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NWBC 2012

The 4th Nordic Wood Biorefinery Conference

Helsinki, Finland
23–25 October, 2012

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Preface

Klaus Niemelä
Chairman of the Organising Committee, VTT, Finland

”*An attempt to discuss fully the influence of chemistry on the utilization of waste wood leads so deeply into practically all fields of chemistry that a paper of this kind must necessarily be limited to a small number of topics*.” This is how S.F. Acree (from Forest Products Laboratory and University of Wisconsin) started his review paper, nearly 100 years ago, on the chemical utilisation of wood, and Acree continued by stating that “*attention is given, therefore, to those phases of this subject which are of most importance commercially and which seem to show greatest promise for the future.”*

Since the days of Acree, enormous advances in chemical, enzymatic, mechanical and thermal utilisation of wood and all other parts of trees have taken place. Therefore, in our modern biorefinery era Acree’s “*this subject*” needs to be understood to cover much more than just the “*chemistry on the utilization of waste wood*”. Taking this into account, the organisers of the NWBC 2012 event sincerely hope that the selected presentations cover “*those phases of this subject which are of most importance commercially and which seem to show greatest promise for the future*”.

Today, the “*greatest promise for the future*” is apparently shown by highly integrated forest industry systems with optimised total energy balances and maximised output of different value-added products; although more robust and simple stand-alone systems also show a lot of potential. This book of proceedings contains numerous examples of industrial and academic views on these approaches for wood-based biorefining. The organisers of the NWBC 2012 wish to warmly thank all the session chairs, speakers, poster presenters and their co-authors for their valuable contributions. This event has benefited from the kind support from the sponsors listed elsewhere in this book. Their support has enabled many young researchers to participate in this conference and to present their studies. Last but not least the organisers wish to give special thanks to Tarja Haapalainen, the technical editor of this book of proceedings.

It has been cited above how Acree started his paper in 1915. This reference is made even more meaningful by ending this short preface by repeating Acree’s final sentence of that publication: “…*the future will probably show that the application of chemistry to the utilization of forest products extends into nearly every field of human endeavor*.”

The organisers wish all conference participants an exciting and stimulating conference.

Reference

Acree, S.F. 1915. What chemistry has done to aid the utilization of wood. J. Ind. Eng. Chem. 7, pp. 913–915.

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Tuesday, 23 October:
Biorefinery – strategy and innovation

Initiating a Public-Private Partnership for biorefineries

Johan Elvnert
Forest-based Sector Technology Platform

Abstract

In Europe today biorefinery research initiatives are plentiful but often fragmented and there are few commitments to pool resources, knowledge and know-how. Furthermore, the research community as a whole and industry alike have not, until now, established a clear way forward for achieving a consolidated route to optimising biorefinery technology and methodology.

In order to promote a more consistent policy environment and the development of new business models and integrated biorefinery value-chains, it would be recommendable for the public and private to form a partnership that transcends traditional value chains, policy areas and research domains and creates critical mass for research, innovation and development of new biorefining concepts.

The EU funded Star-COLIBRI project (Strategic Targets for 2020 – Collaboration Initiative on Biorefineries), a 2-year Coordination Action which ended in 2011, set out to provide the necessary stepping stones for a stronger and less fragmented approach to biorefinery developments in Europe. Towards the end of the project, the European Commission was approached with the suggestion to invite relevant industry representatives to a first discussion about the setting up of a future partnership. Around 40 leading companies and the European Commission is now preparing towards a future public-private partnership called ‘Biobased for Growth’ which may be launched in 2014. Biobased for Growth could potentially allow for a doubling of the pace in which new biorefinery concepts are introduced to the market. How the idea of this potential public-private partnership (PPP) came to life and examples of the complicated political and practical procedure of establishing it is the topic of this contribution.

What is a public-private partnership (PPP)?

The simple way to explain how PPPs in the field of EU-funded Research and Innovation works is to say that the European Commission and a consortium of private stakeholders together manages a “research programme” on a 50/50 principle of shared costs, governance and influence. Research projects funded by this “programme” are selected through open and competitive call procedures, but the industry stakeholders have a very strong influence over the topics of the call. The importance of research PPPs was recognised in the Europe 2020 Strategy put forward by the European Commission in March 2010. The strategy mentions that PPPs are important instruments through which the EU can maximise and accelerate the practical benefits of research for Europe’s businesses and SMEs.

Since 2007, several research PPPs have been established with the European Commission as (one of) the public partner(s). These PPPs are organised in many different ways and also conduct their operations differently. However, there are two distinct categories: Institutional PPPs and contractual PPPs. Institutional PPPs, Called Joint Undertakings (JU) or Joint Technology Initiatives (JTI), require a decision of the European Parliament and the Council and is, when operational, managed by a public European Agency.

The JTIs established have total budgets ranging between € 1 billion and € 3 billion for a 10 year period. In three JTIs (*Innovative Medicines Initiative*, *Clean Sky*, and *Fuel Cells and Hydrogen*), public resources are exclusively composed of EU funds, provided through the budget of the JTI; in the two other (*ARTEMIS* and *ENIAC*), they are combined with funds of the participating Member States or countries associated to FP7, provided through national funding agencies.

Contractual PPPs are established by a legal contract by on one hand the European Commission and on the other hand a private consortium. The daily administration remains with the European

Commission that already manages the research and innovation budget, but the vision and multi-annual roadmap prepared by the private stakeholders serve as the basis for all activities. Under the European Economic Recovery Plan (2008), three contractual PPPs were created to represent a powerful means of boosting research efforts in the large industrial sectors of automotive ("Green Cars"), construction ("Energy-Efficient Buildings") and manufacturing ("Factories of the Future").

Why a European PPP for Biorefining?

First of all, size does matter! While the scope of the partnership must l be focused enough and the participants few enough for the cooperation to be practically manageable, a successful partnership must be wide enough for critical mass. At the scale of European multi-billion Euro PPPs, biorefining happens to be a very suitably sized topic.

Second, the timing is right! A PPP on biorefining would be timely both in the perspective of renewable energy and mitigating climate change, as well as industrial competitiveness and jobs creation perspective. Large companies are investing in research on new biomass pre-treatment methods, conversion processes and new products for old and new markets.

Further on, the shared challenges and opportunities are grand! The benefits of a closer integration of traditional biobased industries go beyond substituting fossil feedstock with a sustainable alternative. It is major opportunity for Europe's industry and citizens.

The actions of the private players in the area of biorefining could greatly influence the successful transition to a more sustainable and competitive European economy, which is the overarching objective of the policy makers, but especially the investment cost and technical risk related to bringing a biorefining concept from the laboratory into running production capacity, is immense.

Meanwhile the public decision-makers actions influence the business of biobased industries and their capability to plan and invest in new biorefinery capacity. For instance, the price of biomass has become increasingly correlated to energy prices, regulated agriculture and food production, rural development policy, taxation on green-house gas emissions and priorities of public investments in infrastructure and research influence strategic business decisions almost as much as market predictions does.

The private stakeholders are ready! Many forest-based companies have started to develop new biobased products to markets which often are equally attractive to energy companies, chemical companies, agrotechnology companies, and thus indirectly also for farmer cooperatives and forest owners. Those sectors have much in common in the biorefinery area and are developing new cooperations, knowing they can add to each others respective strengths.

Seeding an idea of a Biobased industries PPP

The EU-funded Star-COLIBRI project gathered five industry-driven European Technology Platforms representing the biofuels sector, forest-based sector, agritechnology sector, plant breeding sector and sustainable chemistry sector as well as researchers from five different research institutes.

The project looked at models for collaboration between on-going research projects, by identifying gaps and overlaps in on-going research efforts, to make better use of resources, whilst creating critical mass and synergy. It also established a central information repository for biorefinery-related research projects which resulted in the Star-COLIBRI Biorefinery Portal (www.star-colibri.net). Supported by the research community and stakeholders of the five participating technology platforms, the project also published a 'Joint European Biorefinery Vision for 2030' and a 'European Biorefinery Joint Strategic Research Roadmap'. The roadmap which covers the complete area of biorefinery-related research describes prioritised research undertakings from biomass to bio-based products. Advice is also given on some strategically-important actions to be undertaken by policy makers and industry. Finally Star-COLIBRI produced two deliverables about how to organise public research funding and facilitating the creation of a European Public-Private Partnership as a form of intensified European collaboration and it was also the partners of the Star-COLIBRI project that encouraged the European Commission to invite private stakeholders to discuss a public-private partnership.

Biobased for Growth PPP – the work start

This first official meeting, called to by the European Commission in February 2012, established that the industry was ready to invest in a public-private partnership if the format was satisfactory. Forest-based companies such as Billerud, Holmen, Mondi, Metsä Group, Sappi, SCA, Stora Enso, Smurfit-Kappa, Södra, and UPM joined as founding members of the private group preparing for a the PPP with other founding members including energy companies (e.g. DONG Energy and Abengoa Bioenergia) chemical companies (such as Cargill, Clariant, DSM, Kemira and Nortsucker), biotechnology/agro-chemical companies such as Novamont, Novozymes, and Roquette. Farmer cooperatives and Forest owners are also represented in the private group and it is important to emphasize that the private partnership is not a closed club. It is open to new members throughout the duration.

The companies involved in the preparation of the PPP – has estimated that during the period 2014–2020 they would be interested in investing more than €2,8bn in collaborative research, development and demonstration in biobased technologies, assuming that the appropriate policy frameworks are in place.

The PPP initiative is also supported by established European Technology platforms: SusChem, Plants for the Future, the Forest-based Sector Technology Platform, European Technology Platform FoodforLife, European Biofuels Technology Platform, Manufuture; European sector organisations as COPA COGECA, CEPI, EuropaBio, European Seed Association, ERRMA, European Bioplastics, FoodDrinkEurope, and CEFIC.

Biobased for Growth PPP – scope and aims

The focus of a future PPP is threefold:

Feedstock: creating value chains and providing secure and sustainable supply of biomass

Biorefineries: R&D and up-scaling through large scale demo/flagship biorefineries

Markets, Products and policies: ensuring market pull and optimising policy frameworks.

In particular the PPP would aim to address the challenge of integration between existing biobased value-chains

- ✓ Fostering a sustainable biomass supply: Improving output from agriculture, agro-food and forestry in a sustainable and foreseeable manner for feeding the world and producing biobased products with a view of valorising local resources; Building logistics & infrastructure for more competitive transport of various feedstock/biomass to the new biorefineries
- ✓ Optimizing efficient processing: biorefineries as the core processing operations linking biomass supply to market demand, while promoting the most efficient use of biomass
- ✓ Developing markets, products and policies; For instance, many well-known brand owners have stressed their ambitions to replace their packaging materials with biobased materials. The PPP aims to develop and deliver those products and alongside speed up the creation of new markets and new products.

Biobased for Growth – political consensus and the challenges ahead

The European Commission has proposed an €80bn budget for research and innovation from 2014–2020 and this proposal is currently being discussed by the European Parliament and EU Member States. In these times of financial austerity, it is not surprising that any kind of public investment is under immense scrutiny and that the PPP stakeholders are faced with the challenge of showing to European parliament members, commissioners, and ministers that investing 1 billion Euros in a PPP for biobased industries is an investment superior to the many alternatives. The list below illustrates some of the numerous decisions that must to be taken questions to answer in order to build the partnership and convince decision makers:

- ✓ Public financial commitment
- ✓ Impact assessment: How many additional jobs are created? Industry investments?
- ✓ Avoid overlaps with initiatives on bioenergy and sustainable process industries!
- ✓ Explain why existing EU Research Framework Programme is not applicable!
- ✓ Balance of research versus demonstration?
- ✓ Food production versus non-food production?
- ✓ Materials versus energy production?
- ✓ Feedstock limitations? Include algae and other potential biomass sources or not?
- ✓ Are all relevant sectors included in the process?
- ✓ Number of member states represented by the members?
- ✓ Role for SMEs
- ✓ Role of private research institutes and universities?

The budget discussed for the period 2014–2020 is in the range of 2 billion Euro, but a final decision is pending. One of the issues for which consensus has to be established is the balance between research and demonstration activities, where the public representatives generally would like to see more basic research and the industry see the need for innovation support and more funding to demonstration and testing at a larger scale. Another point of discussion is the perceived conflict between food production and non-food production, especially now with this year's dry weather and low crop yields in the US. While the PPP strive to optimize land use and biomass efficiency and not to switch production capacity from food to non-food, Public concerns like these still has to be addressed properly.

Next steps

The establishment of a Public-Private Partnership for Biobased industries would have a very positive impact on the future of the forest-based sector. However, a long and difficult political process has just started and meanwhile private partners have to get organised and prepare a Strategic Research and Innovation agenda. In 2012 or early 2013, a political decision must have been taken by the European Parliament and Council. In 2013, an agency has to be established to administrate the funding of biorefining activities. If these processes go according to plan, the Public-Private Partnership 'Biobased for Growth', with a total estimated budget of 2 billion Euros, will commence its activities in 2014.

Regulatory and legal frameworks for wood biorefineries in EU and Russia

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Abstract

The target of the paper is to clarify, what kinds of challenges have to be taken into account, and in which stage of the innovation process those challenges should be faced when developing wood biorefineries in the EU and Russia. The regulations handled relate to wood and biomass sourcing, products themselves and the environment.

Different EU countries have different policy instruments for renewable energy. Feed-in-tariffs, premiums, quota obligations, investment grants, tax exemptions and fiscal incentives vary from country to country. EU directives are implemented in different ways in the member countries.

What comes to the wood raw material itself, different countries have diverse regulations for wood harvesting. Each country has a forest policy of its own and the states own different stakes of the forests. The forest laws define the forest management and various permits are needed before trees in the forest can be cut. In addition, the regeneration regulations also vary. The topics related to sustainability of the operations have become an important issue and protected areas, landscape, cultural aspects, recreational areas, etc. need to be taken into account.

What comes to Registration, Evaluation, Authorisation and Restriction of Chemical substances (REACH), biorefineries producing bioenergy have a different status compared to the biorefineries producing bioproducts. Biopolymers is a class of its own. Chemicals already sold in the market have been registered in REACH. To get the licence, negotiations with the previous registrants are required in order to agree upon the information and the costs occurred. Non-registered chemicals are another type of challenge.

The environmental and social issues related to biorefineries will be discussed. How deep of an environmental and social impact analysis is required, depends on the product. The question is: how to define the scope. Not only the authorities granting the permits but also the stakeholders must be able to rely on or at least not oppose to the results of the assessment. For risk management purposes, in addition to the environmental and social impact assessment, a social license to operate must be earned. Therefore, the assessment requires clear quantitatively comprehensible sustainability indicators, which can be used as a platform for discussion and argumentation. Moreover, the assessment should cover the whole life-cycle of the biorefinery products from the raw material procurement to the end use of the final product.

Does the framework concentrated in the promotion of bioenergy sector have an impact on the traditional wood-based product industry and in the evolvement of the bioproduct industry? Is it easier to develop other types of renewable energy than bioenergy because of regulations?

Introduction

The target of the paper is to clarify, what kinds of challenges have to be taken into account, and in which stage of the innovation process those challenges should be faced when developing wood biorefineries in the EU and Russia. The regulations handled relate to wood and biomass sourcing, products themselves and the environment.

The article replies to the following questions: Does the framework concentrated in the promotion of bioenergy sector have an impact on the traditional wood-based products industry and in the evolvement of the bioproduct industry? Is it easier to develop other type of renewable energy than bioenergy because of regulations?

Biorefineries

In this paper the term biorefinery is used to describe the production system for bioenergy, biofuel and various bioproducts, which are either in the innovation pipeline or already in the market.

Policy instruments for renewable energy

In the EU the target for energy from renewable energy sources (RES) is 20% by 2020. The highest targets percentagewise have been set for Sweden, Latvia, Finland, Austria, Portugal and Denmark, all above or equal to 30%. The majority of countries, like Germany, France, Italy, Spain and the UK, start from a very modest level but will have to multiply the use of renewable energy by 2020.

What comes to biofuels in transportation, European Commission established a goal of 5.75% by 2010. This target was reached only in France (5.9%), Germany (6.2%) and Sweden (7.3%) of the 15 countries, whose reports have been published. Nevertheless, a new target of 10% was set to 2020. The applicable energy sources are electricity, hydrogen generated from RES and first or second generation biofuels.

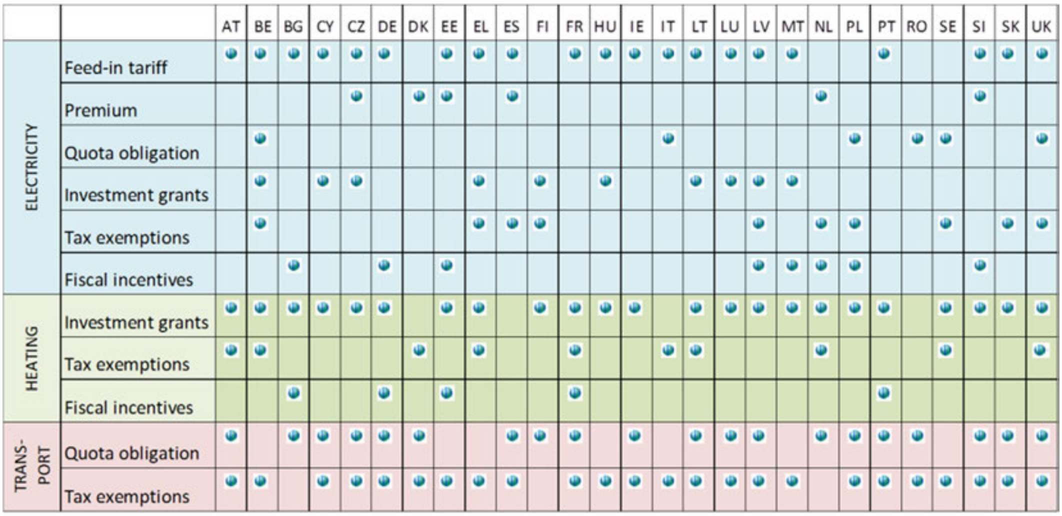
The states have a freedom to choose, how to reach the targets of this Renewable Energy Directive (RED), as shown in Figure 1. Feed-in tariffs, premiums, quota obligations, investment grants, tax exemptions and fiscal incentives are in use. There is variation, how each state applies these “carrots or sticks” from power generation or heating to transportation fuels.

These instruments have not been too effective at least by 2010. The EU Emissions Trading System seems to be more efficient. For example, from the start of 2012, emissions from all domestic and international flights arriving at or departing from an EU airport will be covered by the EU Emissions Trading System. All airlines flying through EU airspace are required to pay 15% of their polluting carbon emissions. Around 4 000 airlines should pay for EU pollution permits. Consequently, several major airlines are moving towards biofuel. As ASTM (used to be American Society for Testing and Materials) approved the use of 50% blend of hydroprocessed esters and fatty acids (HEFAs) fuel to be mixed with conventional kerosene in 2011, the primary reason slowing down the use of biofuel is its availability (and yes, the price).

It can be expected that the growing use of biofuel in aviation speeds up the pace in switching to biofuels also on the ground and in sea transportation, provided that suitable biofuel is available. The world is awaiting for biobutanol, which is not only more close to diesel in its volumetric energy content but is said to easily mix with diesel and to be less corrosive than ethanol.

In Russia the main concept is the Energy Strategy of Russia until 2030. It was adopted in 2009 by the Russian government and concentrates mainly on the more efficient oil, natural gas, coal production and energy security. It contains though a few issues focused on the second generation biofuel. The Russian government resolution in January 2009 set a quantitative target of 4.5% for RES in the energy production. The percentage may first sound low until understanding that hydropower is not counted as RES.

The downside of the policy instruments is the volatility: the instruments may change and do change, maybe not overnight, but at least when switching from one government to another and from a strategy round or budgetary season to the next one. Should the financing decisions for the investments be done by forgetting any impact of the policies prevailing today as they may change before the biorefinery is up and running?



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ELECTRICITY	Feed-in tariff	●	●	●	●	●	●		●	●	●		●	●	●	●	●	●	●	●			●			●	●	●
	Premium					●		●	●		●										●					●		
	Quota obligation		●													●						●		●	●			●
	Investment grants		●		●	●				●		●		●			●	●	●	●								
	Tax exemptions		●							●	●	●							●		●	●			●		●	●
	Fiscal incentives			●			●		●										●	●	●	●				●		
HEATING	Investment grants	●	●	●	●	●	●		●	●		●	●	●	●		●	●	●	●	●	●	●		●	●	●	●
	Tax exemptions	●	●					●		●			●			●	●				●				●			●
	Fiscal incentives			●			●		●				●										●					
TRANS-PORT	Quota obligation	●		●	●	●	●	●			●	●	●		●		●	●	●		●	●	●	●		●	●	●
	Tax exemptions	●	●		●	●	●	●	●	●	●		●	●	●	●	●	●	●	●		●	●	●	●	●	●	●

Figure 1. Different policy instruments in the EU countries.

Regulations for Wood and Biomass Sourcing

Different countries have diverse regulations for wood harvesting. Each country has a forest policy of its own and the states own different stakes of the forests. Forest laws define forest management and various permits may be needed before trees can be cut. The topics related to sustainability of the operations have become an important issue and protected areas, landscape, cultural aspects, recreational areas, etc. need to be taken into account.

EU Forest Law Enforcement, Governance and Trade (FLEGT) will come into force in March 2013. Seven years of discussions reached a result, which limits the production and consumption of illegal timber. As a consequence FLEGT licenses will be issued, independent monitoring will be applied and timber will be controlled at EU borders.

EU Timber Regulation (EUTR) will enter in force in all 27 EU Member States on 3 March 2013. The regulation will prohibit the placing on the EU market not only illegally harvested timber but also products derived thereof. The products include fuel wood, sawn wood, plywood, packing material, pulp and paper, wooden furniture, etc. Only recycled products will escape the loop. Records of suppliers and customers have to be maintained.

It is not possible to forget Russia's membership in the World Trade Organization (WTO), which came into effect in 2012. It will have a positive impact on wood and wood-based product trade in the region.

REACH and CLP

REACH regulation came into force in 2007. It requires the chemical manufacturers and importers to generate data for all chemical substances produced or imported into the EU above one tonne per year. The risk management measures must be identified and communicated.

Plenty of exceptions in the registration exist. The typical reason for exemption is that the substance already belongs to another regulating procedure (fertilisers, detergents, explosives, pyrotechnic articles, drug precursors, plant protection products, biocidal products, hazardous substances in electric/electronic equipment, nanomaterials, eco-labeled products, emissions to air and water, fluorinated gases, ozone depleting substances, food/feed additives or cosmetic products). The exemptions above only apply, when the chemical is used in that particular regulated application as the active substance. Further exemptions are, if the substance belongs under waste directive or is reused as such or recovered, becoming end-of-waste. Also polymers are exempt, but not monomers.

REACH permitting does not apply for substances “used as fuel in mobile or fixed combustion plants of mineral oil products and use as fuels in closed systems”, which opens a question, should and does this allow, fairly enough, biofuel to be exempted as well. There is an EBB (European Biodiesel Board) Biodiesel REACH Consortium to ensure proper registration of biodiesel and related substances. Scientific work and demos are though allowed as long as the material volume is below one tonne per year.

REACH permitting is neither required for intermediate products, which are consumed at the production site. However, if the product is consumed by another company and there is additionally an intermediate storage, permitting is required even at the same site.

The first step is to find out, under which regulation the substance belongs to and if the substance has already been registered. The producer or importer should join the consortium, who registered the substance. Constructive negotiations with the main registrant are needed, to secure that production and sales can be launched as planned. If the substance is new in the EU and has not been registered before, the registration has to be done before starting the operations.

CLP regulation cannot be forgotten either. It regulates classification, labelling and packaging of substances and is aligned with GHS, the respective Globally Harmonized System under the United Nations. The target is to ensure a high level protection of both human health and environment in both industry and transportation, and to allow free movement of substances. The notification has to be delivered one month before the substance enters the market by the producer and/or the importer.

Russia is poised to adopt a regulation consistent with the EU’s REACH. Russia has formed with Kazakhstan and Belarus a Customs Union, where the chemical regulations are handled. The Union became a single economic space as of 1 January 2012. The same regulations will also apply in the Eurasian Economic Community, which in addition to the states of the Customs Union, includes Kyrgyzstan, Tajikistan and Uzbekistan.

Sustainability for biorefineries

To ensure sustainability of operations, a wide set of requirements has to be fulfilled. First, the environmental and social impacts and risks have to be assessed. The labour and working conditions and the potential impacts for the health, safety and security of the workers and the community have to be studied. The land acquisition process has to be handled with care, not only for the production site of the biorefinery but also for the biomass production regions. Special attention should be paid to possible involuntary resettlement and to the (often conflicting) interests of local residents and indigenous people. In case land is not owned, but leased or under some other type of contract agreement, similar caution shall be paid. Both the cultural heritage and conservation of the biodiversity have to be taken into account. The mitigation of the risks and impacts has to be presented.

According to the prevailing EU regulations, all this should be performed for two or three alternate production sites. After approval of this ESIA, Environmental and Social Impact Assessment, the various permits will be applied to one of the sites. All above has to be done before starting the construction of the biorefinery.

In Russia, similar concept is in effect, but in two forms. The first one is SEE, State Environmental Expertise, where all developers have to present the project plans to the Federal or Provincial SEED departments. SEED may hire experts or teams to assist in evaluation of the environmental regulations and the final SEED resolution may be positive or negative. The second concept is OVOS, the assessment of the environmental impacts, in which the developer has to prepare an environmental impact statement and the authorities have to initiate the consultation and public participation process. The environmental impacts are then balanced against the social and economic considerations. OVOS does not apply to all projects as SEE, but to projects listed in OVOS regulations, a list that is broader than the Espoo Convention.

The regulations vary somewhat from country to country also inside the EU. The fact is that no major company is in the position to overlook the sustainability issues today when planning a major investment anywhere in the world. In major investments requiring external financing this is self-evident as financiers would not approve loans if the assessment would end up in a negative conclusion.

Compliance to laws, regulations and licensing requirements does not guarantee sustainability. In addition to meeting requirements prescribed by the legislator, sustainable companies go far beyond. They see themselves as a part of the surrounding environment and accept certain roles and responsibilities in it. They plan, start, execute and exit operations in a way that does not cause harm, but preferably provide benefits to local people and the environment – and at the same time value to the company. This paves the way for gaining acceptance and trust among stakeholders and concurrently reduces risks and possibilities for conflict.

Such a “social license to operate” differs from other permits as it cannot be obtained but has to be earned. The consultation processes of the ESIA and permitting processes is a good help in developing the discussion and co-operation between the bodies. When earned, the “social license” is the best asset for maintaining relations with stakeholders, managing social and environmental risks and cherishing corporate reputation.

Conclusions

This paper covers only such regulations which most obviously have to be complied with in wood biorefineries. Before the green button can be pushed to start a biorefinery, quite a long list of various other permits must have been granted. We shall not forget the various construction and operation related permits, which differ from country to country, from city to countryside, from a region to another.

It may sound that the plentiful regulations would prevent any new type of production plant. At the end, the target is the safety of operators, citizens and pass byers. There are numerous examples, where everything did not go as well as it was originally planned.

There are no regulatory reasons, why a biorefinery would not succeed. The needed assessments, paper work and procedures just have to be implemented first.

Forest biorefineries – sustainable business opportunities in Scandinavia and North America

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Abstract

The goal of this study is to compose a holistic view of the issues affecting the development and implementation of forest biorefineries and present future views for the forest clusters in Scandinavia and North America. The Delphi study was conducted in three phases in 2008–2011: First, an internet survey with related quantitative analyses was conducted. The following two phases were qualitative in their nature with themed interviews and email inquiries, and related thematic analysis. The results from all the Delphi rounds indicate that the key factors for forest biorefinery development and biofuel production are quite similar in the studied countries. High price of oil, national security of fuel supply and long-term policies are the most prominent macro-scale drivers. At the industries level, the successful implementation of a biorefinery business requires efficient exploitation of existing wood biomass resources, availability of financing and collaboration between different value chain actors. At the strategic level an understanding of new markets and management of change as well as development of economic wood fractionation technologies facilitate best the diffusion process. Overall, biorefinery business is seen as a sustainable when taking into consideration environmental, social as well as economic dimensions. Nevertheless, forest biorefinery business will further intensify the pressure of forest-based industries towards forest-ecosystems which in turn can lead to various environmental impacts. Furthermore, both in the Scandinavian and North American forest industries, the conservative organizational culture seem to create an important barrier to restructuring the business.

Introduction

Biomass-based energy (bioenergy) and products (bioproducts) play an important role in society’s transition towards a more sustainable, bio-based economy. Consistently, a bio-based economy with related new opportunities offers ways for diversifying business in the forest cluster. The need to redefine business models is particularly urgent in the mature pulp and paper industry, with its frequent mill closures (e.g. Chambost and Stuart, 2007; Toland, 2007). Widely studied at the moment are lignocellulosic, non-food biomass feedstocks and technologies for converting these sources into economical, low-carbon biofuels (carbon is used as a shorthand for life cycle global warming impact, Farrell et al. 2007) and bioproducts (e.g. FAO, 2011; Hetemäki, et al., 2011; Johnson et al., 2009; Perlack et al., 2005). There has been plenty of interest in biorefineries integrated into the pulp and paper industry. In this study, a forest biorefinery is defined as a multi-product factory that integrates biomass conversion processes and equipment in order to produce a variety of bioproducts such as fuels, fibers, and chemicals from wood-based biomass (e.g. NREL, 2012; Ragauskas, 2006).

However, in addition to considerable opportunities, there are also many risks related to biorefinery implementation. Thus, as the emerging biorefining economies continue to take shape, there is a growing need for realistic estimates of the factors that affect the diffusion process of forest biorefineries both in the global and the national business environments. Overall, the challenges related to biorefineries must not be seen as purely technical problems nor as issues unconnected to society. Nevertheless, studies related to forest biorefineries have largely been technologically focused until recent years (Söderholm and Lundmark, 2009).

The goal of this Delphi study is to compose a holistic view of the issues affecting the diffusion of forest biorefineries in Scandinavia and North America and present future views for the forest clusters in the studied areas.

Theoretical framework

Innovation and new technology diffusion

According to Rogers (2003), *diffusion* is the process by which innovation is communicated through certain channels over time among the members of a social system. Technological diffusion can be also understood as referring to the expansion of the utilization of a new concept, be it a new product, new processes or new management methods within and across economies (Stoneman, 1986).

Although classic models of technological development suggest a straightforward, linear path from basic research and development to technology commercialization and adoption, in practice, technology diffusion is more often a complex and iterative process. Technology can diffuse in multiple ways – depending on the particular technology – across time, over space, and between different industries and types. In addition, the effective use of diffused technologies by companies frequently requires organizational, workforce, and follow-on technical changes. (Baptista, 1999; Freeman, 1996; Peres et al., 2010)

Often, innovation research has focused on technical issues and primarily concentrated only on those stakeholders directly involved in the value-adding activities or market relationships, such as the customers, complimentary innovators and suppliers. Further, technological innovation processes have been studied many times by exploring the importance and relation of research and development (technology push) and activities that encourage commercialization and implementation of new innovations (market pull). (Dosi, 1982; Freeman, 1996; Inoue and Miyazaki, 2008) Other *environmental*, *political, economic*, *social, networking* and *institutional* factors are often given less emphasis. Technology as such cannot guarantee success of an innovation if other aspects related to the innovation are not accepted by stakeholders. (e.g. Baptista, 1999; Coria, 2001; Freeman, 1996; Majahan et al., 2000; Peres et al., 2010)

The diffusion of an innovation rarely takes place in an unchanging environment. Furthermore, diffusion processes of new products and services have become increasingly complex in recent years. (Peres et al., 2010)

Analyzing the Business environment

Johnson et al. (2008) have provided a framework for understanding the environment of the organizations with the aim of helping to identify key issues and ways of coping with change. Environmental influences and trends can be thought of as *layers around the organization*. The outer layer is referred to as the *macro-environment*, which is the most general layer, consisting of broad environmental factors that impact to some extent nearly all organizations. Within the macro-environment sit *industries or sectors*, and the inner layer stands for further *strategic groups*. These are organizations with similar strategic characteristics.

Data and methods

The study uses a Delphi method, which is a technique for obtaining forecasts from selected experts (Landeta, 2006). The research was conducted in three phases in 2008–2011: First, an internet survey with related quantitative analyses was conducted. A total of 125 forest and bioenergy sector representatives responded to the survey, yielding a response rate of 24.5%. The following two phases were qualitative in their nature with themed interviews and email inquiries, and related thematic analysis. The nine respondents, who participated in the first phase, answered the questions in the second research phase. In the third research round a total of 23 representatives participated in the themed, semi-structured expert interviews in the U.S., Canada, Finland and Sweden.

Results and discussion

Forest biorefinery facilities

This study created a picture of a forest biorefinery in the studied areas as a multi-product facility, in which high value-added bioproducts together with biofuels are produced from forest-based feedstock jointly with the other locally available biomasses. As a basic biorefinery concept, respondents indicated facilities with 200 000 to 300 000 or even 500 000 tons per year of biofuel production capacity in which Fischer-Tropsch diesel will be a principal product. Forest residues (logging tops, pre-commercial thinnings, stumps) and mill residues were considered the most significant wood-based biomass sources in future biofuel production. In Finland many respondents also believed that peat will play a significant role in forest biorefinery facilities. Moreover, experts highlighted the evaluation of the potential of various feedstocks in addition to forest residues. Urban organic waste in particular was believed to have future potential. (see also Näyhä and Pesonen, 2012a; b) However, the significance of various low-volume, high-value bio-products in addition to high-volume bulk products were seen as crucial: synthetic polymers, viscose fiber derivatives, fuels, (butanol, ethanol) chemicals, medicines, cosmetics, nanotechnology products, intelligent paper and packaging, and composite materials. Estimates of the importance of new products varied greatly, starting from 10% of total production to the highest estimates of 50%.

Key diffusion factors for the forest biorefineries

It has been shown by this study that the forest biorefineries can be implemented in different ways with case specific variation in raw materials, products, degree of integration and consortia partners. In addition, biorefinery business requires involvement of different industries and collaboration between partners. Therefore, diffusion of forest biorefineries is a multifaceted process that is affected by a variety of issues. The complexity of the diffusion process has also been addressed in many other studies concerning the diffusion of new technologies (e.g. Baptista, 1999).

The results from all the Delphi rounds indicate that the key factors for forest biorefinery diffusion (Figure 1) are quite similar in the studied countries (see also Näyhä et al., 2011; Näyhä and Pesonen, 2012a). Based on three research rounds, the key elements that promote faster development of forest biorefineries are presented in Figure 1.

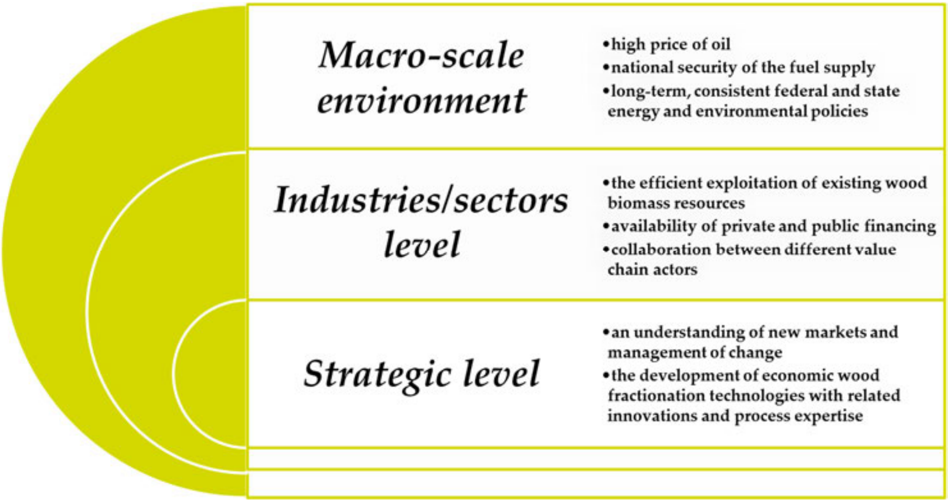


Figure 1. The key drivers for the forest biorefinery diffusion.

4.3 Future views: Sustainability and Restructuring the Business

In the first research round the respondents were asked to choose from four future views – defined as *Business as Usual, Restructuring the Business, Sustainability, and Domestic Competencies* (views are based partly on work of Häyrynen et al., 2007) – the one that corresponds to their impression regarding the future of the forest cluster (Näyhä et al., 2011). *Sustainability* and *Restructuring the Business* best describe the future development of the forest cluster, as 80% of the respondents chose one of the two options. In Scandinavia, the *Sustainability* view got more support compared to North America whereas in North America the *Restructuring the Business* view was more common compared to Scandinavia. According to the *Sustainability* view the forest cluster is successful in a society that respects ecological values and sustainable forest utilization. Sustainability is the key issue also in financial decision-making. Production will be further developed towards energy and raw material efficiency. Biorefineries and related new products sustainably guarantee the forest cluster's success. According to the *Restructuring the Business* view, the competitiveness of the national, traditional forest cluster will disappear, and reliance on old production structures remains highly risky. Investments are aimed at new markets and new business concepts. According to this view, there is a strong interest in an increasing amount of projects geared towards biorefinery concepts and new products.

Interestingly, recent developments in the forest biorefinery sector and the current trends wider in society indicate that the future views chosen as most likely in 2008 have started to actualize in many contexts. A transition towards bioeconomy – which in a broad sense means the exploitation and management of renewable natural resources in a sustainable way – is one of the most prominent trends of the current society (EC, 2011). Respectively, many ideas that are presented in the *Sustainability* view of this research are consistent with the bioeconomy efforts. According to the *Restructuring the Business* view, there is rising interest in and projects working with forest biorefinery concepts and products. These statements have been realized in many terms, as there are many on-going biorefinery projects both in Scandinavia and North America.

Overall, findings of this Delphi study indicate that biorefinery business is seen as a sustainable when taking into consideration environmental, social as well as economic dimensions. Accordingly, environmental sustainability is an important driver for the forest biorefinery business in general. A company's environmentally sustainable image can also be a competitive advantage. Even though the biorefinery business was considered to be sustainable in general terms, the responses also indicated that harvesting feedstock is the part most challenging to manage in the value chain, and its environmental impacts are not sufficiently known. Moreover, according the respondents there should exist applicable sustainability criteria for biomass raw material and its use (Näyhä and Horn, 2012). Furthermore, it was believed that raw material demand of biorefineries cannot be satisfied solely with wood-based biomass. All in all, in every research phase several statements of the respondents indicated that forest biorefinery business will further intensify the pressure of forest-based industries toward forest-ecosystems which in turn can lead to various environmental impacts and challenges. Accordingly, the role of NGOs, particularly various environmental groups, was considered important, especially in the U.S. In the U.S., environmentalists seem to be more of a threat whereas in Scandinavia those groups are seen to go more hand-in-hand with other stakeholders.

North American and Scandinavian forest industries are facing the situation in which restructuring the business is crucial, due to the mature – or even declining – state of many parts of the business. The drivers for change are widely recognized, but pathways for the new business largely still need to be created (see also Näyhä and Pesonen, 2012b). In both the Scandinavian and North American forest industries, the conservative organizational culture and lack of financial resources seem to create important barriers to change. The scope of the change with the needed transformation activities and resources depends largely on contextual features such as the location of the biorefinery, chosen technologies and raw material availability. The role of the forest industry in the forest biorefinery consortium is largely seen as a biomass provider. Operating a commercial-scale forest biorefinery facility requires both new managerial- and operational-level skills. Readiness for change need to be embedded in the organizational culture – and the key for attaining this is open-minded, multi-disciplinary organizational management. Innovative personnel are believed to be found in forest industry companies, yet current culture does not encourage these people to put forward their ideas. The success in the biorefinery business cannot be achieved without collaboration that combines the right set of resources. Nevertheless, it will be challenging to share profits among the partners in the biorefinery consortium.

Conclusions

There is a strong aspiration to move towards a bio-based economy in present society, and bioenergy and bioproducts play an important role in this transition. Though the forest biorefineries will certainly play a role in this process in the coming years, at this point it is very difficult to give exact estimates of how prominent this role will be and how diffusion of forest biorefineries will explicitly proceed. During the research period the perceptions have widened from an exploration of biorefineries from a purely technical perspective to more holistic approaches. Moreover, this study indicates that forest biorefineries have a multifaceted diffusion process in which a variety of issues affect the diffusion. Thus incentives that promote the biorefinery business must stem from several sources.

Incentives for the biorefinery business differ only slightly in the studied areas, and there were no significant differences in the opinions between the sectors that were involved in the study. Therefore it can be concluded that both studied areas seem to have potential for success in the biorefinery business.

One of the most striking aspects to emerge from this study is the rather languid attitude of forest industry companies towards new business and inertia in the strategic management. This is interesting, as the involved industries themselves should work to actively create strategies for managing change and aiming resources towards new business. However, it was also believed that the forest industry has been more future-oriented than has been publicly indicated.

Overall, it seems that the hype that was related to renewables in general and to the biorefinery business has passed, and at all the levels of the business environment more realistic plans and approaches are being made, with the actual steps in the form of commercial-scale biorefineries.

References

Baptista, R. 1999. The Diffusion of process innovations: A Selective Review. International Journal of the Economics of Business 6(1), pp. 107–129.

Chambost, V., Stuart, P.R. 2007. Selecting the most appropriate products for the forest biorefinery. Industrial Biotechnology 3(2), pp. 112–119.

Coria, J. 2009. Taxes, permits, and the diffusion of a new technology. Resources and Energy Economics 31(4), pp. 249–271.

European Commission 2011. European Strategy and Action plan towards a sustainable bio-based economy by 2020. Initiative, November 2011. Available at http://ec.europa.eu/governance/impact/planned_ia/docs/2010_rtd_055_sustainable_bio_economy_en.pdf. Accessed 16.4.2012.

Farrell, E.A. et al. 2007. A Low-Carbon Fuel Standard for California. Part 1: Technical Analysis, University of California Press.

Freeman, C. 1996. The greening of technology and models of innovation. Technological Forecasting and Social Change 53(1), pp. 27–39.

Hetemäki, L., Niinistö, S., Seppälä, R., Uusivuori, J. 2011. Murroksen jälkeen. Metsien käytön tulevaisuus Suomessa [Utilization of Finnish forest in future]. Metsäkustannus, Karisto Oy, Hämeenlinna. (In Finnish.)

Häyrynen, S., Donner-Amnell, J., Niskanen, A. 2007. Globalisaation suunta ja metsäalan vaihtoehdot [Direction of globalisation and forest cluster options]. University of Joensuu, Faculty of Forest Sciences. (In Finnish.)

Inoue, Y., Miyazaki, K. 2008. Technological innovation and diffusion of wind power in Japan. Technological Forecasting and Social Change 75(8), pp. 1303–1323.

Johnson, K., Scholes, R., Whittington, R. 2008. Exploring Corporate Strategy. 8th edition, Harlow, Pearson Education Limited, Essex.

Johnson, B., Johnson, T., Scott-Kerr, C., Reed, J. 2009. The Future is Bright, Pulp and Paper International. October 2009, pp. 19–22.

Landeta, J. 2006. Current validity of the Delphi method in social sciences. Technological Forecasting and Social Change 73(5), pp. 467–482.

Mahajan, V., Muller, E., Bass, F.M. 1990. New Product Diffusion Models in Marketing: A Review and Directions for Research. Journal of Marketing 54(1), pp. 1–26.

NREL National Renewable Energy Laboratory. 2012. Available at http://search.nrel.gov/query.html?qp=site%3Awww.nrel.gov+site%3Asam.nrel.gov&qs=&qc=nrel&ws=0&qm=0&st=1&nh=10&lk=1&rf=0&oq=&col=nrel&qt=biorefinery. Accessed 14.6.2012.

Näyhä, A., Hämäläinen, S., Pesonen, H.-L. 2011. Forest biorefineries – a serious global business opportunity. In: Alen, R. (Ed.). Chapter 4, Biorefining of Forest Resources. Bookwell Oy, Porvoo.

Näyhä, A., Horn, S. 2012. Environmental sustainability-aspects and criteria in forest biorefineries. Journal of Sustainability Accounting, Management and Policy Journal. (Accepted for publication.)

Näyhä, A., Pesonen, H.-L. 2012a. Diffusion of forest biorefineries in Scandinavia and North America. Technological Forecasting and Social Change 79(6), pp. 1111–1120.

Näyhä, A., Pesonen, H.-L. 2012b. The forest industry’s strategic change towards the biorefining business. (Submitted article.)

Peres, R., Muller, E., Mahajan, V. 2010. Innovation diffusion and new product growth models: A critical review and research directions. International Journal of Research in Marketing 27(2), pp. 91–106.

Perlack, R.D., Wright, L.L., Turhollow, A.F., Graham, R.L., Stokes, B.J., Erbach, D.C. 2005. Biomass as feedstock for a bioenergy and bioproducts industry: The technical feasibility of a billion-ton annual supply. U.S. Department of Energy, DOE/GO-102005-2135.

Ragauskas, A.J., Nagy, M., Kim, D.H., Eckert, C.A., Liotta, C.L. 2006. From wood to fuels: Integrating biofuels and pulp production. Industrial Biotechnology 2(1), pp. 55–65.

Rogers, E.M. 2003. Diffusion of Innovations. Free Press, New York.

Stoneman, P. 1986. Technological Diffusion: The Viewpoint of Economic Theory. Ricerche Economiche 40(4), pp. 585–606.

Söderholm, P., Lundmark, R. 2009. Forest-based biorefineries: Implications for Market Behavior and Policy. Forest Products Journal 59(1/2), pp. 6–15.

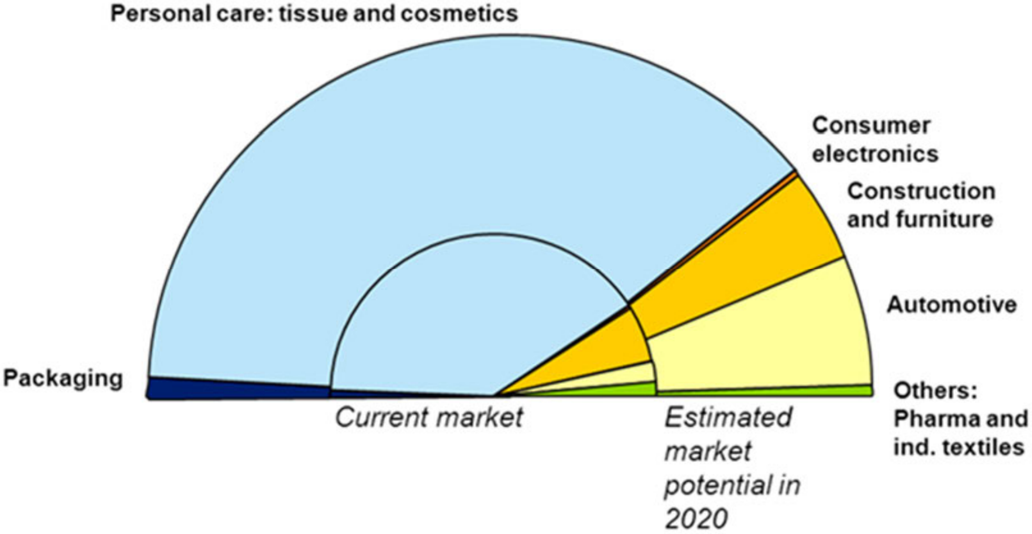
Toland, J. 2007. Hard times in Helsinki, Oslo and Stockholm. Pulp & Paper International 49(12), pp. 5.

Roadmap for advanced bio-based materials

Katja Salmenkivi, Petri Vasara
Pöyry Management Consulting Oy

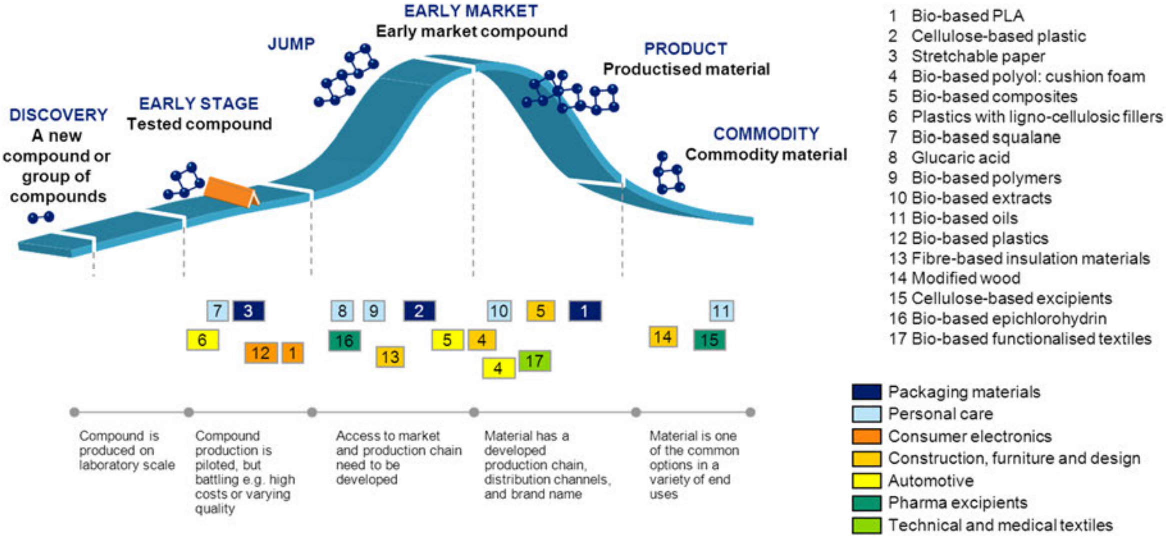
Advanced bio-based materials include a large variety of products. Development and commercialization has taken off thanks to resource constraints, increased demand for green products and discoveries in enabling technologies. In general, the advanced bio-based materials sector is in a phase of expansion on many fronts simultaneously and without coordination. The future looks very promising with aggressive demand growth in several application areas. New materials are continuously being developed, and breakthroughs may propagate quickly across end-uses. Some of the most promising end-use sectors are: Packaging, personal care (tissue and cosmetics), consumer electronics, construction and furniture, automotive, and a group of uses including pharmaceuticals and industrial textiles. Pöyry estimated current market sizes for the advanced bio-based materials to be 22 billion EUR in these respective sectors. Market projections by end-use sector were determined to be as follows:

> *cosmetics and tissue/hygiene (value added consumer products) dominating at 14 bill. EUR and 4 bill. EUR, respectively,*
>
> *construction and automotive follow (2.6 bill EUR and 990 MEUR),*
>
> *technical and medical textiles (470 MEUR) and*
>
> *packaging, pharma and consumer (200 MEUR, 110 MEUR and 40 MEUR).*



Market growth for these new materials relies heavily on the high number of r&d efforts that are taking place on several fronts around the world. The initiatives to follow are actually so numerous that the problem of "information overload" is very much at the forefront – along with quality issues in what is claimed.

The Pöyry BioCurve describes some of interesting initiatives and their development phases from discovery to the total market assimilation. The current status and the future possibilities of the selected example materials are analyzed here by showing their location on the curve. It is critical to pass “the fence” and to be able to jump to the market.



It is important to realize that successful market penetration is not enough when dealing with the bio-based materials industry. The availability of biomass resources, technology development and market demand form a triad of key questions for growth of bio-based materials production. In biomass, there is great variation in the value chain from field to end user depending on feedstock and geographical location. Until now bio-based materials have been produced from major biomass commodities such as starch, sugar, wood and vegetable oils. However, new raw material sources have to be introduced if big scale operations are pursued. It is still in many cases uneconomic and technically not possible to produce many high volume advanced bio-based materials from wood. How about the future? Where can we find the most interesting initiatives adding value in future? Where would the Nordic raw materials, wood have the most interesting opportunities?

The presentation will speculate on where the most interesting product opportunities for Nordic wood based bio refineries could be found by presenting a roadmap for these.

Bio-based chemicals – success by maximizing value and being resource efficient

Anna Holmberg
Arizona Chemical AB, P.O. Box 66, SE-820 22 Sandarne

Contents

Creating value is a core task for any business. The Arizona Chemical (Arizona) value creation model builds on offering the customer a green and innovative product with a high functionality. The green product often substitutes one based on non-renewable raw materials. However, being green is not enough. Instead the “greenness” must be combined with a functionality that brings advantages to the customer’s production process or improves his or her end product. It is only when the green innovation and the functionality are combined that true value can be created.

Arizona applies its value creation model in each of its four focus markets. To the *Adhesive* market, Arizona supply bio-based resins for tack and adhesion in high performance end applications. We also offer tackifiers, which extend the applications of water based adhesives instead of solvent based ones. To *Tire* producers, we provide tread enhancement additives that work with the tire to improve traction and breaking distance. The same additives improve the polymer-filler interaction and thus lower the rolling resistance of the tire and save fuel. In the *Roads & Construction* sector, our innovations allow higher use of recycled material in new pavements rather than being thrown into landfills, which earlier was often the case. Our resins also increase the durability and luminosity of road markings. To the *Personal Care* market, we provide bio-renewable and safe products used in various applications, such as sun screens, lip gloss and mascara.

At Arizona we believe in market driven product development. We interact with the customer to define his or her needs prior to starting the development of a new product. We supply a solution, which is ticked off by the customer prior to any business transactions taking place. According to our experience, applying this “outside-in” perspective is vital in building sustainable and profitable business.

In our daily work, we follow the New Product Blueprinting (NBP) methodology developed by Advanced Industrial Marketing Inc. Firstly; a thorough Market Research takes place with the target of identifying the most attractive opportunities. Secondly, we perform Discovery Interviews with existing and potential customers to uncover unmet needs. Thirdly, we continue with Preference Interviews to be able to prioritize among the discovered unmet needs. Fourthly, we do a Side-By-Side Testing to truly understand competitive offerings that we face in the market place. Fifthly, we define the product objectives to be met and develop this further through Technical Brainstorming. Finally we summarize by concluding whether or not we have a solid Business Case.

We believe that we know what we talk about when it comes to developing bio-refinery business. We run modern refineries with over 80 years of experience. We have a proven track record of commercializing new products and bringing value to the customer. And we are truly market driven with an “outside-in” perspective on business.

When we raise our eyes from the pure business perspective and address the larger political picture, we can see that our world is presently facing several tough challenges. We are going through the worst financial crisis in modern times, we are experiencing a climate change which forces us to rethink many of our old beliefs and we see an ever-increasing fight over resources. To address these challenges, we must develop a resource efficient, low carbon economy. Important focus areas are life cycle thinking, effective use of resources and sustainable products. And we should achieve this while maintaining the high quality of life that we are used to.

To achieve the resource efficient, low carbon economy, Arizona advocates the implementation of four fundamental principles:

1. A natural raw material shall always be used to its full potential through cascading use
2. A level playing field shall exist between users of the same resource

3. Sound business is based on market economics, not on incentives
4. Focus shall be set on creating highest possible value.

Cascading use is all about making the most out of a raw material by securing its full potential. Step by step the intrinsic value is extracted. Side streams to the main production flow are defined as co-products. It is only at the end of the cascade – when no further intrinsic value remains – that the resource should be defined as a residue and be promoted for energy purposes.

A level playing field allows users to compete for the same raw material on fair and equal terms. One application should not be politically favored for another – instead this should be left to the market to decide upon. Political incentives and subsidies create market distortion by “pushing” raw materials into certain applications and by cutting off the natural cascading use prematurely. This results in reduced resource efficiency.

Basing new products on incentives will never build long-term sustainable business. Incentives are politically decided and what might seem like a “safe haven” today can be gone tomorrow. Instead any new product must be strong enough to survive on its own merits in the market economy.

By focusing on creating highest possible value from a raw material, all stakeholders in the value chain are potential winners. It also stimulates innovation and business acumen and thereby benefits the society as a whole.

The importance of the four principles can be exemplified with a real life example. Arizona’s main raw material is Crude Tall Oil, or CTO, which is a co-product of kraft pulping. CTO is a liquid biomass, which is scarce, i.e. its supply is limited. A well-established application is the one Arizona represents, i.e. bio-chemicals. A newer application developed in the last couple of years is to use CTO as a feedstock for a diesel fuel with renewable content.

When comparing the two applications, clear differences can be observed. Bio-chemicals make use of every economically viable component in CTO and upgrade to specialized products. The bio-chemicals continue to create value over time in long life cycle end applications. The biofuels route produces a fuel, which by definition has a short life cycle, and once burned, it cannot any longer contribute to value creation. A further important difference between the two routes is that bio-chemicals are economically competitive without any incentives, while for biofuels, policy instruments are very important – in some cases vital – to make ends meet.

Arizona’s annual sales amount to approx. USD 1 billion, customers are served globally and the company employs over 1 100 people. Arizona has manufacturing sites in North America and in Europe. The executive offices are found in Almere, the Netherlands and in Jacksonville, Florida, US.

Role of COST in European forest and forest products research

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Abstract

This article describes COST – European Cooperation in Science and Technology – its organisation, and main instruments, and how to participate. It further outlines how COST works as a platform for innovation by sharing information and producing new knowledge. Some COST Action examples are presented and the article closes with describing the expected future role of COST in the European Research Area (ERA).

COST coordinates nationally funded research activities through enhanced networking. This is first of all carried out using the so-called COST Actions. Focus is on Europe, but the networking also covers participation from many non-European countries. COST does not fund research as such; its contribution to the ERA comes from the synergies that arise from the enhanced networking of active research groups.

Knowledge is a valuable asset for creating and sustaining advantages for individuals and organisations. An obstacle to knowledge sharing is the fact that knowledge is property. This is reflected in the fact that one is typically rewarded for what one knows, not for what one shares. Therefore, incentive mechanisms are needed in order to motivate individuals and organisations to share their knowledge. COST instruments are designed to face this challenge, compensating networking costs and encouraging innovation through synergies.

About COST and how to participate

About COST

Founded in 1971, COST is the first and widest European framework for the transnational coordination of nationally funded research activities. It is based on an inter-governmental agreement between 35 European countries. COST is funded through the EU RTD Framework Programmes.

COST key features are:

- building capacity by connecting high-quality scientific communities throughout Europe and worldwide;
- providing networking opportunities for early career investigators;
- increasing the impact of research on policy makers, regulatory bodies and national decision makers as well as the private sector.

Through its inclusiveness, COST supports integration of research communities, leverages national research investments and addresses issues of global relevance. Reaching out to over 30.000 researchers across Europe, COST is a building block of the European Research Area, instrumental for successful innovation strategies and global cooperation.

The organisation of COST reflects its inter-governmental nature. Key decisions are taken at COST Ministerial Conferences which are usually held every five years.

The Committee of Senior Officials (CSO) is the highest decision-making body and is charged with the oversight and strategic development of COST. Each COST Member Country appoints up to two representatives to the CSO, one of whom is the COST National Coordinator (CNC), the national contact point.

The Domain Committees (DCs) consist of scientists covering the 9 scientific domains and nominated by the COST National Coordinator. The DCs are

- Biomedicine and Molecular Biosciences (BMBS);
- Chemistry and Molecular Sciences and Technologies (CMST);
- Earth System Science and Environmental Management (ESSEM);
- Food and Agriculture (FA);
- Forests, their Products and Services (FPS);
- Individuals, Societies, Cultures and Health (ISCH);
- Information and Communication Technologies (ICT);
- Materials, Physics and Nanosciences (MPNS);
- Transport and Urban Development (TUD).

Each COST country may appoint one representative to each Domain Committee. The DC reports to the CSO and is responsible for (i) Evaluation of proposals for new COST Actions; (ii) Monitoring of COST Actions in progress and; (iii) Assessment of completed COST Actions. The DCs also supervise the strategic development of their respective domains.

In addition, Trans-Domain Proposals allow for broad, interdisciplinary proposals to strike across the nine scientific domains. A Trans-Domain Proposals Assessment Body (TDP-SAB) is responsible for the assessment of interdisciplinary proposals.

The COST Office implements the CSO decisions and supports the scientific activities, e.g. the COST Actions' and DCs' activities. The COST Office in Brussels is provided by the European Science Foundation (ESF) based in Strasbourg, the implementing agent for COST.

How to participate in COST

Following a bottom-up principle, applicants from any type of institution can submit a COST Action proposal in any field of interest at any time of the year (continuous call). Proposals are collected twice a year and assessed in two stages.

The Preliminary proposals (3–4 pages), submitted using the on-line form (see www.cost.eu/opencall) should provide a brief overview of the proposal and its intended impact. Eligible proposals are assessed by the relevant Domain Committee or Trans-Domain Proposal Standing Assessment Body (TDP-SAB) in accordance with the published criteria (see guidelines on www.cost.eu/opencall). Applicants of the highest ranked preliminary proposals are invited to submit a full proposal. Full proposals are peer reviewed according to the assessment criteria (see guidelines on www.cost.eu/opencall). A final list is established after the oral presentation of the proposal (DC Hearings). The decision of funding a proposal is taken by the CSO within eight months of the collection date and the Action should expect to start within three months thereafter. COST supports the Actions by reimbursing travel and subsistence related to Action meetings, short-term scientific missions, training schools and publications, and it also grants some financial support to the local organisers of Action meetings.

Although the COST Actions form the main instruments, COST also funds two kinds of strategic activities. First, the Science & Technology-driven Activities serve the dissemination of COST activities and outcomes, initiated by the DCs. Three categories of proposals can be presented under this umbrella: Transdisciplinary Science & Technology Strategic Events focusing on S&T development of transdisciplinarity; Domain Specific Science & Technology Strategic Events focusing on S/T novelties; and Action Showcases focusing on dissemination of COST Action outputs. Second, the Policy-driven Strategic Activities aim to give COST the necessary visibility and to reinforce its credibility in the mind of policy decision-makers. These activities are initiated by the CSO or the COST office director. Finally, COST has a small budget reserve for ad hoc strategic initiatives.

COST as a platform for innovation

Knowledge sharing

COST is first of all an organisation that deals with knowledge sharing through networking. Before focusing on what knowledge sharing leads to let us have a look at what knowledge actually is, why it should be shared, and how the sharing may be hampered or boosted.

Knowledge is information possessed in the mind of individuals, it is personalized information. It is related to facts, procedures, concepts, interpretations, ideas, observations and judgements. Knowledge is the result of cognitive processing triggered by the inflow of new stimuli. Information is converted to knowledge once it is processed in the mind of individuals and knowledge again becomes new information to others once it is presented in some interpretable form, for example as text, graphics, words, or as other symbolic forms.

There are several reasons why explicit knowledge (knowledge that can be articulated, codified and stored is said to be explicit, in contrast to tacit knowledge like e.g. the ability to ride a bike) should be shared. First of all, the amount of information and knowledge is growing rapidly, mainly due to the explosion of ICT, increasing education levels and increasing R&D efforts. Although only 5% of those who have ever lived on mother earth are still alive, 90% of the scientists are, and to stay alive in the academic system they are supposed to publish new knowledge. And ICT obviously plays a crucial role enabling us all to access and share this sea of new and old knowledge.

Secondly, a necessary consequence of the increasing pool of knowledge is increased specialization. Let me exemplify with laminated wood. Developing this relatively simple product requires competence in many sub-disciplines of physics, in chemistry (glue), in mechanical engineering (sawmills), in logistics, ICT and forest management – to mention a few. No single individual can keep abreast with all new developments within this broad range of required competencies. Therefore, specialisation is required.

A consequence of the explosion of knowledge and its impact on the evolving society is that education no longer should be regarded as a phase in life, but rather as a life-long experience. This implies a reinforced need for knowledge sharing far beyond what was required a generation ago, and it leaves us the possibility of focusing more on permanent knowledge (long lasting knowledge like the theorems of Pythagoras and Archimedes as opposed to temporary knowledge e.g. on how to run some specific software) during the basic study years. This, together with the problems of recruiting new students to studies in forestry – globally, also calls for special attention to the increased need for knowledge sharing within the forest sector more specifically.

Knowledge sharing may be hampered in several ways. Knowledge is a valuable intangible asset for creating and sustaining advantages for individuals as well as for organisations, networks and projects. An obstacle to knowledge sharing is the fact that knowledge is property and therefore ownership becomes very important. Illustrating is the fact that one is typically rewarded for what one knows, not for what one shares! Therefore, incentive mechanisms may be needed in order to motivate individuals and organisations to share their knowledge. These incentives may take many forms. COST instruments like COST Actions, Exchange visits and Strategic workshops are typical examples, designed as they are for compensating networking costs and encouraging innovation.

Research has identified three important conditions for knowledge sharing between universities and industry. First, the partners must trust each other, second geographic proximity counts and, third, policies for IPR, patents and licences must be in place. Failing of any of these conditions will hamper knowledge sharing.

The explosion of new knowledge makes it more important than ever to tell relevant from irrelevant information in order not to drown in the sea of information. This requires ways of filtering high quality information and knowledge from garbage.

Knowledge sharing may be also be boosted, first of all by fighting against those factors hampering it. This implies putting in place incentive mechanisms that motivate knowledge sharing, ensuring trust and rules for IPRs and patents, and assisting in qualifying information and knowledge, in short enabling easy transfer of knowledge. This implies facilitating establishment of RTD networks, arranging high quality conferences and workshops, identifying knowledge sources and applying ICT in the most helpful way. This is exactly what COST does.

Knowledge sharing in COST

There are 36 member countries in COST, and another 38 countries, most of them non-European, participate in COST Actions. COST creates networks along and across different European dimensions. It has played – and still plays – an extremely important role in networking and sharing success between old and new and not (yet) EU member countries. It is well known that COST has acted as a door opener to cooperation with researchers in many non-EU countries.

COST Actions may cover any part of science. Therefore COST promotes knowledge production and knowledge sharing between research on the one hand and society and industry on the other. Society gains when it comes to policy-making in governmental and regulatory bodies, and the private sector in any kind of industrial production, for example in the forest products industries.

Another dimension which is highly emphasised in COST is the interaction between senior and junior researchers. We believe that there is much to be learned both ways and in interaction, leading to synergies. No doubt this is also very future oriented.

Cost aims at capacity building, and it builds on the bottom-up approach inviting researchers to submit ideas on any topic. Once a new COST Action is established any country is free to sign the MoU and appoint its members to the Action.

COST also puts gender balance into practice, for example through the way proposals are assessed, Actions are monitored and meetings are sought to be arranged in a family friendly way.

No doubt the nationally funded research projects are innovative, but through networking these projects COST enables boosting the innovation even further through synergies.

The knowledge sharing in COST enables participants in research projects to share knowledge in order to create a common understanding of problems at hand, and to coordinate activities. This applies to information seeking, interpretation, analyses etc. including timing and sequencing of research tasks and reporting.

A main reason for public funding of research at national levels is the fact that research projects often involve a higher risk than what the private sector is willing to accept. In this context it should be noted that an important outcome of knowledge sharing is the substantial reduction of risk.

Innovations often seem to arise from synthesis and re-combination of spread pieces of knowledge. These are pieces already existing here and there, and which may serve quite new functions when put together in new and innovative ways.

Transfer of knowledge is a main key to human’s success – from old to young, from skilled to less skilled, building up common knowledge.

Therefore, what is typical for knowledge sharing is that synergies arise. It is only the synergies from cooperation that makes research projects and COST Actions legitimate for EU funding.

Since knowledge sharing leads to synergetic innovation it is now high time that we get rewarded not only for what we know, but for what we actually share!

Some COST Action examples

COST Action FP0901: Analytical Techniques for Biorefineries

Trees, annual and perennial plants, recycled fibres, and lignocellulosic side streams from forest and agroindustry are renewable resources for the development of natural materials, biochemicals, and bioenergy. The chemical complexity of plant materials, the feed material of Biorefineries, renders the analyses of the feed constituents, processes, and valorised products challenging. The main objective of the Action is to develop new and evaluate existing analytical methods related to forest-based and agroindustrial Biorefineries. Thus, the Action covers the analytical methods for the Biorefinery feed material and for processed biochemicals, biomaterials, and process residues. Especially analytical pretreatments will be evaluated. Critical steps are the representativeness of the sampling and samples, the extraction, fractionation, and sample storage methods applied. New methods will be applied and evaluated for their relevance. Other emphasised areas will be development of analytical on-line applications, hyphenated techniques, and applying statistical multi-component analyses to sort out the relevant data from the main data stream. The European forest-based, bioenergy-based and agroindustrial industries will benefit from the Action in receiving relevant information on their developments of sustainable and environmentally benign solutions for novel utilisation of renewable resources. The development of analytical tools will lead to cost effective and sustainable processes and products.

COST Action FP1003: Impact of renewable materials in packaging for sustainability – development of renewable fibre and bio-based materials for new packaging applications.

Paper and board are made from renewable resources and are low carbon footprint materials, therefore giving them an environmental advantage compared to other materials. However, in packaging applications, paper and board are nearly always used in combination with non renewable materials; e.g. barrier materials derived from oil based plastics or aluminium. To give the forest industry a competitive edge this Action will focus on packaging solutions based entirely on renewable resources in order to remove the serious disadvantages associated with future paper and board packaging solutions that continue to rely on non renewable materials. The Action will explore possibilities that the forest itself can offer as a raw material base for different components within a given package, thus exploring the full potential of the fibres. The Action is an opportunity and a strategic objective for the forest sector value chain and will reduce environmental impact thus making it of potentially great importance for contributing to European policy. To fully understand the benefits it is important to assess the solutions from a sustainability point-of-view taking account of the total packaging value chain. That is why the Action also addresses research in e.g. value chain efficiency, end-of-life and supply of raw material.

COST Action FP1105: Understanding wood cell wall structure, biopolymer interaction and composition: implications for current products and new material innovation

The primary objective of the proposed Action is to build knowledge and understanding of fundamental physical (self assembly) processes and biological systems (e.g. genetic control) that drive natural structures and biopolymer composition within the plant/wood cell wall and to use new knowledge of self assembly processes to support the development of new biopolymer based materials. The Action also aims to quantify the impact of new knowledge on our understanding of the mechanical properties of the cell wall and how processes such as pulping, bleaching recycling, cell wall disintegration methods and ongoing tree improvement and biotechnology programmes impact both positively and negatively on structure and composition of the cell wall. The intent is to explore how this knowledge can be used to support ongoing improvement in these areas of activity. An overarching goal is to develop multidisciplinary competence and capability to support these objectives and to work closely with commercial organisations to promote effective dissemination of knowledge and the development of a more economically sustainable Forest Based Sector.

The future role of COST in the European Research Area (ERA)

The COST strategy concentrates strengthening its current key features and on four strategic goals: best performance in its implementation; orienting COST Actions on output; improving cooperation within COST countries and beyond; and ensuring good governance.

The goal with regard to best performance is to remain the most efficient and user-friendly research networking tool for scientists in the ERA. To achieve this COST will agree easy and clear common guidelines for applicants; adapt Action objectives and evaluation criteria to its mission; ensure adequate financial support of Actions; have user-friendly software tools guiding its entire process; clearly define roles and responsibilities of COST's decision-making bodies; and annually evaluate its processes to scope further improvements.

In order to develop the output orientation COST will have key performance indicators linked to objectives;·follow-up completed Actions, with regular impact analysis; design an ambitious dissemination strategy; develop concepts and criteria for strategic activities; and interact strongly with other forums.

Better cooperation within COST countries will be achieved by linking research excellence in Europe; providing networking opportunities for early career researchers; enhancing training prospects for innovative minds; and by delivering support for further coordination of COST countries' national research and innovation policies. In addition COST will be open to scientists from all over the world; develop tailored activities for neighbouring countries; maintain a dialogue with international organisations (such as the OECD, UN, WHO and UNESCO) on topics of mutual interest; and ensure its strategy complements the strategic European framework for international science and technology cooperation.

Good governance will be achieved through simplifying COST rules and procedures to support researchers' needs; implement light-touch and more efficient mechanisms for management and monitoring of COST Actions; clarify responsibilities to ensure a proper sense of ownership of its activities and Actions; and enforce clear commitment to the COST Code of Conduct and the values it expresses.

Finally, in line with the COST Mission and the COST Strategy outlined above, also the COST Position Paper "The COST Framework – A Cornerstone of the ERA", the CSO has recently prepared an Action Plan to "especially contribute by networking and supporting young promising teams in the field of Research and Innovation and contribute to widening pan-European participation, while reinforcing cooperation with near neighbour countries based on mutual benefit.

References

The article is based on the brochure About COST 2012–2013, official COST documents and a presentation given by the author in the European Parliament 7 September 2011.

Understanding wood cell wall structure, biopolymer interaction and composition: implications for current products and new material innovation

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Abstract

The paper outlines a new Cost Action (FP1105) which aims to build our knowledge of fundamental physical processes that drive natural structures and chemical composition within the cell wall and explore how we can use natural self assembly processes to develop new biopolymer based materials. The Action also aims to explore how new knowledge of biopolymer structure and composition of the cell wall can be used in the short medium term to support improvement in existing forest products processes including biorefinery. A further aim is the development of a new platform for the development of new biopolymer based materials. It is also anticipated that new knowledge will lead to improvement in tree breeding and biotechnology programs that support the forest based sector.

Introduction

For several decades scientists have looked at the structure and biopolymer composition of the wood cell wall and the role it plays in the properties of plant fibre-based materials such as solid wood, paper and composites. Despite this work, there are still a number of gaps in our understanding. As an example, a recent paper by Turner et al. 2011 highlighted a new approach to viewing the crystalline cellulose structure of plant cells, that has provided new insights into the architecture of the wood cell wall. The work indicates a complex, fractal cell wall structure in many timber species.

The pulp and paper and broader forest products industry, is under increasing pressure to add value, not only to the primary product of manufacture but also to utilize the residuals in higher value applications. This has led to the evolution of a bio-refinery concept, which requires an “in depth” characterization of a complex package of biopolymers and to understand the processes required to extract different components. Interest in the development of wood as a bio refinery feedstock has led to advances in our understanding of cell wall ultra-structure and biopolymer composition. However, as our knowledge improves there is an increasing awareness that there is much still to learn. Further complexity is added by a poor understanding of how primary industrial processes influence and change cell wall ultra-structure and overall composition, these processes may alter the assembly of the biopolymers in unintentional ways that lead to suboptimal extraction and utilization of the residual material in whole tree utilization processes.

Within the field of biochemistry and genetics there is a growing understanding of some of the factors under genetic control but in other instances, it is clear that there is still a poor understanding of the incredibly complex phenotype (at the cell wall level). Without this understanding, it is impossible to determine the relative contribution of genes, environment and the underlying physical processes in determining the structure, and composition of the cell wall. A hypothesis has been proposed (Turner et al., 2011) that the fractal structure of the tree and the cell itself, along with the majority of biological and inorganic materials that are allowed to self assemble (in what is traditionally seen as a thermodynamically driven process of diffusion limited aggregation), is driven by the underlying fractal structure of space-time. This concept, has gained considerable momentum through parallel and independent research programs in theoretical physics (Nottale and Auffrey (2008). The principle has been demonstrated through the use of a modified Schrödinger equation to model biological functions (morphogenesis, duplication, multiscale hierarchy of organization etc.) and the ubiquitous fractal structures found in biological systems and the physical world. The hypothesis states that these structures are influenced by quantum mechanics and the fundamental geometric structures of space-time in a way that we are only just beginning to understand. The physics underlying this work is already providing new, fundamental insights into the nature and structure of matter.

The new COST Action is aimed at trying to improve our understanding of the multidisciplinary challenges highlighted above.

COST Action structure

The COST Action is divided into three working groups illustrated below (Figure 1).

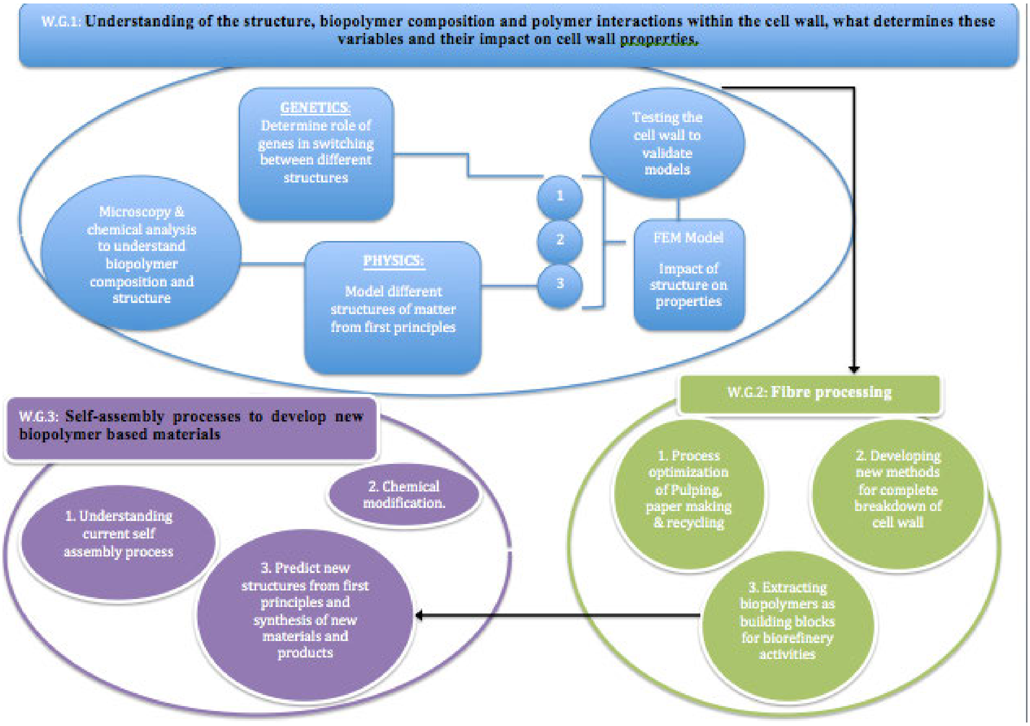

Figure 1. An outline of the three working groups and the key work activities to be included in the Action.

Working group 1: Understanding of the structure, biopolymer composition and polymer interactions within the cell wall, what determines these variables and their impact on cell wall properties

This work will start with the latest findings on the structure of the wood cell wall, which reveal a common link with the structures of a broad range of biological and inorganic materials.

One of the objectives of the working group will be to test the hypothesis, that many “biological structures” are driven by fundamental physical processes, rather than “complex biological systems”, which can be modeled from first principles using quantum mechanics. A second hypothesis to be tested is that the role of genes is to “switch” between different “physical processes” rather than driving the underlying structures we observe in biological systems (A principle first proposed by Erwin Schrodinger in 1943). Working group 1 will focus on collaboration between physics, biochemistry, genetics, analytical chemistry and microscopy to develop a better understanding of, genes, enzymes, macromolecules and environmental factors controlling cell wall formation. It is anticipated that this in turn may assist in the development of more focused breeding and genetic improvement programs.

The key aim will be to develop a collective understanding of the role of fundamental physical processes in defining cell wall structure, composition and biopolymer interaction. This work will include the development of improved models of nano-scale and cell wall structures from first principles that could lead to improved prediction of the characteristics wood, pulp and paper, and other wood based materials properties. As an example, the classical model of a highly oriented S2 layer and its impact on issues such as wood strength, stability and creep needs a re-think. Structural studies will focus on Finite Element Modeling (FEM) of the cell wall, including the interaction of the cellulose skeleton and amorphous biopolymers to better understand the physical properties of the cell. FEM studies will be validated through a program of testing of macro, micro and nano-scale structures for fibrils, cells, paper and small clear wood samples.

Working group 2: Fibre Processing

The second focus area involves using the combined knowledge developed in working group 1 to support ongoing improvement in three key areas of interest. These include:

- Improving existing processes such as pulping, recycling and papermaking. There will be a particular focus on how existing processes impact on biopolymer composition and how they can be modified to improve quality and performance of the end products. There will also be a focus on how processes such as pulping could be improved to facilitate the better utilization of residual products such as hemicelluloses and lignin.
- Development of new or improved chemical, enzymatic and mechanical processes to break down the wood cell wall into individual biopolymers and monomers that can be used as bio-refinery feedstock.
- Investigation and ongoing development of fractionation technologies to look at separating and refining biopolymers into chemical building blocks that could be used for a range of downstream bio-refinery activities.

Working group 3: Self-assembly to develop new biopolymer based materials

This working group will look at developing self-assembly processes that could lead to the development of a platform of new biopolymer based materials and products. Work will include:

- Reviewing and sharing state of the art self-assembly processes. This knowledge will be used as a starting point for the development of new self-assembly processes.
- Functionalisation of biopolymers which can be used as building blocks in the development of new materials.
- Using new knowledge of the underlying physics driving self-assembly processes found in biological and inorganic materials as a theoretical platform for the development of new self-assembly processes. Materials scientists are currently focused on understanding and mimicking biological processes. Many biological systems may well turn out to be purely physical processes. Understanding how these systems work could lead to insights into the development of new self-assembly processes at molecular, nano-meter and macro scales.

The work program proposed is multidisciplinary and requires the development of a new multidisciplinary network and platform of synergistic competencies that can support innovation in both the growing and processing industries. This will be facilitated through workshops, training schools and scientific exchange as well as by supporting the development of multidisciplinary research proposals addressing the objectives of the Action.

COST Action FP1105 was officially started in May 2012 with the first workshop to be held in Stockholm on December 3rd and 4th 2012.

The success of the Action is predicated on participation of a wide range of scientific disciplines. The objective of this paper is to inform a broader audience and to encourage wider participation in the Action.

References

Nottale, L., Auffrey, C. 2008. Scale relativity theory and integrative systems biology: Macroscopic quantum type mechanics. Progress in Biophysics and Molecular Biology 97, pp. 115–157.

Turner, P., Kowalkczyk, M., Reynolds, A. 2011. New insights into the micro-fibril architecture of the wood cell wall. COST Action E54 Book. Fine Structure of Papermaking Fibres. ISBN 978-91-576-9007-4.

Genetically engineered (GE) forest trees as biorefinery raw materials – legislative and scientific status

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Towards Future Forestry

One main driver of future forestry is the increasing world population which recently (October 2011) exceeded 7 billion and it is expected to exceed 9 billion by 2050. Increasing population numbers combined with accelerated climate change including weather extremes, floods, droughts etc. (Nellemann *et al.* 2009) are predicted to increase the need for more food production. The current estimates of Food and Agriculture Organisation (FAO, http://www.fao.org/wsfs/forum2050/wsfs-forum/en/) indicated that food production must increase by 70% in the next 40 years and if more land is not available, 370 million people could be facing famine by 2050. This will also push new demands for forestry and productivity in the future.

According to the FAO report (2010) on Global Forest Resource Assessment, global forests cover 4 billion hectares i.e. 31 percent of the total land area. The total land area designated primarily for wood production has decreased by more than 50 million hectares during the last 20 years and the area designated for multiple uses has increased by 10 million hectares during the same period indicating that also the future forest area will have to serve multiple purposes, including conservation, recreation and wood production. Thus, there is a definite need for efficient timber production using marginal land which is not suitable for economically viable agricultural uses. In their opinion paper in 2002 Fenning and Gershenzon already emphasized the role of plantation forestry on a long-term basis to limit the harvest pressures on natural forests and, furthermore, they suggest biotechnology tools to be applied to tree improvement processes in order to save time.

Bioeconomy / Biorefineries – The Players of Future Forestry

According to the EU White Paper (2011) “The European Bioeconomy 2030”, bioeconomy, including biorefineries as key components, refers to sustainable production and conversion of biomass into a range of food, health and fibre as well as industrial products and energy. Today, world economies are faced by the urgent need to find alternatives to the decreasing fossil fuel resources (especially oil and gas). This means that more support will be directed at the use of renewable energy. The increasing support together with increasing price of oil or CO_2 will definitely lead to higher demand for wood energy, wood fibers and other bio-products such as bio-chemicals, bio-plastics, bio-fuels, food additives etc. derived from sustainable forestry (FPAC, The Forest Products Association of Canada, 2011). Thus, bioeconomy concept will provide multiple new production possibilities which will affect the whole forestry sector.

Genetically Engineered Crop Species

Genetically transformed crops, also called biotech crops, have a 16 years track record of commercial deployment with a cumulative area of over 1 billion hectares planted by 2010 and a total area of 160 million hectares planted in 2011 (James 2011). This makes GE crops the agricultural technology with the highest ever adoption rate and farmers from 29 countries, the global economists and researchers are reporting multiple economic and environmental benefits. At the same time, numerous scientific studies have not found any incidence of harm. Also the preliminary information on the year 2012 (ISAAA press release in August 17, 2012) indicates that US farmers continue to demonstrate overwhelming trust and confidence in biotech crops and the global adoption of biotech crops is expected to continue to grow particularly in developing countries. Furthermore, the EU publication "A decade of EU-funded GMO research under the Framework programmes 2001–2010" describes 50 research projects including 400 research groups, funded by 200 million Euros. In these projects the focus was on science, safety aspects, environmental impacts and risk assessments of genetically modified organisms (GMOs) and the main conclusion was that biotechnology, and in particular GMOs, are not *per se* more risky than e.g. conventional plant breeding technologies.

Genetically Engineered Forest Trees – the History of 25 Years

The first report on GE forest tree species *Populus alba* × *grandidentata* was published in 1987 by Fillatti *et al.* The transformation was done using *Agrobacterium tumefaciens* and neomycin phosphotransferase (*nptII*) as a marker gene and the bacterial 5-enolpyruvyl-shikimate-3-phosphate (EPSP) synthase gene (*aroA*) conferring herbicide tolerance. Since then the transformation protocols have been developed and/or improved for several coniferous and deciduous tree species. Moreover, several new genetic transformation applications (e.g. artificial miRNA, virus induced gene silencing, targeted mutagenesis) are or will be included in the methodological toolbox of forest trees.

Compared to crop plants forest trees may still be considered undomesticated. They are characterized by cross pollination, long generation intervals, long vegetative periods and many of the economically important species are wind-pollinated. Generally, the conventional tree breeding strategies are based on selection of "plus trees" and establishment of seed orchards etc. However, the genetic improvement is limited compared to genetic engineering which is fast and can be designed specifically to end-use purposes. GE trees are also well suited to the already adopted plantation forestry practices and management procedures. To investigate GE trees under natural environments, the trees need and are evaluated in the science-based field trials. Globally, more than 10 tree species have been tested in over 700 field trials. In these trials no negative GE tree specific ecological or health effects have been found (Walter *et al.* 2010). Moreover, in China commercial transgenic poplar plantations along with conventionally bred varieties have been established. The total area of the plantations is 300 to 500 hectares including more than 1.4 million Bt-trees conferring insect resistance. The oldest trees are already 15 years old. Up to date no harm for the environment has been found. This is important information because outbreaks of forest insect pests damage around 35 million hectares of forest annually, primarily in the temperate and boreal zones (FAO report on Global Forest Resource Assessment, 2010).

In the case of GE trees, as in the case of all new technologies, the potential risks and benefits must be identified and quantified. Transgene technology could contribute to preservation of the natural forest and to reduction of deforestation of large areas. However, due to the long life cycles of trees and their particular significance in many terrestrial ecosystems, concerns of potential impacts of transgenic trees have been raised. The public concern is especially focused on potential uncontrolled spread of transgenes via vertical or horizontal gene transfer as well as on pleiotropic and unintended effects on non-target organisms.

Cost Action FP0905

Research on biosafety of GE trees has been initiated in several European and non-European countries and numerous field trials have been used for the science based evaluation. Results of these studies are, however, scattered or difficult to access and there is a need to put together the already existing information. This was also the reason to propose the Cost Action FP0905 Biosafety of transgenic trees: improving the scientific basis for safe tree development and implementation of EU policy directives. The chair of the action is Dr. Cristina Vettori (Italy), the vice chair is Dr. Matthias Fladung (Germany) and the COST Science Officer is Melae Langbein. The main objective of the Cost Action is to evaluate and substantiate the scientific knowledge relevant for biosafety protocols of GE trees by putting together the already existing information generated in various European and Non-EU Countries. This work provides basis for the future EU policy and regulation for the environmental impact assessment and safe development and practical use of GE trees. The activities of the action is arranged in four working groups in which WG1 covers biological characterization of GE trees, WG2 deals with environmental impact assessment and monitoring of GE trees in the whole production chain from plantation to final products, WG3 focuses on socio-economic implications and recommendations for the use of GE trees and WG4 is responsible on management of intranet – internet websites and dissemination (http://www.cost-action-fp0905.eu/).

Legislation

EU legislation

In EU all research and commercial applications using GE methods have to be approved in advance. In case of research and field trials this is done by national authorities of a given Member State (MS). Commercial cultivation (placing on the market) is authorized by a qualified majority decision in the EU regulatory committee composed of MS representatives. The Directive 2001/18/EC of the European Parliament and of the Council on the deliberate release into the environment of genetically modified organisms regulates field trials and placing on the market (import, processing and cultivation) of GMOs. The Directive gives guidance on risk assessment, risk management and monitoring of GMOs. Directive 2009/41/EC of the European Parliament and of the Council on the contained use of genetically modified micro-organisms regulates laboratory research. In Finland, the national Gene Technology Act (377/1995) implements these two directives. Moreover, the national Gene Technology Act also regulates laboratory and greenhouse research carried out with plants and animals.

The main task when preparing a GE application, be it for research or commercial purposes, is environmental risk assessment. The principles of risk assessment are the same as for e.g. chemicals risk assessment.

- Identification of characteristics which may cause adverse effects
- Evaluation of the potential consequences of each adverse effect, if it occurs
- Evaluation of the likelihood of the occurrence of each identified potential adverse effect
- Estimation of the risk posed by each identified characteristics of the GMO(s)
- Application of management strategies for risks from the GMO(s) (in case of field trials and commercial cultivation)
- Determination of the overall risk of GMO(s).

The applicant provides all necessary information of the GE application, the used organisms and the release site ecosystem, including climate, flora and fauna. The applicant carries out the risk assessment and the authorities evaluate and approve the assessment. The EU regulation identifies some potential adverse effects of GMOs. Environmental adverse effects could include effects on the dynamics of populations of species in the receiving environment and the genetic diversity of each of these populations. Also effects on biogeochemistry (biogeochemical cycles), particularly carbon and nitrogen recycling through changes in soil decomposition of organic material would be considered as adverse effects.

The EU legislation does not include specific guidance on how to carry out risk assessment of GE trees.

International agreements and guidance

The Cartagena Protocol on Biosafety (hereafter Protocol) is an international agreement on biosafety as a supplement to the Convention on Biological Diversity. The Protocol seeks to protect biological diversity from the potential risks posed by living modified organisms (LMOs) resulting from modern biotechnology. In accordance with the precautionary approach, the objective of the Protocol is to contribute to ensuring an adequate level of protection in the field of the safe transfer, handling and use of LMOs that may have adverse effects on the conservation and sustainable use of biological diversity, taking also into account risks to human health, and specifically focusing on transboundary movements. The Protocol entered into force in 2003. Each Party implements the Protocol in their national legislation.

During four last years there has been intensive work on the development of risk assessment guidance under the Protocol. This guidance includes a risk assessment roadmap, specific guidance on different types of LMOs and guidance on monitoring. This guidance and its status will be discussed in Hyderabad, India in October 2012 where the 6th Conference of the Parties to the Convention on Biological Diversity serving as the meeting of the Parties to the Protocol meets. This guidance includes specific guidance on risk assessment of GE trees.

OECDs Working Group on Harmonization of Regulatory Oversight in Biotechnology (hereafter Working Group) works to ensure that the information used in environmental risk/ safety assessment of GE organisms, as well as the methods used to collect such information, is as similar as possible among countries. Its aim is to improve mutual understanding, increase the efficiency of environment risk/safety assessment and avoid duplication of effort. It also reduces barriers to trade. The most important current projects include e.g. environmental considerations to be taken aboard an environmental risk assessment process. The Working Group has prepared several biology publications on different tree species.

References

Cartagena Protocol on Biosafety to the convention on biological diversity (2003).

Consensus Documents for the Work on Harmonisation of Regulatory Oversight in Biotechnology: Biology of trees: Norway spruce (Picea abies); White spruce (Picea glauca); Poplars (Populus spp.); Sitka spruce (Picea sitchensis); Eastern white pine (Pinus strobus); European white birch (Betula pendula); Jack pine (Pinus banksiana); North American larches (Larix lyalli, L. occidentalis, L. larciana); Western white pine (Pinus monticola); Douglas-Fir (Pseudotsuga menziesii); Lodge pole pine (Pinus contorta); Black spruce (Picea mariana). http://www.oecd.org/env/chemicalsafetyandbiosafety/biosafety-bio track/consensusdocumentsfortheworkonharmonisationofregulatoryoversightinbiotechnology.htm.

Directive 2001/18/EC of the European Parliament and of the Council on the deliberate release into the environment of genetically modified organisms and repealing Council Directive 90/220/EEC.

Directive 2009/41/EC of the European Parliament and of the Council on the contained use of genetically modified micro-organisms.

EU White Paper, 2011. The European Bioeconomy 2030.

FAO, 2010. Global forest resources assessment 2010. FAO Forestry Paper 163, Rome http://www.fao.org/docrep/013/i1757e/i1757e.pdf.

Fenning, T.M., Gershenzon, J. 2002. Where will the wood come from? Plantation forests and the role of biotechnology. Trends Biotechnol 20, pp. 291–296.

Fillatti, J.J., Sellmer, J., McCown, B., Haissig, B., Comai, L. 1987. Agrobacterium mediated transformation and regeneration of Populus. Mol Gen Genet 206, pp. 192–199.

FPAC, 2011. The new face of Canadian forest industry. The emerging bio-revolution. The Biopathways project. http://www.fpac.ca/publications/BIOPATHWAYS%20II%20web.pdf.

James, C. 2011. Global status of commercialised biotech/GM crops: 2011. ISAAA Brief No. 43, ISAAA, Ithaca, New York.

Nellemann, C., MacDevette, M., Manders, T., Eickhout, B., Svihus, B., Prins, A.G., Kaltenborn, B.P. (Eds.). 2009. The environmental food crisis – The environment's role in averting future food crises. A UNEP rapid response assessment. United Nations Environment Programme, GRID-Arendal. http://www.grida.no.

Walter, C., Boerjan, W., Fladung, M. 2010. The 20-year environmental safety record of GM trees. Nat Biotechnol 28, pp. 656–658.

Used wood sorting, utilization and recycling in different value chains

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Abstract

Wood waste generated from end of life products forms a significant source of wood material. Estimations of 29.6 Mm3 of recovered wood to be utilized in 27 countries in Europe and the additional potential of at least 52.5 Mm3 exist (COST E31 & UNECE document). Remarkable share of the identified resource is either not recycled at all, or is used in a low value applications.

DEMOWOOD project *Optimisation of material recycling and energy recovery from waste and DEMOlition* WOOD in different value chains is introduced. It is part of WoodWisdom-Net Research Programme *Sustainable, competitive processing and end-use concepts for forest-based industries*. In DEMOWOOD, recovered wood includes all kinds of wooden material available at the end of its use as a wooden product. General aim of the project is to investigate valorization concepts for increasing the added value of waste wood in value chains for pulp production (TMP) for paper products, for particle board production, for CHP plants and for liquid biofuels production. Project results will help in saving the forest resource and increasing the use of a renewable re-source, in reducing the GHG emissions in the materials and in energy sectors and in reducing the environmental impact of waste wood management. Project coordinator is Institut Technologique FCBA. Work package specific objectives are presented.

Introduction

Wood is a material which is in very wide use in Europe. It is used in large quantities in many different sectors and is a part of our everyday lives. Wood waste generated from end of life of wooden products forms a significant source of wood (also called as post-consumer recovered wood).

COST Action E31, “Management of Recovered Wood”, presented its findings on the amounts of recovered wood available over twenty European countries. A summary of these findings is presented in Table 1.

Table 1. Results of a survey conducted by COST Action E31 (Merl et al., 2007).

	Quantity (ton/year)
Reuse	535 142
Recycling	10 872 383
Energy	9 996 395
Composting	916 822
Others, unknown	4 147 127
Landfill	3 125 083
Total	**29 592 953**

Based on COST E31 findings, estimations are quoted in the UNECE document (Hetsch, 2009): 28.6 million m^3 of recovered wood are estimated to be utilized in 27 countries in Europe and the additional potential is estimated to be at least 52.5 million m^3. Recovered wood is the largest potential source for additional wood supply for society growing needs if native forest is not accounted (which is the main wood supply). Remarkable share of the identified resource is either not recycled at all, or is used in a low value applications.

One of the great advantages of wood is that it can be recycled several times before, eventually, being disposed of by incineration with energy recovery. The price of recovered wood has been increasing every year throughout Europe.

The particleboard industry is a traditional user of industrial wood residues and recovered wood. This sector is experiencing increasing competition for its raw material supply, mainly from the fast growing green energy generating sector. The harsh raw material competition forces the European wood-based panel industry to search for new material sources and the waste wood becomes, more than before, an industrial material source. In the six main European countries over 30% of the raw material is coming from recovered wood in the particleboard production.

The pulp industry is not using recovered wood up to now, because in many cases the purity requirements for the pulping process and for the paper quality and for characteristics have stopped its use as a raw material. Recovered wood may be contaminated and contain non biomass materials.

The biomass energy field is the fastest growing sector among the wood users. The European and member states policies are strongly supporting the development of renewable energies and namely of biomass energy. The European Committee for Standardization has published 27 technical specifications regarding solid biofuels between 2003 and 2006, and they have been upgraded recently to EN-standards; the most important ones are regarding classification and specification of solid biofuels (wood chips and hog fuel) (EN 14961). However, demolition wood, which is in the scope of DEMOWOOD project, is not included in EN 14961. The EU-project BioNormII (2009) has addressed the issue of waste wood classification in the context of EN 14961 – part 1. The results of BioNormII will be in benefit in DEMOWOOD project, where the issue is addressed more on a conceptual level.

There are million tons of waste wood which are disposed by landfilling or incineration, or combusted without efficient energy recovery. These generate environmental impacts and can even reduce the positive environmental profile of wood product. Increasing the level of material recycling and energy recovery from recovered wood is today, to a very large extent, a regulatory objective and a European wide public policy.

DEMOWOOD project

DEMOWOOD project *Optimisation of material recycling and energy recovery from waste and DEMOlition WOOD in different value chains* received its funding through 2nd Joint Call for Research and Development Proposals within the WoodWisdom-Net Research *Programme Sustainable, competitive processing and end-use concepts for forest-based industries*

Project started in January 2011 and will end in December 2013. Total budget of the project is 1 750 k-€ of which public funding 900 k-€.

In DEMOWOOD, the main sources of recovered wood are packaging materials, demolition wood, timber from building sites, and fractions of used wood from residential, industrial and commercial activities.

General aim is to investigate valorization concepts for increasing the added value of waste wood in value chains for:

- pulp production (TMP) for paper products
- particle board production
- CHP plants and liquid biofuels production.

Project results will help in saving the forest resource and increasing the use of a renewable resource, in reducing the GHG emissions in the materials and in energy sectors and in reducing the environmental impact of waste wood management.

Driving force for the project is that 25% of the identified resource is either not recycled at all, or has a low-value use. Additional potential is estimated to be at least 52.5 Mm3 of recovered wood (Hetsch, 2009).

Project coordinator is FCBA (French Institute of Technology for forest based and furniture sectors). DEMOWOOD is structured according to Figure 1:

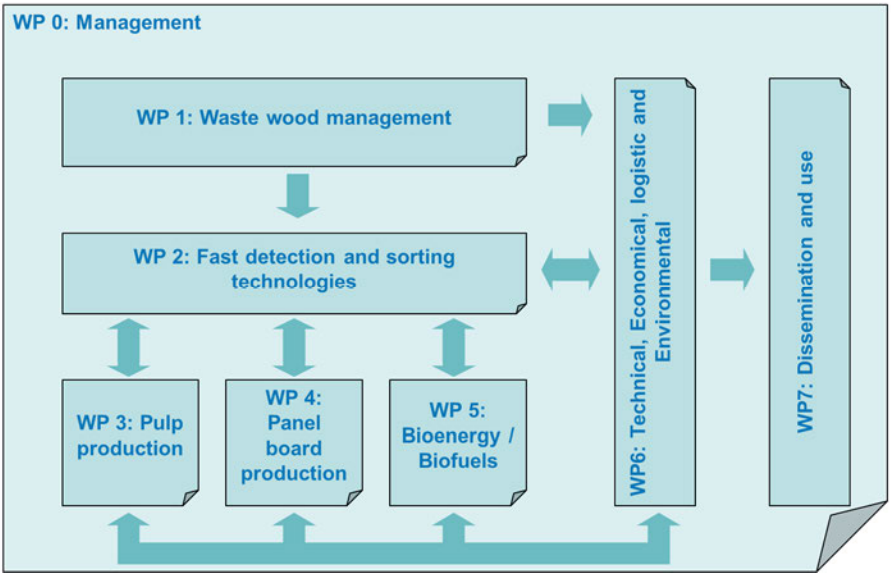

Figure 1. DEMOWOOD project structure.

Work packages in DEMOWOOD

Waste wood management inventory

Work package 1 *Waste wood management inventory* objective is to obtain an overview about the waste wood sources in Finland, France, Germany, Switzerland and Austria.

Waste sources considered are the construction / demolition sector, and end-of-life furniture. Both the original sources of waste wood, and the present management practices by the waste management sector, are analyzed.

A typology of waste wood is defined, to characterize the different types of sources in terms of material and chemical contamination, amounts available and collected; localisation of these sources, price levels and logistics of collection are also estimated. The types and classes of waste wood as sorted presently by the waste management actors will be characterized in the same way.

The national classification systems (legal, normative and industrial practices) will be recorded and analysed and suggestions for harmonisation and rationalisation of classification systems at European Scale is made.

Fast detection and sorting technologies

Work package 2 *Fast detection and sorting technologies* focuses on evaluation of detection and sorting technologies in the range of waste wood recycling.

Special focus is on the needs of paper industry, panel production and energy recovery. Together with other work packages also the requirements arising from recycling and energy recovery (including bio-fuels) are evaluated, as well as the current adequacy of existing technologies. Based on this, better or new solutions are searched for performing the sorting and detection processes.

Enhanced separation of metal particles is also evaluated as the detection of emissions of formaldehyde, VOC, PCB and lindane. The project partners will look for fully new ways of detection and sorting technologies and make recommendations for new developments.

Mechanical pulp production

The recovery and the sorting of wood wastes delivers raw materials to be used as furnish for the production of thermomechanical (TMP) fibres.

The objective of the workpackage 3 *Mechanical pulp production* is to demonstrate the interest of introducing such raw materials in a conventional TMP process and to determine the impact on the pulping process, on the pulp quality, on the pulp bleachability and on the generated effluents.

Maximum content of wood wastes into conventional wood used in TMP process that does not affect the process is determined.

Panel board production

Particleboard production of Germany and France together reached in 2008 almost one third of the whole European production.

German particleboard producers and recycling companies, as operators of waste treatment installations, have to apply the German “Ordinance on the Management of Waste Wood”. According to this directive for the production of particleboards, only certain categories of waste wood are permitted (A I and II). These categories contain wood in its natural state (only mechanically treated and most insignificantly contaminated with foreign bodies), or bonded, painted, coated, lacquered or otherwise treated wood with no halogenated organic compounds in the coatings and no wood preservatives (A II). In practice, the coatings of category A II to A IV (A III: contaminated with halogenated organic compounds; A IV: treated with wood preservatives) are difficult to distinguish in the plant, so that for safety reasons the producer rejects the material from all three categories.

Aim of work package 4 *Panel board production* is to largely increase the amount of recovered wood from categories A II to A IV, fulfilling the conditions set in the regulations for producing particleboards. The innovative idea is to consider all recovered wood (A II to A IV) being the same, and process it through a cleaning system which breaks the wood down to particles of medium size and sort clean wood chips out, as well as to produce other more contaminated fractions for other uses. On all wood treatments, which are applied on the top surfaces of the wood, an envelope of treated wood is formed. Once chipped into smaller particles, the chips will either be free of treatment or be contaminated.

Traditionally used separation techniques and newly developed technologies (WP 2) are tested to obtain the highest amount of clean wood from the recycling process.

Bioenergy and biofuels

The behaviour of used wood as a fuel is in principle similar to that of clean wood. Used wood is often dry, thus the net calorific value can be higher than for common fresh wood fuels (e.g. bark). Used wood (i.e. waste wood) has higher amount of contaminants, which may accelerate deposits in the boiler as well as corrosion, as well as change the composition of ash. Thus the development of sorting practices and advanced processes to upgrade used wood is critical.

The quality of shredded used wood has improved significantly compared to previous production process (only shredding and magnet) and is approaching the quality of clean wood fuels. In Finland shredded used wood can be classified as clean biofuel (out of the waste fuel class) based on the limit values presented in the report of the Finnish Technical Research Centre (VTT-R-04989-08).

Objectives of the work package *5 Bioenergy and biofuels* are:

- Determination of the combustion characteristics of waste wood in pilot scale experiments and assessing combustion alternatives
- Determination of the suitability of waste wood to biotechnical ethanol production in laboratory scale experiments and production of data for the model of ethanol production and feasibility evaluation
- Recommendations for improvement of quality of waste wood for fuel handling and efficient combustion.

Technical, economic and environmental assessments

The objectives of work package *Technical, economic and environmental assessments* are:

- To generate and select end of life waste wood utilization pathways according to the project scope
- To look at sustainability for the selected pathways, especially taking into account material recycling, energy recovery and economics
- Further, the effects of logistical aspects are considered. Environmental benefits for selected pathways are evaluated based on Life Cycle Assessment (LCA) principles.

Different pathways for sustainable utilization of end of life waste wood are created according to project scope. They are based on common practices today and on efficient techniques handled in other work packages. The target is to improve material recycling and energy recovery. Especially pathways to paper products and to wood panels, and issues of energy recovery are under consideration according to project scope. The most promising pathways are selected for further evaluation.

For the selected concepts process/mill level material and energy balances are created as input-output models. Material recovery and utility consumptions are considered. Direct costs and income estimates on the basis of the created models are calculated.

Different waste wood utilization pathways with the concept specific reference level, and with the possible concept alternatives, are compared by using specific mill level key figures. Profitability comparison is based on direct costs (investment costs can be considered, if information is given by project partners) and sensitivity for the main cost components will be studied.

The environmental assessment is carried out based on LCA principles. Parameterized database based on the data collected is created. Sensitivity analyses are performed on the following aspects: The influence of parameters linked with logistics (truck load, truck consumption, transport distances between the different sorting, treatment and recycling sites), the relevance of local utilization of waste wood and the importance of taking into account temporary carbon storage in the calculation of greenhouse gas effect depending on the number of years the carbon is stored.

Acknowledgements

Partners in the project are from Germany, France and from Finland. Institutes and industries are listed below. They all are active members of DEMOWOOD project, and participating in the work. The material presented here is based on project plan and on contribution of all the partners listed below, involving a large number of experts:

- Institutes: *Germany:* Papiertechnische Stiftung (PTS) and Fraunhofer-Institut für Holzforschung – Wilhelm-Klauditz-Institut (WKI); *France:* Institut Technologique FCBA and Centre Technique du Papier (CTP); *Finland*: VTT
- ➢ Industry: *Germany*: Entsorgungstechnik Bavaria GmbH, Schumann-Analytics Pfleiderer Holzwerkstoffe GmbH, TITECH GmbH and RTT Steinert GmbH; *France*: SITA Recyclage, Veolia and Norske Skog Golbey; *Finland*: Lassila & Tikanoja Oyj (L&T) and Finnish Wood Research (FWR).

References

1. BioNormII. 2009. Pre-normative research on solid biofuels for improved European standards. Project number 038644. 1.1.2007–31.12.2009. EU's 6th framework programme.

2. Hetsch, S. 2009. Potential Sustainable Wood Supply in Europe. Geneva Timber and Forest Discussion Paper 52. UNECE.

3. Merl, A., Humar, M., Okstad, T., Picardo, V., Ribeiro, A., Steierer, F. 2007. Amounts of Recovered Wood in COST E31 Countries and Europe. COST E31 Final Conference, Klagenfurt, May 2nd to 4th, 2007.

The Forest Refine project – development of efficient forest biomass supply chains for biorefineries[1]

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Abstract

The need for energy is continuously increasing globally, due to e.g. increases in industrialization and population. Unfortunately, petroleum is in danger of becoming short in supply within coming decades. In this paper existing and planned biorefinery initiatives in Sweden and Finland are identified and described. Standing volumes, annual growth and harvested volumes of forests in Sweden and Finland are described together with an overview of forest biomass supply chains. Raw material quality demands of biorefineries may differ from those of traditional forest industries and energy plants and efficient supply chains for the provision of biorefineries with forestry biomass have to be designed and developed. The Forest Refine project is a Swedish/Finnish cross-border co-operation working to improve the whole forest supply chain. The participants have comprehensive knowledge about biorefining, forest energy supply chains and traditional forest supply chains.

Keywords: Forest biomass, wood biomass, bioenergy, biorefinery, fractioning, characterization, forest supply chains

Introduction

The global need for energy is continuously increasing as a result of, for example, increases in industrialization and population. Globally, petroleum is the single largest energy supply source, accounting for 33% of the total primary energy supply in 2009 [1]. The transportation sector consumed 62% of the oil products [1]. There is an awareness that petroleum is in danger of becoming short in supply within coming decades. It is estimated that 54 of the 65 major oil producing countries have already peaked in production and that others are close to their peak [2]. Sweden and Finland have already replaced most of the oil used for heating with biomass but more than 90% of the transports still rely on fossil oil import. As it stands now, it is more difficult to find renewable solutions for the transport sector than for heat and electricity production.

In Sweden and Finland, forest biomass resources have provided the basis for significant industrial activities for more than a century. Sawn timber products and pulp and paper products have dominated the use over a long time but the use of forest biomass for energy purposes has grown rapidly over the past decades. In the near future, the use of forest biomass in biorefineries is expected to increase. The infrastructure and supply chains of forest biomass that are present today have been developed mainly to supply the production of sawn timber, pulp, paper, heat and power and may therefore not be optimal for future biorefineries. Biorefineries will most likely be limited in size, because the relative bulky forest biomass must be transported economically from a limited supply area. The cost for harvest, transport, storing and handling of the biomass is of prime importance when calculating the overall cost for biorefining. Biorefineries are long term investments with several decades of expected operation time that will be affected by future changes in, for exam-

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ple, raw material costs, transport costs and end-product markets. Therefore, it is important to develop efficient forest biomass supply systems that are as robust as possible with respect to these uncertainties, and which can supply biorefineries with a sufficient amount of raw material at competitive cost.

The Forest Refine project is a Swedish/Finnish cross-border co-operation where the participants have comprehensive knowledge about biorefining as well as wood supply chains. It is run by BioFuel Region between January 2012 and April 2014. Swedish participants are BioFuel Region, Swedish University of Agricultural Sciences (SLU) and Processum Biorefinery Initiative. Finnish participants are Finnish Forest Research Institute (METLA), Centria University of Applied Sciences, Ostrobothnian Rural Institute and Kokkola University Consortium Chydenius.

Clusters, networks and research

Biorefinery-related research is conducted at almost all Swedish and Finnish universities and at research institutes such as **Innventia** (Sweden) and **VTT** (Finland). There are many biorefinery-related clusters and centres for coordination of research, development and innovation.

Swedish examples are: the **Biorefinery of the Future,** comprising industry, academy and society coordinated by **Processum biorefinery initiative,** located in Örnsköldsvik; **NumberOne** forest industry network centered in Sundsvall; **ETC (Energy Technology Centre)** in Piteå, focusing on thermochemical processes; **Swedish Gasification Centre,** with academic and industrial stakeholders within biomass gasification technology; **Swedish Knowledge Centre for Renewable Transportation Fuels (f3)** centre for the development of fossil-free fuels for transportation; **Wallenberg Wood Science Center** for research on new material products from forest is a joint initiative of the **Royal Institute of Technology (KTH)** and **Chalmers University of Technology**.

Finnish examples are: the **Finnish Bioeconomy Cluster FIBIC Oy** (previously Forestcluster Ltd) organising companies, research institutes and universities to implement a Strategic Research Agenda; **CEEN Ltd** (Cluster for Energy and Environment) coordinating industry driven energy and environmental research. FIBIC Oy and CLEEN Ltd are part of the **Strategic Centres for Science, Technology and Innovation (SHOK); Benet Bioenergy Network** with 6 expert organizations, administrated by the Benet Ltd; the **Forest Industry Future** cooperation between Finnish centres of expertise seeking new solutions for the industry, especially small and medium-sized firms; the **Energy Technology** cluster focusing on manufacturers of energy technology equipment.

Forest supply chains

The total standing stemwood volume of Swedish and Finnish forests is around 3 200 and 2 284 million m^3 (Mm^3), respectively. The annual growth is about 120 Mm^3 in Sweden and 104 Mm^3 in Finland. In average, the volume of all felled stems (including unharvested stems) was 90 Mm^3 in Sweden and 63 Mm^3 in Finland. Hence, the volume of standing stemwood increased by around 30 Mm^3 and 41 Mm^3, as an annual average, in Sweden and Finland, respectively. Almost all of the harvested roundwood is used domestically – only 1 Mm^3 is exported.

In 2010, 16 and 19 Mm^3 of wood, consisting mainly of bark and forest chips, was consumed in heat and power plants in Finland and Sweden, respectively. Additionally, 6.7 Mm^3 of wood was consumed by households, mainly as firewood, both in Sweden and in Finland. [3, 4, 5]

Harvesters are employed to fell, delimb and cross-cut the trees into pulpwood and sawlogs while forwarders transport the logs to the roadside. The logs are then transported to the pulp mills and saw mills by trucks. The harvest of energy biomass (logging residues, stumps and small diameter trees) is integrated with the harvest of sawlogs and pulpwood, which makes the production of energy biomass more cost-efficient. Typically, the collection and terrain transport of logging residues to the roadside is done in spruce dominated stands by modified forwarders. The logging residues are either chipped at the roadside and transported by trucks to the end-users (heating or combined heat and power plants) or transported as loose material to a terminal or an end-user and chipped there. Stumps are, typically, extracted by tracked excavators with purpose-built heads and transported to the roadside by modified forwarders, where they are stored for a couple of seasons and then transported by truck to the end user. Small diameter trees from early thinnings are cut by small harvesters and transported to the roadside by forwarders. The trees are either chipped at the roadside or transported to an end user and chipped there.

In the Finnish National Forest Programme, a goal has been set to increase the use of forest chips. The aim for annual use is 8–12 Mm^3 by the year 2015. In 2010, the Government's ministerial working group for climate and energy policy stated that the consumption of forest chips in heat and power plants is aimed to be increased to 12–13 Mm^3 by the year 2020 [3]. Although in Sweden no such target has been set, it is estimated that the annual consumption of forest chips in heating and power plants will be around 10 Mm^3 by 2020 (in 2010 it was 6 Mm^3).

Biorefinery initiatives in Finland and Sweden

This section reports on a survey of existing and planned biorefinery projects in Sweden and Finland. The information has partly been gathered from web pages and secondary sources, which may not always be up to date, and will be verified in forthcoming work of the Forest Refine project. A selection of projects is given in Table 1. A comprehensive list will be published in a work report [6].

The projects apply different technologies to separate wood components. Cellulose hydrolysis and ethanol technology has been demonstrated and is considered ready for larger-scale applications, but no such projects have been announced. Existing demo plants are seeking new forms for continued operation, or ending operations.

Seven out of totally eight Finnish and Swedish bioenergy projects that applied for NER300 investment grants (a financing instrument funded by emission allowances set aside in the "New Entrants' Reserve") were gasification projects and one project concerned pyrolysis of biomass. After the recent release of a prioritisation list for the NER300 grants, only one out of three Finnish projects appears to proceed with their plans. Further, Finnish UPM is pursuing a project in France.

A number of pyrolysis projects are underway, where the pyrolysis oil will primarily replace fuel oil but could in the future be upgraded to motor fuel. There are also projects for demonstration of biomass torrefaction – a pre-treatment of biomass to simplify long distance transports and processing. Torrefied biomass could replace fossil coal in existing power plants.

The pulp industry is active within the development of new biorefinery processes, for example to develop of pulp fibers into new types of materials and products (e.g. textiles, composite materials, nanocellulose etc.); upgrade residue streams to marketable products (black liquor gasification; lignin extraction, fermentation of hemicellulose; gasification or hydrolysis of fibre sludge); implement processes for co-production of process steam and marketable products (gasification, pyrolysis); extract useful substances from incoming raw material (hemicellulose pre-extraction). Tall oil from pulp mills is increasingly being used as feedstock for motor fuels and various chemicals.

Extraction of small-volume, high-value substances from wood is more of a niche area where some research and development is ongoing, concerning, for example, antioxidant substances and repellents for animals feeding on young trees. There is a growing interest from the chemicals industry to develop large-volume based chemicals from forest biomass.

Table 1. A selection of Swedish and Finnish biorefinery activities.

Project etc.	(1)	(2)	Description
Hydrolysis & Ethanol			
EPAB	D	S	Pilot plant for cellulosic ethanol production in Örnsköldsvik (~200 m^3/yr). Owned by Umeå University, Luleå University, SEKAB.
NBE Sweden	D	S	Development plant for cellulosic ethanol production in Sveg (3 000 t/yr). Owned by NBE Co. Ltd., HMAB, Härjedalen municipality.
ST1	P	F	St1 biofuels are currently producing ethanol from sugar- and starch-containing waste in several plants and are researching technology for ethanol production from cellulose.
Chempolis	D	F	Chempolis Ltd is an R&D company developing biorefinery technologies, specialised in non-food, non-wood raw materials. Has a biorefinery park in Oulu.

Gasification			
BLG DME DP1	S	S	Black liquor gasification demonstration plant. Pressurised (30 bar), oxygen-blown entrained flow gasifier (3 MWth) with a DME demo plant. Technology developed by Chemrec AB.
IVAB	S	S	Pressurised entrained flow wood powder gasification pilot plant (1 MW, 15 bar) in Piteå.
MIUN	S	S	Circulating fluidized bed, indirect gasification (150 kW) with fuel synthesis, Härnösand.
WoodRoll	S	S	Indirect gasification technology demo (150 kW) in Köping. Developed by Cortus.
Chalmers	D	S	A 2–4 MWth indirectly heated gasifier integrated on the return leg of a 12 MWth CFB boiler
Värnamo IGCC	D	S	IGCC demo plant (18 MWth). Planned rebuild for syngas production was cancelled. Mothballed.
NSE Biofuels	D	F	Neste Oil and Stora Enso built a wood gasification demo (12 MWth) in Varkaus. Syngas combusted in lime kiln. The aim was a commercial BTL plant, but it has not been prioritised for NER300 support.
Vaskiluodon Voima	P	F	140 MW gasification plant for CHP under construction in Vaasa
Vallvik biofuel	P	S	Planned black liquor gasification plant with methanol production at the Rottneros mill in Vallvik. Applied for NER300 support but has not been prioritised.
Rottneros biorefinery	P	S	Planned gasification plant for methanol production at the Rottneros mill in Rottneros. Applied for NER300 support but has not been prioritised.
WoodRoll Köping	P	S	Cortus is planning 5 MW gasifier with upscaling to 25 MW in a second step.
Hagfors	P	S	Planned fluidized bed gasifier for methanol production (1 000 000 t/yr) by Värmlandsmetanol. Uhde selected as technology supplier.
Norrtorp	P	S	Prestudy for 250 MW methanol and SNG plant by Värmlandsmetanol, EON, SAKAB and others.
GoBiGas	P	S	20 MW plant for SNG under construction by Göteborg Energi. An 80–100 MW unit is planned for a second phase. Has been prioritised for NER300 support.
E.ON Bio2G	P	S	SNG plant planned by EON, up to 200 MW. On the reserve list for NER300 support.
UPM Rauma	P	F	Planned gasification/FT plant in either Rauma (Finland) or Strasbourg (France). Strasbourg plant prioritised for NER300 support and Rauma plant on the reserve list.
Ajos BTL	P	F	Planned gasification/FT-plant. Metsä group recently withdrew from the project. Vapo Oy are pursuing the project and are seeking new partners. Prioritised for NER300 support.
Pyrolysis & Torrefaction			
Metso	D	F	2 MW pyrolysis R&D plant in Tampere.
Pyrogrot	P	S	Planned pyrolysis oil plant at the Billerud pulp mill in Skärblacka. Prioritised for NER300 support.
Fortum	P	F	Plant for pyrolysis oil production (50 000 t/yr) in Joensuu.
Green Fuel Nordic	P	F	Three facilities for pyrolysis oil production to be built. Expected output 270 000 t/yr.
BioEndev	D	S	Torrefaction demonstration plant planned in Umeå.
Torkapparater	D	S	Torrefaction demonstration project located on Gotland.
Preseco	D	F	Bio-char demonstration plant in Lempäälä.
Pulp-mill based			
Domsjö	P	S	Production of specialty cellulose, ethanol and lignin at industrial biorefinery site in Örnsköldsvik.
Södra Cell	P	S	Development of new materials such as specialty cellulose and composite materials. Lignin extraction from black liquor.
SunPine/Preem	P	S	Production of diesel (Evolution Diesel) from tall oil.
Arizona Chemicals	P	S	Production of a range of chemicals from tall oil.
UPM BioVerno	P	F	Planned tall oil based diesel (BioVerno) production facility in Lappeenranta.

(1) Demonstration/development (D) or production (P) plant. (2) Geographic location: Finland (F) or Sweden (S).

Discussion

The raw material quality demands of future biorefineries may differ from those of traditional forest industries and energy plants. This will have an influence on the raw material supply chains. Important parts of the supply chain include harvest, terrain transport and storage at landing, terminal handling and fractioning, characterization of different fractions, delivery and, finally, processing at the biorefinery. Forest biomass (the tree) can be divided into its tree parts (e.g. stemwood, bark and needles) and main chemical components (cellulose, hemicelluloses, lignin and extractives). The relative amounts of tree parts and chemical components vary within tree species and among different tree species depending on factors such as age and growing conditions. Extractives normally represent only a few percent of a tree, but may be a source of highly valuable chemical substances. It is thus of importance to utilize all the available raw material efficiently. It has been suggested that biomass should be utilized in a similar manner as crude oil; with large amounts of the biomass used as fuels, while smaller but economically significant amounts are further refined to products of higher value. Optimum use requires that the advantages and disadvantages of each type of forest biomass (e.g. stem wood, bark, foliage, stumps and roots of the different species) can be identified for each application. For example, in contrast to current heating plants, which often prefer a low share of fresh needles, a future biorefinery may prefer a high share of fresh needles to maximize the production of valuable chemicals.

The optimal technology and wood conversion process used as well as plant size will vary depending on the available local feedstock and the supply system used. If raw material is upgraded (by e.g. tree component fractioning) at a terminal, the raw material supply area can be increased thus allowing larger refining processes to take place. To avoid increased competition and biomass shortage, new biomass terminals, in which the biomass is fractionated into various assortments and supplied to different biorefineries, might be required to utilize every component of the biomass in the best possible manner.

The forest biomass resources are extensive in Sweden and Finland, but the supply chain has to be optimized for high cost-efficiency of the biorefinery processes. However, today it is not known what tree- and wood components will meet the demands of the whole biorefinery industry. Neither is it known how the logistical systems from the stump to the plant will affect the quality of the desired feedstock. It is the industry and the end product which will set the requirements on the physical and chemical composition of the forest biomass. The concept of biorefining covers a wide range of possible industrial activities, which is also reflected in the variety of development paths followed in current projects. Industrial complexes that utilize all components of a tree are plausible, as well as specialized industries that process only specific tree parts. It is also conceivable with an industry structure where the majority of the industries process by-products from a few types of industries that process primary forest raw material. Existing pulp mills or future large-scale biofuel plants are examples of candidates for such primary forest raw material processing industries. Each alternative biorefinery structure puts different demands on the raw material supply chain. The continued study of different supply chain and biorefinery options could help forest owners and biorefinery stakeholders in making the right priorities for the future.

The project's purpose is to analyze and improve the raw material supply to biorefineries. The idea with the project outline is to work with the whole supply chain from the forest to a biorefinery. This also includes calculation of potential amounts available for several decades in northern Sweden and Finland of different biomass components. This is vital information for the design and localization of a biorefinery.

References

1. IEA. 2011. Key World Energy Statistics 2011. Paris, France: International Energy Agency.

2. Aleklett, K. 2005. The Oil Supply Tsunami Alert', Association for the Study of Peak Oil and Gas (online). Available: http://www.peakoil.net/Aleklett/Oil_Market_Tsunami_Alert.pdf.

3. Finnish Forest Research Institute, 2012. Finnish Statistical Yearbook of Forestry 2011. Ylitalo, E., (ed.). ISBN 978-951-40-2330-9.

4. Finnish Forest Research Institute, 2010. Wood Fuel Used for Energy Generation 2010. Ylitalo, E., (ed.). Forest Statistical Bulletin, 2011, 7. ISSN 1797-3074 (In Finnish.)

5. Swedish Forest Agency 2011. Swedish Statistical Yearbook of Forestry 2011. ISBN 978-91-88462-95-4.

6. Joelsson, J.M., Tuuttila, T. The history and current development of forest biorefineries in Finland and Sweden. Work Report of the Forest Refine project. (Forthcoming.)

ForestSpeCs findings on byproducts of forest industry: could bark be more valuable than timber?

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Abstract

The EU-project FORESTSPECS provides research based biological and technical understanding and solutions needed for upgrading wood related residues and humic substances to value-added chemicals and materials. Only through such knowledge-based approach it is possible to develop innovative applications to the potentially huge variety of bioactive substances available in these by-products, currently considered as waste. These substances represent a rich source of aromatic and other complex structures, whose upgrading to value-added speciality chemicals and materials provides an opportunity to the forest sector to create new types of value chains. Application opportunities include medical, pharmaceutical, agricultural, and environmental remediation uses.

We focus our study on wood residues, such as the bark of *Betula, Pinus, Picea, Larix, Abies* and *Populus*, as well as on peat, as raw material. The work consists of innovative natural products chemistry, extraction and process technology; as well as basic research on the mode of action and the structure-function relationships in order to increase the knowledge-base, essential for the emerging bio-economy. Products arising from the use of these rapidly renewable natural raw materials could replace petrochemical-based products not only in high value-added segments (e.g. medicine, cosmetics, plant protection), but also in technical products such as adhesives, coatings, surfactants and chelating agents. Furthermore, this project creates options for adding value to the total resource of processed wood and peat residues, e.g. in remediation and soil conditioning, so that no wastes remain, and the overall operations are environmentally sustainable and economically attractive. The outcomes of this project are expected to be of significant importance to the forest, farming, medical and pharmaceutical sectors, with major positive spin-off impacts to human health and the environment.

The ForestSpeCs project

The FP7 research project “Wood Bark and Peat Based Bioactive Compounds, Speciality Chemicals, and Remediation Materials: from Innovations to Applications” (ForestSpeCs) had as a starting point the vision to replace certain large-volume, oil-based chemical materials with bio-renewable and innovative products based on wood-related residues and humic substances. In particular, the project has aimed to find ways to produce high value added, bioactive compounds such as pharmaceuticals and biological plant protection products, to develop new environmentally benign industrial chemicals and polymers, and to create economically attractive options for the total use of processed wood and peat residues either as a whole, or after extraction of the main bioactive fractions, for example in soil remediation. After almost three years of research by seven academic and two SME partners from Finland, Russia, Germany, Switzerland, and the UK, emerging economic opportunities for adding value to forest “waste” appear wider than ever.

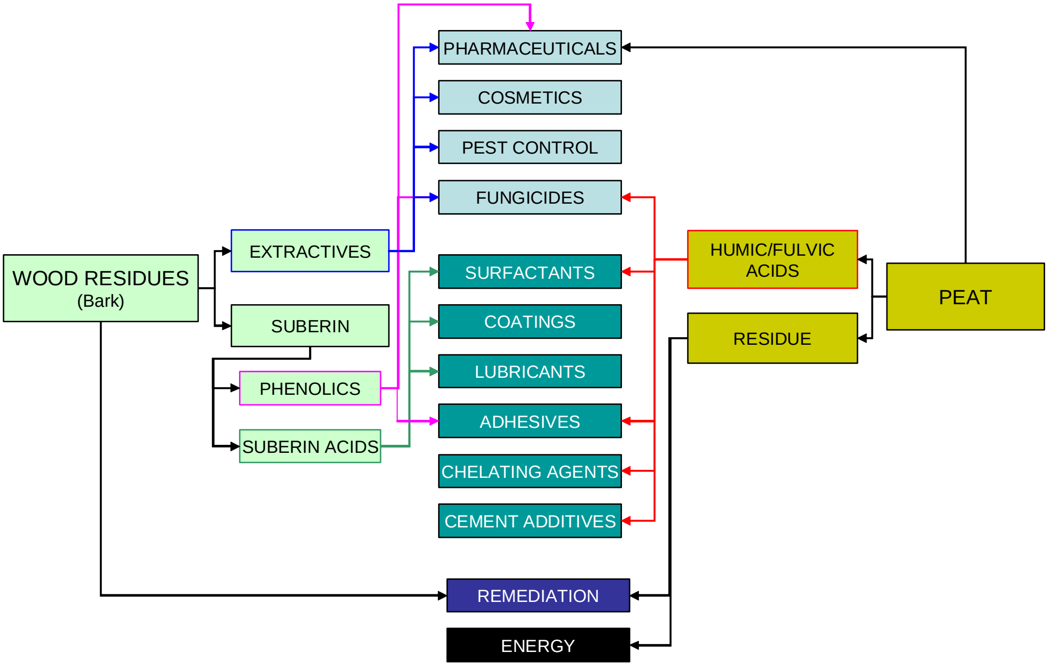


Figure 1. The strategy and value chain for upgrading of wood residues and substances of humic origin to value-added chemicals and materials in *FORESTSPECS*. The chart describes the two main types of basic raw materials as the starting points (bark on the left and peat on the right hand sides of the chart), the value-added secondary raw materials (towards the middle), and their possible application areas (middle of the chart) as bioactive substances (upper part, light blue), speciality chemicals (middle part, turquoise), as core substances in remediation materials (lower part, dark blue), or as sources of energy (bottom; not a topic for *FORESTSPECS*).

Upgrading forest residues: a wealth of opportunities

The Helsinki-based ForestSpeCs-project has been searching for innovative ways to utilize high-volume side products of the forest industry, with focus on bark from the most important tree species and on humic substances available in peat. Bark as a raw material represents excellent opportunities for commercial development based on the huge variety of bioactive compounds contained in bark. Furthermore, bark is an abundant source of rapidly renewable organic biomass, and therefore of great interest as a source for energy and other large-scale applications such as landscaping materials and growth substrate.

A race for the resource

Annually about 20 million m^3 of bark is produced in the EU. It has long been considered as waste, and its current main application options include use in landfills, burning for energy, organic mulch for landscaping, composting to produce soil, and many minor uses. Bark is becoming highly attractive in the search for renewable energy based on biomass, and is a key resource in the calculations concerning future sources of energy. However, other uses may be more attractive because of higher economic value. Besides energy, the other large-scale application area for bark is its potential to replace peat as a growth substrate for horticulture, and as soil amendment to remediate poor and contaminated soils.

Growth substrate

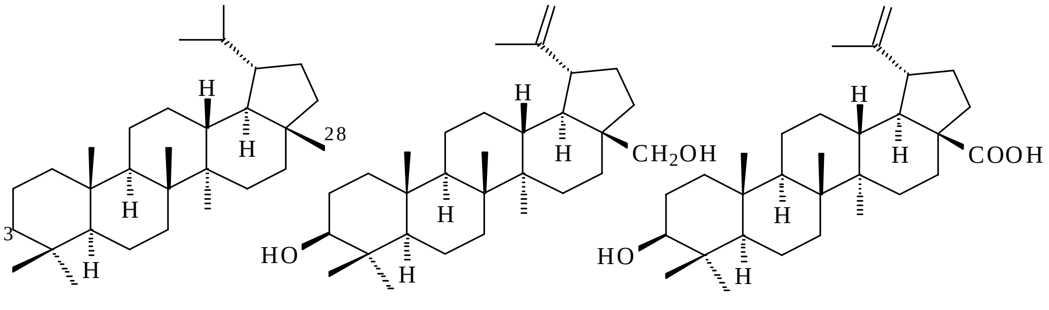
Bark already is composted to some extent to produce growth substrate for home gardening and the horticulture industry. Almost all growth substrate currently, however, is based on the slowly renewable peat abundant in some countries, but scarce in most. Several countries are now completely banning the use of peat for this purpose, and an intensive search for other sources is ongoing. Improved composting processes, researched in ForestSpeCs, could make bark the most important option as peat replacement. Interestingly, the horticulture industry in Europe uses annually close to 20 million m^3 of peat – almost the same volume as the total production of bark – and home gardening equals or even exceeds that in terms of volume. Thus for a complete replacement of peat, the domestic production of bark in Europe is not enough, and if everything is used for the production of growth substrate, nothing remains for the energy sector.

Remediation of poor and toxic soils

In many parts of the world, the biological productivity of the soil is severely limited by the lack of organic matter. Bark can form a base for improving such soils and may become an important tool in combating desertification. Bark from certain tree species is highly resistant to decay, which might be useful under some tropical conditions where rapid loss of organic matter from the soil is a problem. Furthermore, bark is an excellent growth substrate for specific micro-organisms, which can add important ecological functions to the composted bark. ‘Designer-composts’ can be produced for specific purposes, such as bioremediation of soils contaminated with heavy metals or organic toxic pollutants. Experiments in the ForestSpeCs project show for example a high potential to remediate toxic landfills from the mining industry, helping to re-vegetate such sites and to convert them into productive forest.

Compounds for cosmetics and specialty chemicals

Bark and peat are rich sources for specialty chemicals and complex organic molecules, which can easily be extracted and used as such, or as a starting point for chemical processes. Promising applications studied in ForestSpeCs include the use of betulin (the white compound in birch bark) and its derivatives in cosmetics, applications of suberin derivatives as surface active compounds, biodegradable lubricants, and binders for coatings and composite materials. Peat derivatives could become important in many industrial processes such as wood gluing e.g. in particle board and plywood applications, as flotation agents in the mining industry, as chelating agents in water purification and as additives (super plasticizers) in cement and concrete. While numerous highly promising application areas have been discovered, progress is slowed down by the lack of industrial availability of the compounds of interest. For example, high-grade betulin would have good markets, but so far only small amounts are available.



1 2 3

Figure 2. Structures of lupane skeleton (1), betulin (2) and betulinic acid (3).

Bioactive compounds for medical and other uses

Some of the most exciting discoveries in ForestSpeCs are the many highly bioactive compounds found in several bark species. Several of these have already well-known medical applications, or applications in the food and feed industry as functional components of dietary significance. For example several specific, highly valuable medical compounds are found in ample quantities in bark, and could form a basis for a flourishing commercial exploitation. One of them is the main component is a plant extract currently entirely supplied to the world market by China. The current production process is complex, with low yields of variable quality, and often connected with pesticide residue problems. This can now easily be obtained at high quantities from bark of European origin from trees that fulfil organic production criteria. One of the most important discoveries in ForestSpeCs may be in the area of plant protection. Compounds from certain bark species have exhibited excellent properties in the control of important plant pests and diseases in large-scale cultivations. These bioactive compounds appear to equal or even outperform the current synthetic pesticides, some of which will be banned from use during the next few years.

Adding value to waste

A comparison of the options to add value to forest industry waste reveals that while the energy value of bark is approximately 20 € per ton (with oil price at 60 USD per barrel), the current sales prices of one ton of bark for landscaping is about 100–150 €, and for composted bark about 150–200 € per ton. The commercial value of the compounds obtainable from one ton of bark for cosmetic, medical and plant protection uses are astronomical compared with any of the other uses. Additionally, after extraction of specific compounds, the remaining biomass can still be used for energy, or for composting, or some other purpose.

Table 1. Economics of bark residues.

Use of bark	Value €/t
Energy	20
Mulch	100
Ordinary compost	150
Pulverized health pills	200 000
Value of extracted, purified compounds	Depends on supply/demand

Supporting processes in biorefineries by correct water treatment

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Kemira Oyj

Introduction

The term biorefinery has many definitions, which are used in different occasions and contexts. Based on the definition by the International Energy Agency (IEA), a biorefinery is the sustainable processing of biomass into a spectrum of marketable products and energy. However, when looking at the material streams within a biorefinery, a biorefinery seems to be a water pumping and treatment installation. Water quantity and quality management (WQQM) includes the control of incoming raw water quality, optimization and reuse of process water, and minimization of wastewater. In a biorefinery the techniques and rules of industrial water and wastewater treatment generally apply. The main challenges and also benefits in a biorefinery WQQM can be found in the internal process water treatment and utilization of waste streams. The amount of water consumption in typical biorefinery schemes are 3 to 9 times that of the main product. In addition to that, water recycle streams can be larger than the consumption, easily by a factor of 3. Proper WQQM can bring significant savings in operation and production costs. As an example from food and beverage side in 2011, the Coca Cola Company eliminated $500 million in operating expenses by applying water efficient solutions [1].

Raw water treatment technologies

The used raw water treatment methods depend on the biorefinery process. Different treatment methods can be used for different operations: heating, cooling, processing, cleaning, and rinsing processes to minimize operating costs and risks. Insufficient control of raw water quality can cause serious problems in the biorefinery processes e.g. scaling and corrosion in pipes, vessels, and steam boilers. Raw water treatment contains several steps which are briefly described below.

Suspended solids

Turbidity relates to the amount of suspended solids in water. Specially designed coagulants and flocculants can remove suspended solids very effectively. However, slowly settling flocs can cause difficulties in the coagulation processes. These flocs can be fragile and negatively affected by hydraulic forces in settlers and filters. To strengthen these flocs and facilitate the settling, coagulation aids can be used. Organic polymers are the most widely used flocculants in raw water treatment. These synthetic polymers are organic electrically charged high-molecular-weight compounds. They improve the coagulation and flocculation process even at low water temperatures from natural sources.

Disinfection

The role of disinfection is the control of harmful microorganisms and the protection of water distribution systems from microbial growth. Every biorefinery needs specific strategy for disinfection.

Before disinfection, the water needs to have low colour and turbidity and low number of particles which all can consume disinfectant. Therefore raw water may need pre-treatment. Depending on the quality of the water, removal toxins, heavy metals, pesticides and nitrate ions may also be needed. Disinfection can be carried out by heat, chemically, or physically with UV radiation or membranes. Heat is used only for small water quantities due to the high energy need. Chemical disinfection uses chlorine or oxidizing agents such as chlorine dioxide, chloramines, hypochlorites, performic acid, and ozone. UV radiation is an effective method to reduce microorganisms by influencing the genetic material and prevent re-growth. Low turbidity is essential to ensure efficiency of UV treatment. The method is gaining popularity and it is often used in combination with other disinfection methods. Protozoa including *Cryptosporidea oocytes*, which are resistant to most chemical disinfection methods, can be removed by fine filtration.

Desalination

Desalination is most commonly used to produce potable water from seawater or brackish water, but industrial water including ultrapure water can also be generated by desalination. There are two primary desalination methods: thermal and membrane desalination. In thermal desalination, raw water is vaporized and then condensed as pure water. Membrane desalination uses a semi-permeable membrane to separate the dissolved salts from water. Membrane desalination is less energy intensive and has taken over the thermal one in most parts of the world.

Depending on the water quality and the desalination technology used, the specific steps in desalination vary. The pre-treatment step is critical for keeping the membrane surface clean from organic and inorganic fouling leading to a drop in flux, salt rejection efficiency, and ultimately short filtration cycles. In the pre-treatment, suspended solids are removed and salt precipitation and microbial growth are prevented. One conventional pre-treatment method is chemical coagulation, flocculation and sedimentation.

Scale control by specific polymeric antiscalants increases membrane and equipment lifetime. These antiscalants are designed for minerals encountered with brackish, sea or high dissolved solid content water. Products need to be compatible with most membranes and the chemicals used in water pre-treatment.

Corrosion inhibition

Raw water can be corrosive leading to increased risk of damage to the process equipment. A variety of substances, including copper and iron, can be dissolved from piping and equipment and thus contaminate the water. Several factors affect corrosion: pH, alkalinity and calcium concentration. These all can be controlled by chemical adjustments.

Color

Color is caused by dissolved organic matter e.g. humic and fulvic acids, or mineral impurities such as iron and manganese. Reduction of color is a control parameter for prevention damage to the process. Chemical coagulation is an effective method to achieve color reduction.

Metals

Heavy metals are in many cases adsorbed to suspended solids. Removal of suspended solids thus reduces heavy metal content. Heavy metals can also be dissolved in the raw water. The adjustment of the pH to a level where heavy metal hydroxides are formed enhances removal by precipitation.

Waste handling

Large investments are needed in the treatment of effluents from the water-intense biorefinery industries. The targets of these investments are the compliance with legal discharge limits, the minimization of the environmental impact of the industrial activity, and the production of pure water mostly for reuse, but also for release to the natural recipient. Many modern biorefinery production sites fulfil the target of zero release, meaning full recycling of purified wastewater back to the process.

Carbon (C), nitrogen (N) and phosphorus (P) are the main chemical components of wastewater in the solid and liquid phase. The enrichment of those nutrient compounds in the water cycle leads to uncontrolled biological growth, production disturbance, and process instability. Carbon occurs as solids in the form of sludge, or as dissolved polymeric or short-chain compounds. Nitrogen and phosphorus occur in form of inorganic ions like ammonium and phosphate, but also as organic compounds like proteins and DNA debris. In addition, wastewater contains minor amounts of sulphur, alkaline earth metals, alkali metals, and other waste from the processes. The amount of oxidizable organic matter is analysed as Chemical Oxygen Demand (COD). The reduction of COD characterizes the performance of the wastewater treatment process. Inside the EU, strict rules apply for the discharge of COD, nitrogen, and phosphorus to the natural recipient.

The wastewater treatment process is a sequence of different process steps where the single compounds are degraded and eliminated. The quality of the effluent determines the actual treatment setup.

Low solids effluent

Effluents with low solid content are treated by an anaerobic step, a subsequent aerobic treatment, and some after-treatment steps e.g. by clarifier, reverse osmosis or evaporation. Due to the lack of essential nutrients in the influent, a selection of macro and micro nutrients is added before entering the wastewater circuit in order to get a better degradation of the carbonaceous matter. Macronutrients like phosphate and nitrogen are added to the inlet of the anaerobic treatment in form of phosphoric acid and ammonium. The target is to achieve the balance of the nutrients C:N:P. Micronutrients are added in form of special metal mixtures. There is often a lack of important metals like cobalt, nickel, selenium or tungsten, for an effective microbial metabolism. With the optimum nutrient supply, the anaerobic microbes are able to metabolise soluble carbonaceous matter to methane. An increased biogas yield in the anaerobic step minimizes the COD load to the subsequent aerobic treatment.

High performance IC-reactors (internal circulation) transfer almost all easily available COD to methane within a few hours (3 to 5 h) of hydraulic residence time (HRT). Pellets consisting of anaerobic microbes form a bed that is passed by the liquid with the degradable COD. Long-chain compounds are converted to easily degradable short-chain compounds. In a final step, they are transformed to methane by methanogens. A subsequent aerobic treatment degrades the remaining COD, N and P producing biological sludge. The sludge is separated in clarifiers, by filtration, or decanter centrifuges. It can be reused in the process after e.g. hydrolysis, but is also disposed by incineration and landfilling.

As the anaerobic treatment produces energy in form of methane, and the aerobic treatment consumes energy in form of air blowing power, operators of such facilities are keen to optimize the anaerobic step.

High solids effluent

Effluents with high solid contents are treated by a process that consists of a primary treatment in form of a settler, of a secondary treatment (biological treatment), often followed by a tertiary treatment (after-polishing). Each of the three treatment steps produces a primary, secondary or tertiary sludge. The three sludge types are mixed and forwarded to a final anaerobic digestion for waste volume minimization and methane production.

In the primary treatment, the solids are eliminated and concentrated to a primary sludge. In the secondary treatment, the clear phase undergoes a biological treatment consisting of interchanging aerated and non-aerated steps where N and P are eliminated under consumption of COD. The resulting biological sludge is thickened in a clarifier. In many cases this treatment is sufficient to fulfil purity standards. A tertiary step is necessary for the achievement of a very low discharge limit. Here a chemical sludge is produced.

As the mixed sludge from this treatment contains large amounts of solid matter, the transformation to biologically degradable matter, the so called hydrolysis, takes several days depending on the chosen setup. Due to digestion grades of 60 % and reasonable methane yields, this method is chosen for effective energy generation and waste volume minimisation for disposal.

Membranes in wastewater treatment

Membrane Bioreactors (MBR) offer some advantages compared to the conventional wastewater treatment. The MBR setups are compact and have a high retention performance for harmful compounds. MBRs produce a high quality effluent. The purified wastewater can easily be reused in industrial processes and agriculture. MBRs produce only small sludge volumes compared to conventional treatment plants. However, the energy consumption per volume treated water represents more than 60 % of the total operating costs.

Sludge dewatering

The main target of sludge dewatering is the minimisation of volumes for transport and disposal, since e.g. fees for incineration and landfilling contribute to almost 50% of the waste handling costs. In recent times, the view on waste has changed dramatically, as it is considered to be a valuable source of energy, and raw materials can be recycled back to the process. The policies of the production sites, strict environmental regulations and release limits put high demands on this final treatment step. As a consequence, efforts are made to produce as pure waste streams as possible.

The addition of process aids is the key to comply with the high demands for an effective solid-liquid separation. Typical process aids for dewatering are flocculants (organic polymers) and coagulants (metal salts). They minimise the repelling forces between the solid particulate matter so that the waste streams from centrifugation or filtration result in pure solid and clear liquid fractions.

The benefits of process water treatment and WQQM in biorefinery – case examples

General biorefinery process water scenario

The technologies vary depending on the biorefinery raw materials, products and unit operations. Biorefineries can be classified in many ways: by product, by process, or by raw material. All biorefineries handle large amounts of water. Even Fischer-Tropsch gasification uses significant amounts of water in syngas scrubbing.

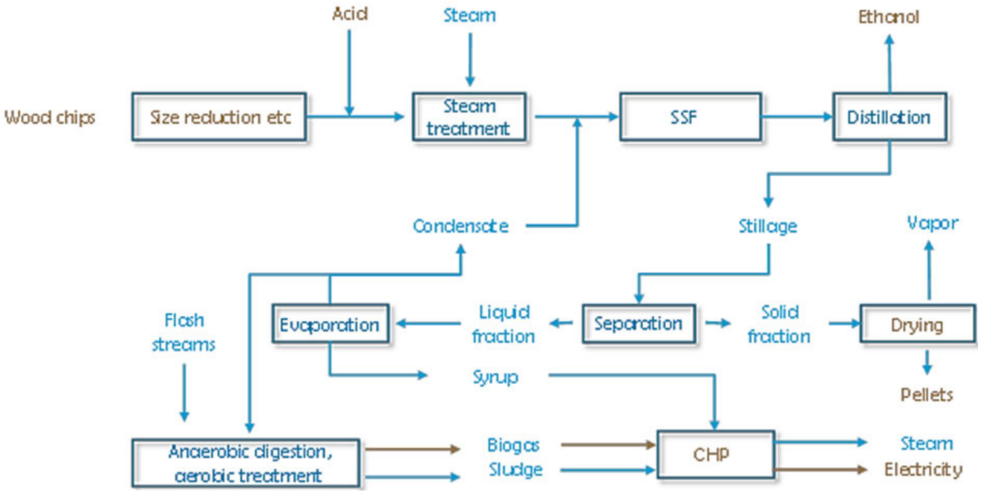

Figure 1. A lignocellulosic biorefinery. Simultaneous saccharification and fermentation (SSF). Combined heat and power boiler (CHP). Redrawn [2].

A lignocellulosic biorefinery is schematically presented in Figure 1. This biorefinery uses wood chips which are steam exploded in mildly acidic conditions as raw material. In this step the dry matter content is 30%. Then the biomass is diluted to 20% concentration by recycled water. In this scheme cellulose hydrolysis to sugars and fermentation take place simultaneously. When fermentation is complete the ethanol is distilled. The waste stream of stillage distillation contains lignin in the solid fraction, which is separated and eventually pelletized. The water fraction is evaporated and the condensed vapor is used as dilution water and partly goes to wastewater treatment. The concentrated fraction is fed to the boiler. The state of art dry biomass concentration in pretreatment is 30%, and in hydrolysis slightly less, and at the end of fermentation water content is close to 80% (Table 1). The flux of recycled water is more than seven times that of the product ethanol (18 500 kg/h). Only with adequate WQQM the operation costs will be economically feasible.

Table 1. Water concentration and water flow rates in a biochemical biorefinery [3].

Step	Water concentration [%]	Water flow rate [kg/h]
Corn stover	20	20 800
Pretreatment	71	224 000
End of fermentation	84	378 000
Wastewater		93 000
Water recycle		132 000
Water consumption		80 000

Bioethanol production

Bioethanol is the most common product of published biorefinery schemes. There are many different technologies proposed, but also similarities. Here we look at a biological, enzyme hydrolysis biorefinery as an example in WQQM related issues.

The most common pretreatment step in a biochemical biorefinery is dilute acid assisted steam explosion. This makes lignocellulosic biomass more susceptible for enzymatic hydrolysis. After the pretreatment, pH is adjusted to a suitable level for the subsequent steps. This is done by base addition raising the ionic strength of the water and possibly requiring salt removal in the water recycle. Water is used prior to the enzymatic hydrolysis in order to adjust the dry matter concentration. This water must be free of enzyme and yeast inhibitors and have a correct ionic level. The inhibitors found in recycled water include furan derivatives (furfural and 5-hydroxymethylfurfural), phenolic compounds, weak organic acids (levulinic, formic, and acetic acid), and heavy metal ions (nickel, aluminum, chromium). The removal techniques of these inhibitors include ion exchange resins, active charcoal, laccase enzymatic detoxification, alkali treatments, and overliming with calcium hydroxide. The application of these usually causes sugar losses and additional filtration steps. Thus careful process design is needed for efficient operation.

In distillation deposits, especially lignin compounds can be formed on the heat surfaces. Here an antiscalant might prolong the distillation time and reduce wastewaters from washing step.

In bioethanol production, the stillage contains large amounts of organic solids, organic acids and salts, thus creating a large chemical oxygen demand (COD) and making the recycling a challenging operation. Grain ethanol process is able to process stillage into a feed product. In lignocellulosic ethanol biorefineries, the volumes of this stillage are larger than in grain processes, as biomass concentration is lower in the process. Thus handling of stillage will form a significant part of the costs, even though the lignin content of the stillage can be used as an energy source. The solid fraction separation of stillage must be efficient to facilitate economic evaporator operation. If that is carried out by centrifugation, evidence exists that flocculants can improve the efficiency.

The water vapors to be released to atmosphere (e.g., from drying) must be treated to reduce volatile organic compounds (VOCs) and odor to the required level.

A recent NREL report [3] gave the following water balance for an ethanol plant of 18 000 kg ethanol per hour production while the plant had a water consumption of 5.35 litres per litre ethanol. However, the recycled amount of process water in the process was 376 000 kg/h i.e. 2.5 times that of raw water, and 20 times the produced ethanol amount. In this example, the recycled water stream from boiler and cooling tower blow down, pretreatment flash and stillage evaporation waters. These streams are collected, anaerobically and aerobically treated, clarified, filtered by reverse osmosis, and partly evaporated before recycling back to process. The cost for the water treatment (equipment, installed cost) is 21% of total installed cost for the plant. The variable operation cost coming from raw water treatment represent 0.5%, wastewater treatment chemicals 4.3%, boiler chemicals 2.3%, and cooling tower chemicals 0.1% of total variable operational costs.

Utilization of algae in biorefinery

Cost-effective methods of harvesting and dewatering the algal biomass are needed for algae biorefinery to become economically feasible. Chemical flocculation and floc separation by sedimentation or flotation can be efficient methods for separation of algae. Further, dewatering of the separated, low-dry-content biomass, can be achieved by traditional filtration or by centrifugation. This dewatering can be improved by chemicals. Utilizing inorganic coagulants and polymer flocculants in the range of 100 ppm and 1 ppm levels respectively, separation efficiencies over 98% have been achieved. The treatment conditions (chemicals, dosages, timing) is affected e.g. by algae type, concentration, pH, and charge. The end-use and downstream processing of the algae biomass may also restrict the types of chemicals to be used. In subsequent dewatering of the biomass by filtration method, chemicals have enhanced dewatering as well as preventing blockage of the filter medium. Dry mass contents up to 15–20% have been achieved. Kemira has developed a method to monitor and optimize the harvesting efficiency. The same flow cytometry based method can also be applied for algae cultivation monitoring.

Production of micro crystalline cellulose at pulp mill

Micro crystalline cellulose (MCC) is a versatile product, which can be used in many industrial applications, e.g. in food, pharmaceutical, cosmetics, paper and board and many other applications. The challenges of MCC production have been rather small production capacity, the lack of efficient recovery of used acid, as well as utilization of effluents. The Clean Technologies Research Group at Aalto University has together with Kemira been investigating the possibility to integrate MCC production to an existing kraft pulp mill [4]. The new biorefinery process can utilize almost 100% of the wood biomass converting it into MCC with a high yield, whereas hydrolysis products can be used as a raw material for bioethanol. In addition, utilization of on-site pulp mill chemicals as well as existing chemical recovery can be achieved.

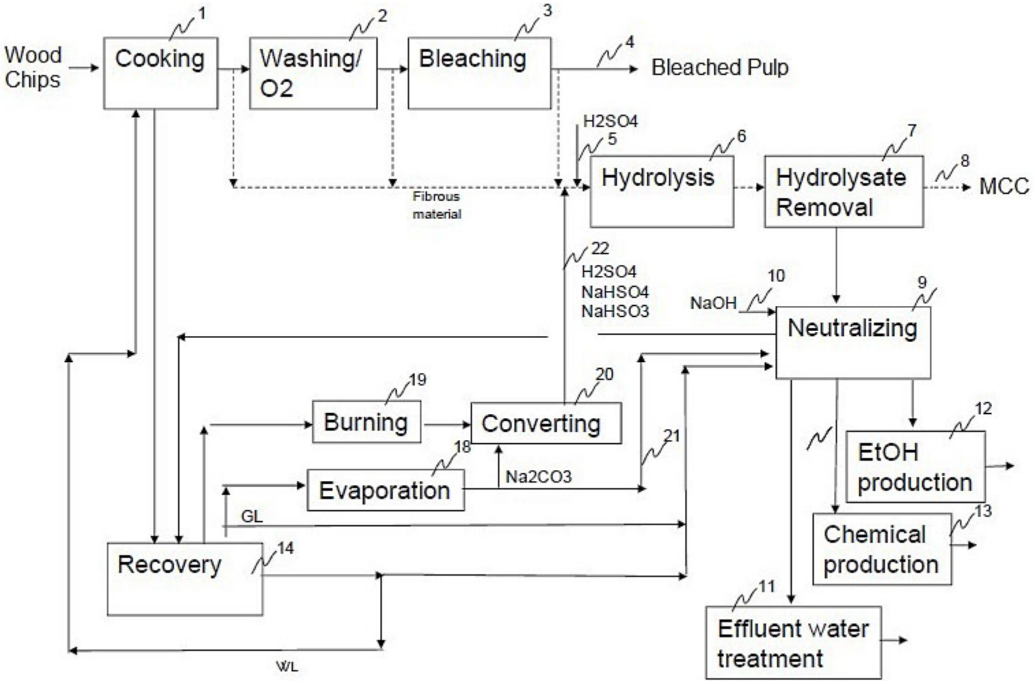

Figure 2. Integration principle of novel MCC process to a kraft pulp mill.

In the traditional production of MCC high loads of hydrolysis products (COD) are discarded in to the wastewater treatment plants. This affects the production costs negatively in the form of raw material loss and wastewater treatment. However, in this specific MCC production concept also wastewater and wastewater management was taken in to account. Hydrolysis stream, containing valuable sugars after neutralizing, can be utilized as a raw material for sustainable way to produce green chemicals such as ethanol and xylan or methane. Dissolved sugars from MCC process can also be treated in the existing effluent treatment system if not utilized in e.g. bioethanol production.

Production of organic acids from dilute side streams

Organic acids, such as formic, acetic, propionic, and lactic acids, are conventionally produced by industrial processes using non-renewable natural raw materials predominantly in the form of mineral oil. However, side streams of bioethanol production could be considered as an alternative raw material for production of small organic acids. References of bioprocesses have been published from the 20's to recent years [5, 6]. However, most of the described processes have been found economically non-feasible due to either an extensive raw material purification need (in case of crude glycerol), or due to too low final productivity and dilute product concentrations in the fermentation broth.

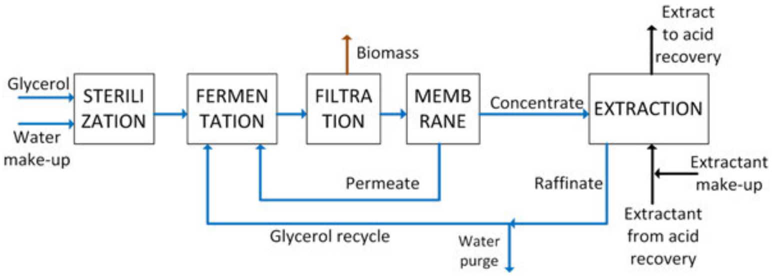

Figure 3. Fermentation process with closed loop process.

The process is very water intensive and in the previous approaches valuable raw material was partly discarded into large wastewater stream. Treatment of this stream would have been very costly. New process design described in the Figure 3. enables not only significant wastewater reduction but also high glycerol conversion to valuable products, minimal chemical consumption for pH adjustment in both fermenter and extractor, improved acid yield in extractor, smaller extractor size and lower investment cost. Furthermore, low extractant residue of total recycle minimizes toxicity effects in fermentation. The loop closure was enabled by extraction and membrane process.

Due to process modifications and closed water loops the wastewater discharge was reduced overall by 85%. However, the real driving force was the 30 % reduction in the production cost of biobased acid due to new process design enabled by water treatment based on extraction and membrane separation.

Conclusions

Water is the single largest component in biorefinery mass balance. Although the cost of raw material and the yield are the largest factors in biorefinery economy, the correct WQQM can bring savings in capital and operational cost.

Correct and adequate raw water treatment ensures smooth, trouble free operation and increases equipment lifetime. Balancing economically water recycles in biorefinery optimises costs, reduces wastewater volumes, and saves energy.

Efficient wastewater treatment can produce energy while fulfilling environmental regulations, and minimizes waste treatment costs.

References

1. Frost & Sullivan. 2012. CEO 360 Degree Perspectives of the Water and Wastewater Treatment Market in the Global Food and Beverage Industry, M7DE-15, August 2012.

2. Barta, Z., Reczey, K., Zacchi, G. 2010. Techno-economic evaluation of stillage treatment with anaerobic digestion in a softwood-to-ethanol process. Biotechnology for Biofuels 3(21), http://www.biotechnologyforbiofuels.com/content/3/1/21.

3. Humbird, D., Davis, R., Tao, L., Kinchin, C., Hsu, D., Aden, A., Schoen, P., Lukas, J., Olthof, B., Worley, M., Sexton, D., Dudgeon, D. 2011. Process Design and Economics for Biochemical Conversion of Lignocellulosic Biomass to Ethanol, Dilute-Acid Pretreatment and Enzymatic Hydrolysis of Corn Stover. NREL/TP-5100-47764, May 2011.

4. Dahl, O., Vanhatalo, K., Parviainen, K. 2011. A Novel Method to Produce Microcellulose, WO2011154600.

5. Sherman, J.S. Propionic acid fermentation by the use of mixed strains of propionic bacteria, US1865146.

Wednesday, 24 October: Industrial developments

Actual and future trends in dissolving pulp manufacture

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Abstract

Herein, we report about existing and novel dissolving pulp processes providing the basis for an advanced biorefinery. The SO_2-ethanol-water (SEW) process has the potential to replace the acid sulphite process for the production of rayon-grade pulps, owing to a higher flexibility in the selection of the raw material source, substantially lower cooking times, and the near absence of sugar degradation products. Special attention is paid to developments that target toward the selective and quantitative fractionation of paper-grade pulps into hemicelluloses and cellulose of highest purity.

This target has been accomplished by the IONCELL process where the entire hemicellulose fraction is selectively dissolved in an ionic liquid in which the H-bond basicity and acidity are adequately adjusted by the addition of a co-solvent. At the same time, pure hemicellulose can be recovered by further addition of the co-solvent, which then acts as a non-solvent. The residual pure cellulose fraction may then enter a Lyocell process for the production of regenerated cellulose products.

Introduction

The upturn of dissolving wood pulps (DWP) in the market during the last 10 years may be attributed to a consistent growth of regenerated cellulose fiber production, particularly in China, where 61% of the current global rayon production capacities are located [1]. The annual DPW production in 2011 was 4.2 million t, of which 2.9 million t accounted for commodity applications, *e.g.* rayon, while the residual 1.3 million t were converted to specialties, *e.g.* to cellulose acetate [1].

Market studies clearly indicate that this trend of increasing demand of regenerated cellulose fibers and thus dissolving pulps will prevail during the next decades.

The global production of textile fibers is predicted to increase from 72.5 million t in 2010 to 133.5 million in 2030 by both an increase in per capita consumption (10.5 to 15.5 kg per capita and year, respectively) and population (6.9 to 8.3 billion) [2]. The inherent physiological properties of cellulose fibers ensure an adequate moisture management that cannot be achieved by synthetic fibers. Since these properties are requested in many fiber products, a minimum constant share of cellulosic fibers, including both natural and man-made fibers, of 33 to 37% on the global fiber consumption has been projected [2]. With this assumption, the annual per capita consumption of cellulosic fibers will increase from its present 3.7 to 5.4 kg in 2030. At the same time, the cotton production will stagnate at a level of about 26 million t per year (3.1 kg per capita in 2030) due to the estimated shrinkage of the cotton growing area and the concomitant increase of the annual specific yield from presently 800 to 925 kg per hectare in 2030. The only way to compensate for the resulting cellulose fiber gap of 1.7 kg per capita is to invest in additional capacities of man-made cellulosic fiber production (viscose, Lyocell, cellulose acetate, cupro, etc.), which, in absolute terms, translates into an additional annual global production of 14.8 million t (from the present 4.2 to 19.0 million t in 2030) [3]. The growing demand for highly purified cellulose pulps is, however, not only limited to textile applications, but it also concerns the manufacture of cellulose acetate for high value-added films, plastics, and coatings as well as cellulose mixed ethers for lacquers and printing, cellulose ethers, and cellulose powder, which have found important applications in the food and pharmaceutical industries. Moreover, dissolving pulps seem to be the preferred substrate for the manufacture of nanofibrillated cellulose (NFC), a future precursor of advanced materials.

Parallel to the necessary investments in new viscose and Lyocell fiber capacities, additional capacities in the production of dissolving pulps, the raw material for the manufacture of man-made cellulose fibers, have to be installed. Dissolving pulp refers to pulp of high cellulose content, comprising a minimum amount of inorganic and non-cellulosic organic impurities [4].

Currently, dissolving wood pulps are produced by the acid sulfite and the vapor-phase prehydrolysis kraft (PHK) processes, which were both developed in the 1950s. While the former remained technically largely unchanged, a modern displacement cooking procedure was adopted to the steam prehydrolysis kraft process [4].

The growing demand for high purity dissolving pulps, however, requires the development of novel process concepts which that both the realization of advanced biorefinery concepts and the manufacture of pure cellulose pulps, revealing a quality profile comparable to that of cotton linters. Changing from steam to water prehydrolysis (autohydrolysis) allows the selective separation of major parts of hemicelluloses in the form of oligo- and monosaccharides and acetic and formic acids. Unfortunately, sticky precipitates are formed from dissolved acid soluble lignin, which currently hampers the commercial application of autohydrolysis as a pre-treatment of alkaline delignification processes [5]. Andritz recently developed cooking system upgrades for retrofit to DPW operation in continuous digesters, including a prehydrolysis reactor vessel for water prehydrolysis. In the meantime, this technology has been delivered or is about to be delivered to several customers in Asia [6]. For the batch cooking technology, the processability of water prehydrolysis is ensured by an in-situ adsorption of the released reactive lignin fractions on activated carbon, as recently suggested [7, 8].

Autohydrolysis of hardwood accelerates the delignification rate during subsequent kraft or soda-anthraquinone (SAQ) pulping, presumably due to better accessibility and the cleavage of LLC bonds as demonstrated by kinetic studies [9, 10]. Thus, milder cooking conditions, expressed in lower H-factor and/or chemical charges, are sufficient to achieve the requested degree of delignification. However, alkaline delignification methods following autohydrolysis pre-treatment of wood, even under mild conditions, are associated with high cellulose losses due to β-elimination (peeling) reactions. Cellulose yield remains almost unaffected by autohydrolysis up to relatively high intensities, while the degree of polymerization (DP) is decreased by the hydrolytic cleavage of glycosidic bonds, thus creating new reducing end groups (REGs). Since the extent of alkaline peeling reactions is proportional to the concentration of REGs, subsequent alkaline treatment, such as kraft pulping, leads to substantial yield losses [11, 12]. The combination of prehydrolysis with acid sulphite cooking is, however, no alternative because of insufficient delignification owing to the deactivation of lignin structures towards sulfonation [13]. Thus, novel process concepts need to be developed that allow the selective and quantitative removal of hemicelluloses and lignin, to realize advanced biorefinery concepts and to satisfy the growing demand for high purity dissolving pulps.

This study provides an overview on novel process concepts for the manufacture of dissolving pulps comprising both further developments of existing technologies as well as radical innovations.

Experimental

Raw material

Birch, spruce, and pine wood chips were delivered from a pulp mill in Finland and *Eucalyptus globulus* from plantations in Uruguay. The chips were screened (SCAN-CM 40:01) upon delivery and subsequently stored in a freezer. The composition of the wood chips is summarized in Table 1 (% on odw).

Table 1. Composition of wood chips.

Species	Cell	(A)X	GGM	KL	ASL
Birch	43,1	27.2	2.5	21.7	4.4
E. globulus [14]	48.7	21.1	1.9	22.7	4.7
Spruce [15]	44.1	8.0	17.7	*27.7	
Pine	41.1	8.5	17.2	25.9	0.7

Calculation according to Janson [16]. KL = Klason lignin; ASL = acid soluble lignin. (*) total lignin

A commercial ECF-bleached birch kraft pulp comprising contents of 25.4% xylan, 1.0% glucomannan, and 73.6% cellulose (according to Janson [16]) was used for the conversion to a dissolving pulp by CCE and IONCELL treatments.

Autohydrolysis

Hot water extractions were conducted in a 10 L batch reactor equipped with a heat exchanger and temperature control. A predetermined amount of deionized water was added to reach a liquid-to-wood (L:W) ratio of 3:1 g/g. A high-pressure pump was used to continuously recirculate the water through the chip bed. The intensity of *standard* autohydrolysis was described by the P-factor using an activation energy of 125.6 kJ/mol as determined for the removal of fast reacting xylan [4, 17], while for the intensity of *reinforced* autohydrolysis, an activation energy of 180 kJ/mol was applied to compute a modified P-factor, log P-X_S, corresponding to the removal of the recalcitrant xylan fraction in birch wood [18].

Pulping experiments

Soda anthraquinone (SAQ) of birch chips and SO_2-Ethanol-Water (SEW) treatments of spruce chips were conducted in an oil-bath reactor, containing 8 rotating autoclaves of 225 ml each. In SAQ cooking, an aqueous solution containing caustic soda (22% NaOH on odw) and AQ (0.1 or 1.0% odw) was added, reaching a L:W ratio of 3:1 g/g. Sodium borohydride (SBH) was added as a reductive stabilization agent to the SAQ pulping liquor. The temperature in the reactor was raised to 150°C and kept constant for 60 min, reaching an H-factor of about 200 hours. SAQ pulping of *Eucalyptus globulus* chips was conducted in a 10-L digester with forced liquor circulation, using the continuous batch cooking (CBC) mode [19]. The same equipment was used for acid sulfite pulping of spruce chips with the standard procedure being described in [20]. The detailed composition of the acid sulfite cooking liquor and reaction temperatures is provided in the Results part. The cooking liquor for SEW fractionation of spruce chips was prepared by injecting gaseous SO_2 into a cold ethanol/water mixture (55% v/v) until a concentration of 1.88 mole/L was reached. More detailed information can be found in [15].

Selected SEW and PHSAQ pulps were ECF bleached to full brightness. The applied bleaching sequences are listed in Tables 2 and 3.

Pre- and post-alkaline extraction

Alkaline pre- and post-extraction (CCE) of *Eucalyptus globulus* chips and kraft pulp are described in [14] and those of birch chips in [21].

IONCELL process

The birch kraft pulp was treated with a mixture of [emim]OAc and a molecular co-solvent in a vertical kneader at 60°C for 3 hours. The dissolved xylan was precipitated by further addition of the co-solvent. The solvent mixture was removed by thorough washing in hot water prior to analysis.

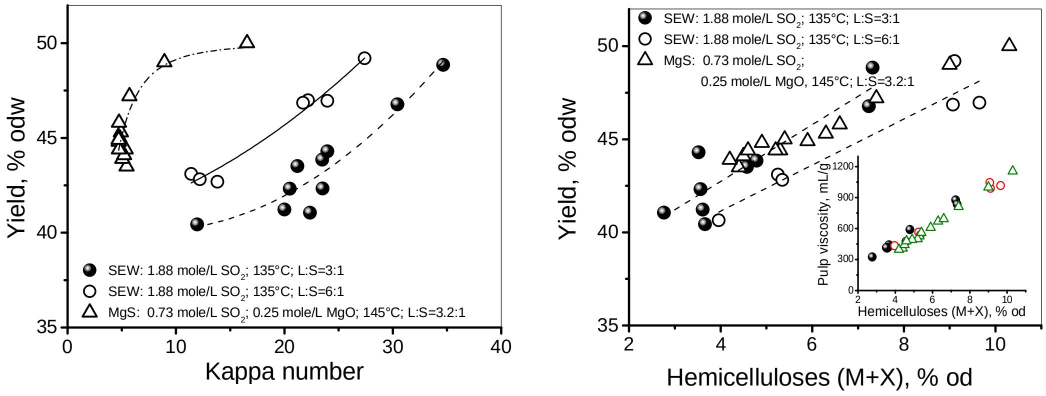
Analytical methods

Chemical composition of wood and pulp samples was determined after a two-stage total hydrolysis, according to the analytical method NREL/TP-510-42618. The ASL was measured in a Shimadzu *UV-2550* spectrophotometer at a wavelength of 205 nm and using an absorption coefficient of 110 L/(g·cm) [22]. The monosaccharides were determined HPAEC-PAD in a Dionex ICS-3000 system. The kappa number and intrinsic viscosity of the pulps were determined according to the SCAN-C 1:100 and SCAN-CM 15:99 methods, respectively. Molar mass distribution of pulps was determined by gel permeation chromatography (GPC) in DMAc-LiCl solution according to Schelosky [23].

Results

Acidic fractionation processes

Acid sulfite (AS) pulping offers a good basis for the realization of the biorefinery concept, allowing the recovery of the three lignocellulosic polymers as pure cellulose pulp (DWP), monomeric sugars, and lignosulfonate in economically attractive quantities. In several industrial AS dissolving pulp plants, products from hemicelluloses (furfural, ethanol, yeast, acetic acid) and lignin (lignosulfonates, vanillin) are produced, enhancing the profitability of the mills. AS pulping, however, shows immanent drawbacks characterized by its low flexibility in the selection of raw material sources, long overall cooking time due to very slow impregnation, inefficient recovery of cooking chemicals, and the conversion of substantial amounts of monomeric sugars to aldonic acids. SO_2-ethanol-water pulping (SEW) has the potential to be a viable alternative to metal-based acid sulfite cooking [15]. The presence of ethanol in the cooking liquor moderates its acidity and allows fast transport of the pulping agents to the reaction sites inside the wood. In this way, the overall cooking time can be substantially reduced. Further, ethanol is known to be a better solvent for lignin and lignosulfonate than water. The absence of a base in the process modifies the recovery cycle to simple distillation of ethanol and unreacted SO_2. Ethanol does not participate in the reactions and can thus be recovered almost quantitatively. Since the pK_a of $SO_2.H_2O$ increases from 1.8 in pure water to about 2.7 in 55% v/v ethanol-water (30°C), the $[HSO_3^-]$ and $[H^+]$ concentrations are significantly lower in the SEW liquor than in an AS liquor. As a consequence, the degree of sulfonation of the dissolved lignin is substantially lower ($S/C_9 \sim 0.24$ for spruce at 1.88 mole/L SO_2 [15]) as compared to the lignosulfonates originating from acid sulphite pulping ($S/C_9 \sim 0.50$ for spruce at 1 mole/L SO_2 [24]). The low $[HSO_3^-]$ also prevents the formation of aldonic acids from dissolved monosugars, which allows higher and easier sugar recovery. Delignification to very low kappa numbers as known from AS dissolving pulp cooking is, however, not possible in SEW cooking, due to lower $[HSO_3^-]$ and $[H^+]$ (Figure 1a). At a given pulp viscosity (or yield) the kappa number of spruce SEW pulps cannot be reduced below 10, while spruce AS pulps show kappa numbers below 5.



(a)

(b)

Figure 1a. Yield vs. kappa number of AS and SEW cooks of spruce. **1b.** Yield vs. hemicellulose content of unbleached SEW and AS pulps.

Figure 1b reveals a comparable relationship between the yield (viscosity) and the hemicellulose content in the pulps from both acidic processes, which, however, shows a dependency on the L:W ratio.

ECF-bleached SEW and AS dissolving pulps exhibit comparable properties. They both meet the specification requested for rayon pulps (Table 2). Surprisingly, acceptable rayon pulp properties were achieved without hot caustic extraction (HCE), as exemplified for the SEW-2 pulp. This was confirmed by a good to very good quality of the viscose prepared by the SEW-2 pulp using Treiber's method [25] (Figure 2).

Table 2. Specification of ECF-bleached SEW- and MgS rayon pulps from spruce (average of two bleaching series). SEW-1: 1.88 mole/L SO_2, L/W = 6/1, 60 min at 150°C, 55% v/v EtOH, 60 min; SEW-2: like SEW-1, but L/S = 3/1, 50 min. MgS: 1.07 mole/L total SO_2, 0.24 mole/L MgO, L/W = 3.2/1, 110 min at 145°C.

Process	Sequence	Total yield % odw	Brightness % ISO	Viscosity mL/g	R18 %	Xylan %	Mannan %
SEW-1	EO-D-Q-P	39.8	90.2	478	94.4	1,7	1,5
SEW-2	O-D-EP-Q-P	41.7	89.3	478	93.2	1.7	2.2
MgS	E-O-D-P	40.9	89.9	552	94.8	1.7	1.9

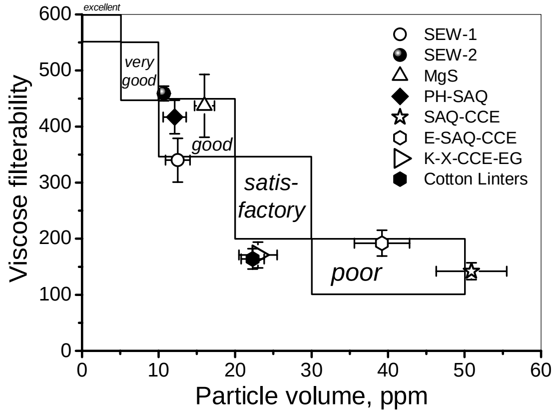


Figure 2. Filterability vs. particle volume of viscose samples prepared from different dissolving pulps.

Alkaline fractionation processes

The manufacture of high-purity dissolving pulps (R18>96%) with a narrow molar mass distribution (MMD) is conveniently accomplished by the two-stage PHK or PHSAQ processes. Currently, the sugars and acetic acid from the hydrolysate are not recovered prior to the alkaline delignification step because prehydrolysis is almost exclusively conducted in vapor-phase. Now, with the development of technically feasible water prehydrolysis processes for the continuous and batch production, the hydrolysate can be used as a source for food additives and platform chemicals [6, 7]. The concomitant production of platform chemicals and rayon pulp from birch wood was studied in lab trials. While the amounts of xylose, xylo-oligosaccharides, and acetic acid in the hydrolysate were confirmed experimentally, the final yields of the purified platform chemicals, furfural and acetic acid, were assumed, based on literature data and industrial experience. In an additional experiment, the potential of increasing the pulp yield through the addition of sodium borohydride (SBH) to the cooking liquor was investigated. The results are shown in Table 3:

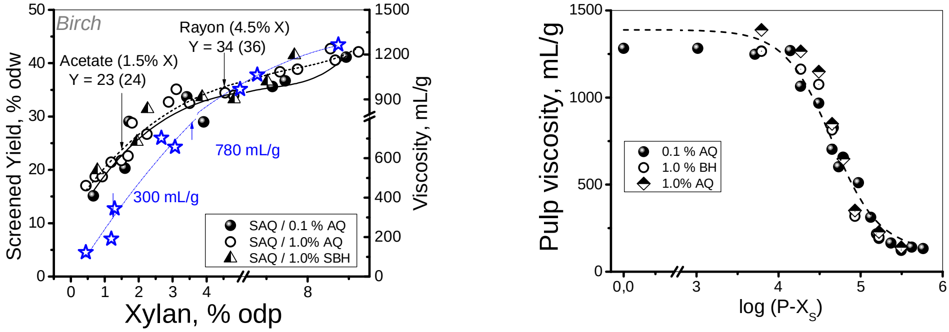
Table 3. Summary of process conditions, product specification and yields of alkaline fractionation of birch wood.

Processes	**Unbleached**		**ECF bleached pulp**					**Extract**		**By-products**	
	Kappa	**Yield**	**Yield**	**R18**	**Xn**	**[η]**	**B**	**Xyl**	**AcOH**	**F**	**AcOH**
		%odw	%odw	%	%	mL/g	%ISO	%odw	%odw	%odw	%odw
PHSAQ	8.3	36.8	34.1	95.8	4.7	507	90.4	*8.4	1.2	4.9	1.0
PHSAQ-B	8.2	38.8	36.2	95.5	6.0	572	91.4	*8.4	1.2	4.9	1.0
K-CCE	18.0	51.5	39.6		6.5			**8.3	n.d.		

PH: L/W = 4/1; 65% of hydrolysate recovered; P-factor = 1 000; SAQ(B): L/W = 3.5/1; 22%EA; 0.1%AQ; (0.5% SBH); H-factor = 300–350; Bleaching: O-A-D-EP-P; (*) 50% monomer, 50% oligomer; (**) as polymer: Mw = 11.7 kDa. 80 mol% xylose conversion to furfural (F) [26]; 85% AcOH recovery based on industrial experience.

The addition of SBH resulted in 1.5% higher cellulose and 0.6% higher xylan yield. Thus the addition of REG stabilizers is no viable option, since it deteriorates cellulose purity, which cannot be compensated unless prehydrolysis intensity is increased, which in turn reduces both yield and viscosity. The recovery of more than 8% xylose on odw from the released hydrolysate and its potential conversion to 4.9% furfural on odw significantly contributes to the economy of the fractionation process. Hence the sales of the DPW production increase by almost 60 €/t of wood, assuming the current furfural market price of 1 200 €/t (~ 15–20% of the DPW sales).

The birch PHSAQ dissolving pulp shows rather low cellulose purity (Table 3), which is sufficient for rayon application as confirmed by reasonably good viscose quality (Figure 2), however, not sufficient at all for cellulose acetate production, where a residual xylan content of 1.5% constitutes the minimum requirement. In a series of experiments, where the intensity of prehydrolysis was gradually increased to very high levels, the relationship between pulp yield after subsequent SAQ cooking and the resulting xylan content and the viscosity of the unbleached pulps was monitored. Figure 3a reveals the substantial yield loss from 34% to 23% on odw when the xylan content is reduced from 4.5% to 1.5% by intensified prehydrolysis.



(a) **(b)**

Figure 3a. Yield and viscosity related to the xylan content in a PHSAQ pulp as a function of prehydrolysis intensity expressed as log(P-X_S) as shown in Figure **3b** [11].

The low pulp yield combined with the low pulp viscosity of 300 mL/g excludes this production concept for the manufacture of acetate grade pulps. Hardwoods with substantially lower xylan content than birch, such as *Eucalyptus urograndis* or *saligna*, might be a suitable raw material source for the production of low-quality acetate grade pulp by means of PHSAQ cooking only, avoiding additional refining steps.

In recent years, several studies focused on the conversion of paper-grade to dissolving pulps by simply extracting the hemicelluloses (mainly xylan also in the case of SW pulp) in aqueous 1.5–3.0 M NaOH solution at 20–30°C (CCE) [19, 27]. In this way, cellulose yield is not affected, which constitutes a clear commercial benefit over the PHK procedure (Table 3). Further, the CCE-treated kraft pulp (K-CCE) reveals a higher alkali resistance, expressed as R18, and a more narrow molar mass distribution (MMD) than the PHK-pulps [19]. However, an alkali-insoluble xylan fraction (≥4%) of high molar mass remains in the pulp even at high NaOH concentration [28]. Further drawbacks of a CCE treatment constitute the partial conversion to cellulose II occuring at NaOH concentration > 2 M as well as the aggregation of the microfibrils, which, upon drying, results in a compaction of the supramolecular structure. These alterations of the cellulose structure, possibly together with the entrapped high molar mass xylan, partly explain the poor quality of the viscose made from CCE-treated pulps (Figure 2). Different to PHK and AS dissolving pulps, the outer cell wall layers, P and S1, of CCE-treated paper-grade pulps are preserved to a greater extent [19, 29]. Thus, the swelling capacity of the S2 is restricted by the rigidity of the outer cell wall layers. The reduced swelling capability in turn causes a lower accessibility and, therefore, lower filter values with high particle numbers, as illustrated in Figure 2. The high swelling resistance due to a thick primary wall [30] is presumably also the reason for the poor viscose quality prepared from cotton linters (Figure 2). It was shown that an endoglucanase post-treatment could improve the accessibility of a CCE-treated kraft pulp, which translates to a slight improvement of the viscose pulp reactivity (Table 3). At the same time, it allows the precise adjustment of the degree of polymerization of the pulp [27].

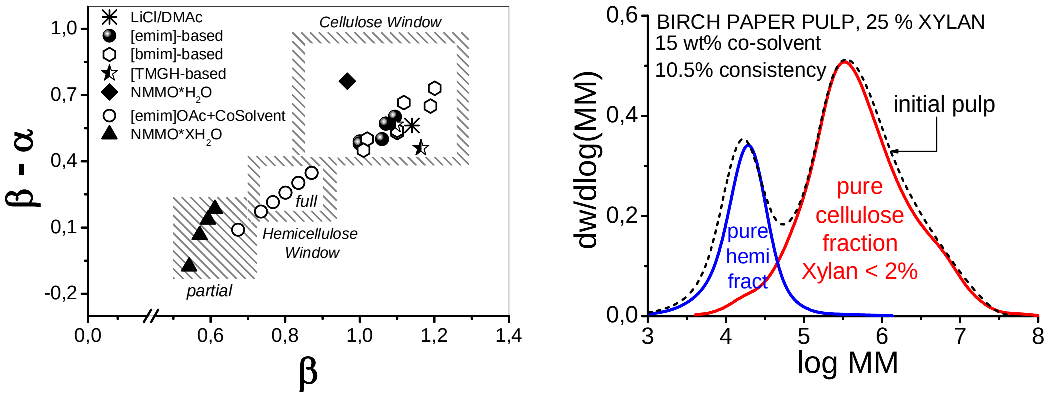
The undiluted filtrate of the CCE stage is a rewarding source of polymeric xylan because the amount of concomitant impurites, such as lignin, extractives or hydroxyacids, or alkaline sugar degradation products, is low. In a first step, the xylan is concentrated by ultrafiltration followed by diafiltration to maximize the xylan-to-NaOH ratio. The xylan is precipated by the addition of an alcohol or a non-solvent or simply by acidification. The xylan yield depends mainly on the raw material source and the conditions in the CCE step. From a birch kraft pulp, 8.3% of xylan on odw and from a *Eucalyptus globulus* kraft pulp, 6.6% [31] of xylan on odw were isolated as dry powder when using 2.5 M NaOH solution at 20°C [32] and 2.25 M NaOH solution at 30°C for one hour, respectively (Table 3). Since polymeric xylan from alkali extraction of hardwood has no definite market yet, no value can be attributed to this product. For example, alkali-extracted xylan can be modified to a film for packaging application after derivatization to a water soluble polymer as recently demonstrated by the conversion to carboxymethyl xylan (CMX) of different DS values [32].

Ioncell process

Although about 50% of the hemicelluloses and about 10% of cellulose are lost during kraft cooking [33], it is by far the most selective process for the separation of lignin from lignocellulosic biomass. Thus, the resulting paper-grade pulp is the most attractive raw material for the manufacture of pure and high molar mass cellulose and hemicelluloses, provided that a process can be developed that allows the selective separation of these polymers. As previously shown, the existing protocols for the removal of hemicelluloses, such as autohydrolysis or alkaline extraction, are all accompanied by unwanted side and degradation reactions or partial conversion of cellulose I to cellulose II. This can largely be avoided by solvent extraction using an aqueous Ni(tren) solution [34, 35]. However, this protocol is handicapped by the necessity of an effective removal of the residual nickel and by the fact that glucomannan from softwood pulp remains almost insoluble under these extraction conditions.

In 2002, Rogers et al. first demonstrated that some ionic liquids (ILs) could solubilize cellulose [36]. Currently, [emim]OAc is regarded as one of the best, if not the best cellulose solvent. In an attempt to predict the cellulose dissolution properties of ILs, the empirical concept of net-basicity, β-α, was suggested, which accounts for the acidity imparted by the cation [37]. It was shown that all ILs reported to dissolve cellulose are located in an empirical solubility window defined by $0.35 < \beta\text{-}\alpha < 0.9$ with $\beta > 0.8$, expressing a necessary balance between acidity and basicity.

In the considerations to find a solvent system that could selectively dissolve hemicelluloses from a hemicellulose-rich pulp, *e.g.* paper-grade kraft pulp, it was hypothesized that the requirements for a solvent regarding H-bond basicity are lower as compared to those for cellulose-dissolving ILs. The lower molar mass, the amorphous structure, and the reduced ability to form inter- and intramolecular H-bonds due to the absence of the exocyclic hydroxymethyl group should facilitate dissolution. Indeed, the addition of a defined amount of a molecular co-solvent to [emim]OAc to lower H-bond basicity, β, and the net basicity, β-α, was successful in the quantitative and selective dissolution of hemicelluloses from a hemi-rich paper-grade pulp (Figure 4a), while both polymers remained completely unchanged in molar mass and yield (Figure 4b).



(a) **(b)**

Figure 4a. Net basicity, β-α, plotted against β, showing the solubility windows for cellulose and hemicellulose, respectively. **4b.** Molar mass distribution of birch kraft pulp and the pure components, cellulose and xylan, separated thereof by selective dissolution of the latter in [emim]OAc+Co-solvent.

In this way, a new process, IONCELL, was developed, which allows the conversion of a cheap paper-grade pulp to a dissolving pulp of highest purity. At the same time, pure xylan can be recovered by further addition of the co-solvent, which then acts as a non-solvent. The residual pure cellulose fraction may then enter a Lyocell process for the production of regenerated cellulose products.

Conclusions

There is no doubt that the existing dissolving pulp processes, AS and PHK, constitute a commercially attractive biorefinery platform. While biorefinery concepts have already been realized in industrial scale on the basis of the AS process, this was not the case for the PHK process so far. Now, with the development of technically feasible water prehydrolysis processes, the way is open to utilize the wood hydrolysate as a source for high value-added chemicals. The novel SEW fractionation process has the potential to replace the AS process owing to a higher flexibility in the selection of the raw material source, substantially lower cooking times, and the near absence of sugar degradation products. However, no differences are seen in the properties of the dissolving pulps resulting from both acidic processes.

The general drawback of the industrial processes is that they experience severe cellulose losses once the demand on purity increases beyond the typical rayon grade quality. All existing protocols for the removal of hemicelluloses are associated with loss reactions or, in the case of the conversion of a paper-grade pulp by cold caustic extraction, with a partial conversion of cellulose I to cellulose II as well as residual hemicelluloses contents too high for the manufacture of high-purity cellulose products.

Based on systematic investigations of the solubility properties of ILs towards polysaccharides, the IONCELL process was recently developed, which permits the production of high-purity dissolving pulps from a hemicellulose-rich paper-grade pulp. Owing to the high selectivity and efficiency, the IONCELL process could be the breakthrough for a new generation of dissolving pulp processes, provided that the selected ILs can be recycled in an economically feasible way.

References

1. Brice, R. 2012. High purity cellulose through 2020. In: The Cellulose Gap 2012: Monte Carlo.

2. Haemmerle, F.M. 2011. The cellulose gap. Lenz. Ber. 89, pp. 12–21.

3. Shen, L., Patel, M.K. 2010. Life cycle assessment of man-made cellulose fibers. Lenz. Ber. 88, pp. 1–59.

4. Sixta, H. 2006. Pulp Properties and Applications, In: Handbook of Pulp, H. Sixta (Ed.) Wiley-VCH. Pp. 1009–1067.

5. Leschinsky, M., Sixta, H., Patt, R. 2009. Detailed mass balances of the autohydrolysis of Eucalyptus globulus 1t 170C. Bioresources 4(2), pp. 687–703.

6. Wiley, E. 2011. The Practicalities of converting to DP technology. Andritz Pulp&Paper.

7. Guetsch, J., Sixta, H. 2012. Regeneration of spent activated charcoals used for lignin removal from prehydrolysis-kraft prehydrolysates. Ind. Eng. Chem. Res. 51(25), pp. 8624–8630.

8. Guetsch, J., Leschinsky, M., Sixta, H. 2011. Process for improved processability of hydrothermolyzates of lignocellulosic material by hydrolysis and adsorption.

9. Schild, G., Mueller, W., Sixta, H. 1996. Prehydrolysis kraft and ASAM paper grade pulping of eucalypt wood. A kinetic study. Das Papier 50(1), pp. 10–22.

10. Rauhala, T. et al. 2011. Effect of autohydrolysis on the lignin structure and the kinetics of delignification of birch wood. Nord. Pulp Pap. Res. J. 26(4), pp. 386–391.

11. Borrega, M., et al. 2012. Potential of hot water extraction of birch wood to produce high-purity dissolving pulp after alkaline pulping. Bioresour. Technol. 2012. (Submitted.)

12. Testova, L. et al. 2012. Cellulose degradation in alkaline media upon acidic pretreatment and stabilization Carbohydr. Polym. (Submitted.)

13. Fasching, M. 2005. Prehydrolysis sulfite revisited. Macromol. Symp. 223, pp. 225–238.

14. Sixta, H. et al. 2011. Progress and challenges in the isolation of xylan from Eucalyptus Wood. In: 5th International Colloquium on Eucalyptus Pulp. Porto Seguro, May 8–11.

15. Iakovlev, M., Heiningen, A.v. 2012. Efficient fractionation of spruce by SO_2-ethanol-water treatment: closed mass balances for carbohydrates and sulfur. ChemSusChem 5, pp. 1625–1637.

16. Janson, J. 1974. Analytik der Polysaccharide in Holz und Zellstoff. Faserforschung und Textiltechnik 25, pp. 375–382.

17. Sixta, H. 2006. Multistage Kraft Pulping. In: Handbook of Pulp, Wiley-VCH, Editor, Wiley-VCH. Pp. 325–365.

18. Borrega, M., Nieminen, K., Sixta, H. 2011. Degradation kinetics of the main carbohydrates in birch wood during hot water extraction in a batch reactor at elevated temperatures. Bioresour. Technol. 6, pp. 1890–1903.

19. Schild, G., Sixta, H. 2011. Sulfur-free dissolving pulps and their application for viscose and lyocell. Cellulose 18, pp. 1113–1128.

20. Sixta, H. et al. 2004. Influence of beech wood quality on bisulfite dissolving pulp manufacture. Part 1: Influence of log storage on pulping and bleaching. Holzforschung 58, pp. 14–21.

21. Sixta, H. et al. 2011. Progress and challenges in the separation and purification of xylan from hardwood. In: 3 rd Nordic Wood and Biorefinery Conference (NWBC) 2011. Stockholm, March. Pp. 22–24.

22. Swan, B. 1965. Isolation of acid-soluble lignin from the Klason lignin determination. Svenska Papperstidning 68, pp. 791–795.

23. Schelosky, N., Roeder, T., Baldinger, T. 1999. Molmassenverteilung cellulosischer Produkte mittels Groessenausschlusschromatographie in DMAc/LiCl. Das Papier 53(12), pp. 728–738.

24. Wollboldt, P. 2011. Lignosulfonate characterization. Wood KPlus.

25. Treiber, E. 1962. A small scale laboratory viscose plant for testing rayon grade pulps. Das Papier 16, pp. 85–94.

26. Xing, R., Qi, W., Huber, G.W. 2011. Production of furfural and carboxylic acids from waste aqueous hemicellulose solutions from the pulp and paper and cellulosic ethanol industries. Energy&Environm. Science 4(6), pp. 2193–2205.

27. Gehmayr, V., Schild, G., Sixta, H. 2011. A precise study on the feasibility of enzyme treatments of a kraft pulp for viscose application. Cellulose 18, pp. 479–491.

28. Wollboldt, P. et al. 2010. Accessibility, reactivity and supramolecular structure of E. globulus pulps with reduced xylan content. Wood Sci. Technol. 44(4), pp. 533–546.

29. Sixta, H. 2000. Comparative evaluation of TCF bleached hardwood dissolving pulps. Lenz. Ber. 79, pp. 119–128.

30. Temming, H., Grunert, H. 1973. Temming Linters. Peter Temming AG, Glueckstadt.

31. Sixta, H., Schild, G. 2009. New generation kraft process. in 2nd Nordic Wood Biorefinery Conference. Helsinki.

32. Alekhina, M. et al. 2012. Preparation and characterization of biodegradable carboxymethyl xylan based film. Carbohydr. Polym. (Submitted.)

33. Sjöström, E. 1993. Wood Chemistry. Fundamentals and Applications. Academic Press.

34. Janzon, R. et al. 2008. Upgrading of paper-grade pulps to dissolving pulps by nitren extraction: yields, molecular and supramolecular structures of nitren extracted pulps. Cellulose 15(5), pp. 739–750.

35. Puls, J., Janzon, R., Saake, B. 2006. Comparative removal of hemicelluloses from paper pulps using nitren, cuen, NaOH and KOH. Lenz Ber 86, pp. 63–70.

36. Swatlowski, R.P. et al. 2002 Dissolution of cellulose with ionic liquids. J. Am. Chem. Soc. 124(18), pp. 4974–4975.

37. Hauru, L.K.J. et al. 2012. Role of solvent parameters in the regeneration of cellulose from ionic liquid solutions. Biomacromolecules, on-line.

Andritz's new technology applied to dissolving pulp grades – a different approach

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Andritz Oy

Abstract

Sulphite cooking has dominated the production of dissolving pulp in the past. Because of environmental reasons, sulphite cooking has decreased and instead has become pre-hydrolysis kraft cooking. Earlier is was done only with batch cooking technology, but due to increasing demand of dissolving pulp, a process based pre-hydrolysis kraft cooking done with continuous cooking technology has been developed. This new solution has been through extensive laboratory trials and subsequently installed and operated within an existing pulp mill originally designed for bleached kraft market pulp. The new process and equipment design have addressed the negative experiences encountered on previous attempts to apply continuous cooking technology for dissolving pulp manufacturing. Both new and existing pulp mills can benefit from the new process solution, which is also allowing campaign production of dissolving pulp or paper grade pulp with the same fiber line. The quality of the hydrolysate taken out from the system is extremely good, which makes it possible to use it for further refining.

Introduction

Dissolving pulp (DP) demand from cellulose experienced extreme volatility in 2010 to 2011. This was due in large part to the increased consumption of textile fiber in Asia as well as a series of difficult cotton harvests and increasing environmental pressure on the production of textile fibers from cotton and synthetic oil based derivatives. Prices for DP doubled from typical levels and maintained these high levels for several quarters. These high prices instigated a global interest in the ability to convert existing market pulp capacity into DP grades.

In recent history, dissolving pulp from cellulose had been dominated by batch cooking technology. A perception had been formed from the 1980s and 90s that continuous cooking presented too many difficulties in stable operation to produce a high purity product like DP. Some of the best documented evidence for continuous cooking technology in DP manufacture can be found in the 1981 paper discussing a conversion project at Ahlstrom Varkaus using a two vessel cooking system [1]. This process was based on the acid hydrolysis of birch, which is among the highest hemicellulose containing wood species and therefore very challenging for DP manufacture. There were also additional installations using single vessel cooking systems located in Russia and Brazil.

Andritz initiated a vigorous DP process development program based on continuous cooking in 2008 when the first indications of market volatility appeared. Several new technology solutions had been fully developed over the previous decades that added to the attractiveness of such a development program, including Diamondback chip steaming [2], TurboFeed chip pumping [2], Lo-Solids Cooking [3] and new control technologies.

Laboratory investigations clearly showed the latest continuous cooking technology could be easily adapted to produce DP with a reduced wood consumption and an improved overall energy efficiency. While this initial laboratory work was performed on North American softwoods, similar studies have since been performed duplicating the results on various furnishes including other softwood, hardwood and Eucalyptus species from around the globe.

Laboratory results

Due to the synergy with hemicellulose based byproducts, straight away Andritz focused on water prehydrolysis instead of the previous acid prehydrolysis process. A water or auto-hydrolysis process was first developed in the 1960s in Germany [4]. The process relies on the naturally forming acetic acid reaction products generated to maintain an acidic pH typically below 4. By controlling the retention time and temperature of the reaction, a desired hemicellulose removal rate can be achieved. In addition, acid soluble lignin and organic acids are extracted from the chips during the auto-hydrolysis phase of the DP process.

Following auto-hydrolysis, the chips are washed with hot water to recover the hemicellulose extracted and acetic acids generated. This dedicated washing step is a novel feature of the new system and it enhances the removal of hemicelluloses from chips. It is designed to improve recovery of the valuable byproducts while limiting the carryover of undesirable byproducts into the digester vessel. If allowed to carryover, these byproducts will consume large amounts of alkali in a neutralization step prior to the alkaline cooking phase.

The hemicellulose extracted chips are cooked in the digester to reduce kappa level to the desired target. With the efficiency of the auto-hydrolysis process, the kappa level out of the digester can be raised several kappa units above the typical target for batch cooking. The higher kappa target can improve yield by several percentage points.

Both laboratory and mill results have shown the pulp is extremely easy to oxygen delignify, reaching a kappa level of 3–5 units independent of wood species. Bleaching can be done in a variety of sequences.

ECF or Light ECF (ECF with very small amount of ClO_2 and with O_3 stage) sequences are typically used for bleaching.

Process design

The major drawback of the previous continuous cooking systems appeared as repetitive and uncontrollable scaling within the process. This scaling manifested itself primarily around the location of drastic pH change. In the two vessel system, Figure 1, with the traditional chip feeding technology of the period the metallurgies were insufficient for the process conditions and therefore extra equipment was introduced to protect the high pressure feeder from extremely low pH environments. The Dragos separator isolated the 4–5 pH environment around the high pressure feeder from the 1–2 pH environment in the impregnation vessel. While this addressed the problems with materials of construction, it increased the level of complexity in an already challenging cooking system to keep in precise control.

Additionally, the two vessel reference developed a scale control program that required the system be converted to kraft pulp every 2–3 weeks in order to remove scale buildup particularly in the bottom of the impregnation vessel and around the screens. This scale could be removed by the switch from acidic to alkaline conditions.

Single vessel systems were also being used to produce dissolving pulp. In addition to the limitations in chip feeding technology, a major pH change was occurring within the cooking vessel that was difficult to control. As the chip volume and digester flow variations occurred, the pH interface location also moved up and down in the cooking vessel. This promoted scaling and it was common for these single vessel systems to take more frequent conversions to paper grade for several days at a time for cleaning.

While both system types produced dissolving pulp for many years in campaign form with kraft pulp, eventually the drawbacks in the system design resulted in the conversion back to full time kraft pulp production. Some of these conversions to produce only kraft pulp also coincided with difficult market situation of dissolving pulp grades in the mid 1980's.

Given the experiences that DP could be manufactured using continuous technology and the promising results with the new auto-hydrolysis process in the laboratory, Andritz developed and sold its first DP system conversion in January of 2011, Figure 2. The conversion was made to a 2009 Andritz single vessel installation successfully making market pulp from Eucalyptus. With the addition of the pre-hydrolysis vessel (PHV) and auxiliary equipment, the system was successfully converted to DP production by November of 2011.

The inclusion of the Diamondback (DB) chip steaming system, where extremely effective chip steaming removes substantially all the air, is a key to the new process. Air-free chips allow for extremely rapid liquid penetration and reduced times for heat transfer. The volume of chips is evenly metered into the system with the DB system allowing for precise control of L/W ratios and heating in the top of the PHV, over 60°C in only several minutes in the vapor-phase top.

After a defined retention time dependent on wood species, the water with acetic acid is extracted from the vessel through internal screens similar to digester vessel screens. Due to a slightly exothermic reaction, the extraction temperature is typically 5C higher than the top liquor phase temperature of the PHV. Hot water added to the bottom of the vessel is also extracted from the screens to create a counter-current washing zone similar to a Hi-Heat washing zone within the digester. This wash zone further removes those reaction products still within the chips at the time of extraction by displacement and diffusion.

In the transfer between reactors, white liquor can be added to already begin the neutralization process. At the top of the digester, the main addition of white liquor is added to neutralize any acidic liquor that carry into the digester. This addition also ensures that the concentration of dissolved organics does not exceed the threshold for precipitation and can instead be removed in the first digester extraction. As the chips are fully impregnated with water, diffusion of the alkali into the chips is extremely fast. Very low reject levels have been observed in the laboratory and in the mill operation using the new auto-hydrolysis process.

Using Lo-Solids Cooking principles, filtrate is added to further wash dissolved organics through displacement and diffusion from the chips while adding additional fresh white liquor for the final delignification phase in the digester. Delignification continues to a wood specific limit to preserve viscosity and overall yield. For Eucalyptus, 9–12 kappa is the target out of the cooking system.

Finally, the extracted hydrolysate from the PHV and the extraction liquors from the digester can be processed separately or together to recover heat energy, keeping the operational cost of the system in control while avoiding excessive hot water generation. By selecting a kettle type reboiler as the heat recovery unit, any steam generated and used in the bin is free from the risk of alkali contamination.

In washing, screening and bleaching, no major changes were done. DP pulp is easy the oxygen delignify, reject amount after cooking is extremely low, ClO_2 consumption has decreased about 50% and COD load in effluent 33% compared to kraft pulp.

Results

After initial startup and before complete optimization occurred, mill DP samples were evaluated against the laboratory simulations and other mill's DP with similar Eucalyptus chips. Table 1 shows this comparison on final bleached pulp. Optimization has further improved pentosan content (<2.5%) and alpha cellulose content (95–97%).

Andritz was released from site coverage within 2 months of startup. Among the most positive results, the mill has been able to produce dissolving pulp for over 3 months before their first scheduled maintenance downtime. DP quality has been good with several viscose fiber producers providing positive feedback. Competing DP fiber suppliers have also indicated the quality to be acceptable for potential future conversion discussions. Several additional conversion projects have already been sold and are in execution phase.

While additional optimization work on the system remains as with any new technological development, the future of continuous cooking technology used for dissolving pulp manufacturing is again colorful and bright.

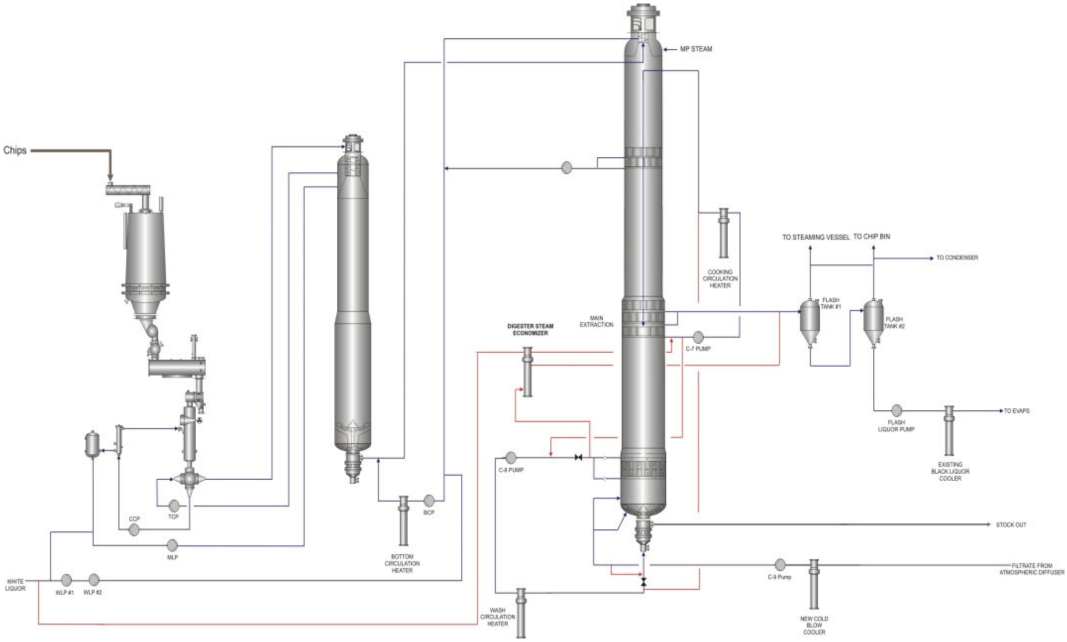

Figure 1. Traditional two vessel cooking system with acid pre-hydrolysis.

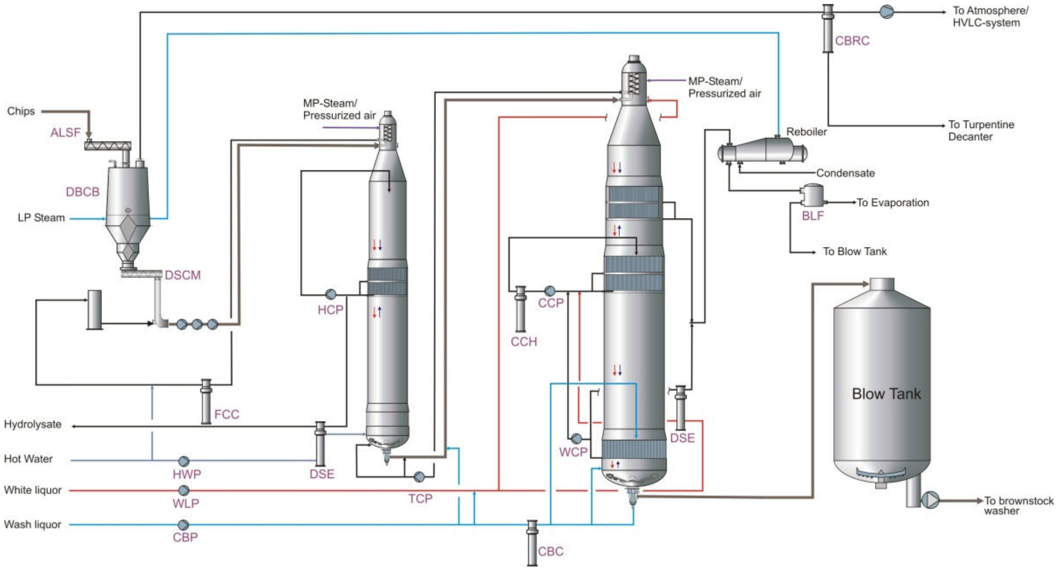

Figure 2. Andritz's new dissolving pulp cooking system with pre-hydrolysis vessel.

Table 1. Comparison of laboratory, mill and published targets for Eucalyptus based dissolving pulp.

	Andritz DP Results Lab / Mill		South American DP Producer Eucalyptus Specs		
Species	**Eucalyptus**	**Eucalyptus**	**Standard**	**Special**	**High Grade**
Viscosity	400–550	520	350–599	250–599	500–599
Brightness	91+	90.2	88–90	89–92	> 90.5
S18	1.4–2.8	3.3–3.8	3.0–4.0	2.3–3.0	< 2.3
S10	2.1–3.8	4.7–6.4	~7	4.0–7.0	4.0–5.5
Ash	0.11–0.14	0.13	0.03–0.12	0.03–0.10	0.03–0.08
Extractives	< 0.20	<0.10	< 0.20	< 0.15	< 0.10
Alpha	94.5–97.4	94.7	94.5–96.0	95.0–96.0	95.5–96.5
R18	97.2–98.6	96.2	96.5–97.0	96.5–98.0	>97.2
R10	96.2–97.9	93.6	~93	93–95	~95
Pentosans	3.0–4.0	3.0	3.0–4.0	2.5–3.5	1.5–2.5

References

1. Arhippainen, B., Nevalainen, P., Marttala, T., Blom, U., Hänninen, E., Nikula, M. 1981. Development of the Alva Prehydrolysis Process (parts 1 and 2).

2. Wiley, W.E., Stromberg, B. 2003. The Development of an Innovative Chip Feeding System for Continuous Digesters.

3. Marcoccia, B., Laakso, R., McClain, G. 1996. Lo-Solids pulping: principles and application.

4. Rydholm, S. 1965. Pulping Processes.

5. Sixta, H. 2006. Handbook of Pulp.

Forest biorefinery cluster – a possible path to biobased products

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Abstract

The forest biorefinery provides an opportunity to increase the profitability of the pulp and paper mills in North America and Scandinavia by producing value-added biobased products. Different technological routes to generate fuels and chemicals are available, however clear choices on what to produce must be taken. The objective of this study is to assess the technical feasibility, advantages and challenges of a hypothetical forest biorefinery cluster built around a pulp and paper mill. The cluster consists of a dissolving pulp mill with biorefinery for furfural production on its site and a chemical plant for tetrahydrofuran and a polytetramethylene ether glycol production. The cluster is technically feasible. The participants in the cluster initiative produce biobased products, share resources, access new markets and generate profits. Partners' location, capital sourcing, selling products to new markets and interactions with new customers are among the challenges to be addressed.

Introduction

Today, many companies, especially in the chemical and pharmaceutical sector, seek biobased raw materials and products; it is expected that the demand for biochemicals increases in the long term. It is estimated that the market for biobased plastics, in particular, will reach 3.45 Mt by 2020 [1]. However, the market potential of biobased products is closely related to fossil fuel prices [2], which in the future will probably rise substantially and new business opportunities for biobased products will be opened. Considering biorefinery produced chemicals, polymers seem to have the greatest market potential in the future [3].

In an integrated forest biorefinery (IFBR) biobased products can be generated, together with pulp and paper (P&P), by using available and underutilized wood components as a feedstock. Various technological routes to produce fuels and chemicals are available, however clear choices on what to produce will have to be made. These choices have to be based on company's own competencies [4]; it is apparent that the selection of the technological path will be unique for each mill, depending on its business plan, process constraints and infrastructure in place. However, the choice of product is not only a technical decision but it is related to the current and expected economic environment. The IFBR may generate a final market-ready product or an intermediate product for further transformation. It is likely that the additional transformation will be made by other industrial sectors, for example the chemical industry, as it has the required knowledge and equipment in place. This could be an attractive option for companies currently manufacturing products derived from fossil fuels. A direct interface between the IFBR and the chemical industry may be developed [5]; this interface can be established within the boundaries of a biorefinery cluster, where a P&P mill, a biorefinery plant and a chemical making plant collaborate by sharing resources in a sustainable way.

An industrial cluster is a group of companies that cooperate with each other and with the local community to efficiently share resources leading to improved environmental quality, economic gains, and equitable enhancement of human resources for both the business and local community [6]. The advantages to be gained from the cluster could result from the use and share of a common primary feedstock, mutually beneficial supplier and consumer relationship, heat and power generation as well as market accessibility for final products. Despite the strength of the forest industry arising from the availability of biomass, existing infrastructure and supply chains, the lack of capital is among the main constraints to the development of biorefinery cluster [3]. Factors such as geographical constraints, P&P process, the energy and material requirements should be taken into account while developing a cluster. The proximity of the product's end user or the target market to the biorefinery cluster is also important if further transformation of the product is required and would not be carried out within the IFBR [7].

The objective of this study is to evaluate the feasibility of a forest biorefinery cluster consisting of a dissolving pulp mill with a plant for hemicelluloses conversion into furfural and a nearby chemical manufacturer producing tetrahydrofuran (THF) and converting it into polytetramethylene ether glycol (PTMEG). Future opportunities for biobased chemicals generated in the cluster are first evaluated. Then, the structure of the forest biorefinery cluster, together with the corresponding technological pathways, is described and potential benefits for the participants in the cluster are assessed. Finally, challenges in partnership development are discussed.

Future perspective for biobased chemicals

Due to low production costs, China is the largest producer of furfural and THF today [8–10]. The world market for furfural is estimated at about 200 000–210 000 t/y, and there will be a steady growth in furfural demand in the future [10]. Today, the THF market is about 200 000 t/y [11], but it is expected that it will exceed 800 000 tons by 2017 [9]. A major part of the growth will occur in China and PTMEG is the fastest growing market for THF [9, 11]. This indicates that biobased PTMEG, THF and also furfural have market potential in the future. Biobased chemicals are real opportunities for a forest biorefinery cluster.

Today, the share of biobased THF and PTMEG is quite small compared to the total production of these chemicals. For that reason, large chemical companies, which have a scale advantage, may not be interested in such a small niche. This could be a good opportunity for medium sized enterprises for which a smaller market is attractive. This could be the case of the chemical manufacturing plant involved in the forest biorefinery cluster. By creating a cluster, the chemical industry partner and the pulp mill get access to competencies required for production, marketing and sales of chemicals.

Case study definition

A dissolving pulp mill is the core of the proposed hypothetical cluster. Dissolving pulp is a low yield chemical pulp with high cellulose content suitable for making rayon, cellulose acetate and cellophane. The process for producing dissolving pulp is a variation of the Kraft process with a pre-hydrolysis stage prior to pulping. During pre-hydrolysis hemicelluloses are solubilised by action of steam, water or chemicals to produce monosaccharides (arabinose, xylose, mannose, galactose, glucose), oligosaccharides (galactoglucomannan, glucuronoxylan), and other minor chemical components (weak acids, furans, phenolic compounds). The hemicellulosic sugars can be converted into a range of value-added products. A biorefinery for furfural production is considered in the present study, as furfural is a high-value product and a building block in the chemical industry. The pre-hydrolysate stream is usually diluted, therefore it is recommended to concentrate it using membranes in order to save energy and decrease operating costs. The concentrated pre-hydrolysate is then transferred in a reactor, where C_5-sugars are converted into furfural by dehydration in the presence of an acid catalyst. Furfural is separated and purified using azeotropic distillation.

The furfural generated in the biorefinery is shipped to the nearby chemical making plant where it is used as a feedstock for THF production. THF is a precursor of PTMEG, a raw material for the production of polyurethanes, elastic fibers (Spandex or Lycra), elastomers, and copolyesters. The current industrial process for THF production involves catalytic dehydration and cyclization of 1,4-butanediol to THF, the intermediate 1,4-butanediol being obtained from fossil resources [12]. The production of THF using a biobased process was employed between 1949 and 1961 by a major chemical company but was abandoned because of the competition with the THF from petroleum feedstocks [13]. However, chemicals production from biobased resources has regained interest in the recent years.

The THF production from furfural involves two steps – the decarbonylation of furfural to furan and its subsequent hydrogenation to THF. The decarbonylation is done in the presence of palladium as a catalyst. Furfural is usually refluxed under pressure at 200°C, while furan and CO are continuously removed from the reaction mixture by distillation [8]. The resulting furan is hydrogenated to THF in the presence of Raney-nickel catalysts.

In the chemical making plant, THF is further converted to PTMEG. It is first polymerized over a heterogeneous catalyst in presence of acetic anhydride to form polytetramethylene ether diacetate (PTMEA). The non converted THF, recovered from the reactor effluent by stripping, is purified and recycled to the reactor. Then, PTMEA is converted to PTMEG by reacting with an excess of methanol in presence of a basic catalyst. Methylacetate (MEAC) is formed as a by product. The subsequent process steps are neutralization of crude product, filtration, and recovery of purified methanol and disposal of methanol-MEAC azeotrope. Finally, oligomers from crude PTMEG are removed by vaporization at high vacuum and additives are introduced to the finished polymer [14].

Technical feasibility of the cluster

The dissolving pulp mill is supplied with 2 000 odt/d of hardwood chips, fresh water and chemicals. Fresh water is treated, heated and used in different process areas. Steam is produced by burning the delignification liquor in the recovery boiler and power is generated in a cogeneration plant. The mill produces 720 odt/d dissolving pulp and generates around 4 000 t/d dilute pre-hydrolysate, from which 20 000 tones of furfural are produced annually.

The IFBR exports to the chemical plant furfural, heat and power. The water effluents produced in the chemical making plant are treated in the effluent treatment system of the pulp mill. Furfural conversion into THF proceeds at 80% yield, which represents an annual production of 16 000 tones. In the chemical making plant, about 80% of the THF is converted into PTMEG at the rate of 13 000 t/y. From the technical perspective the collaboration between a P&P mill with a biorefinery plant on its site and a nearby chemical making plant is feasible. The participants involved in the cluster initiative produce biobased products, share resources and generate profits.

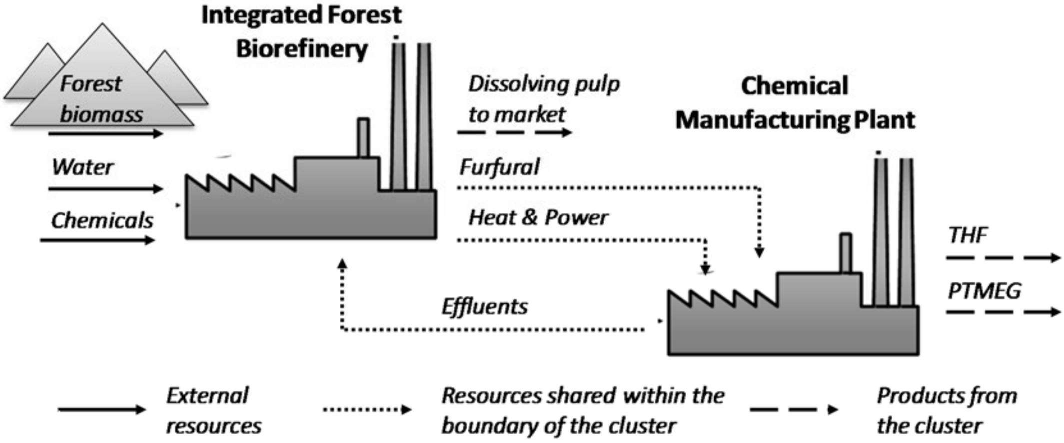

Figure 1. Overview of the biorefinery cluster.

Benefits of the partnership

Profitability of biobased chemicals depends on prices of raw materials and energy. Furfural produced in the dissolving pulp mill based biorefinery is a valuable feedstock for the chemical making plant, since it costs less that the feedstock shipped from China. Buying furfural from the nearby company avoids expensive transportation costs. The geographic proximity of the companies is an important factor for the profitability of the cluster [7]. In addition, the P&P mill sells to the chemical company heat and power at an advantageous price. Sharing infrastructure, such as heat and power plant and effluent treatment system reduces the operation costs of the chemical manufacturing plant. Using fewer resources also reduces the environmental impacts of the cluster.

Several studies have shown that partnerships have many benefits in business in general [15–21] and this applies also to the forest biorefinery cluster. The partnership between the P&P mill and the chemical manufacturing plant adds a competitive advantage for both companies and in that way increases their market share and revenues. By means of collaboration the companies involved in the cluster get an access to key resources such as raw materials, information and capital. Partnership between these companies also enables the chemical producer to manufacture biobased products and gets for the P&P company an access to the chemical market. In addition, collaboration provides new contacts outside of the cluster, which can bring new knowledge, complementary skills and competences to both companies. It is also possible to share risks of new business area by collaboration.

Challenges of partnership development

The production of biobased chemicals needs capital resources. The process for furfural production using pre-hydrolysate from dissolving pulp mill requires investments for reactor, concentration and separation equipment. Heating, cooling and power resources used in the furfural biorefinery and in the chemical making plant are supplied by the utility system of the pulp mill. However, investments for piping required to transport utilities and resources, as well as for grid should be made.

Producing biobased chemicals is a new business area to the P&P industry. Biochemicals are different from pulp or paper to handle and sell. There is also much legislation in the area, since various statutes and norms regulate chemicals production, warehousing and transport. The P&P company uses many chemicals also in its present business, but still legislation of chemicals could be a new world to it and it has much to learn. In addition, production of biochemicals needs also new technical, chemical and business know-how. So, the P&P mill and the chemical company have to assess their existing competencies and the need for learning new capabilities which are required on the new markets [22]. In addition, they have to find an access to the chemical market and overcome barriers to entry, since existing chemical producers will probably try to prevent new competitors. In other words, the P&P mill and the chemical manufacturer have to think about how they could compete with Chinese companies who dominate the present furfural, THF and PTMEG markets.

A price of the product is often crucial factor in purchase decisions. For that reason, the biobased chemicals produced within the cluster should not be substantially more expensive than fossil based ones. In general, it is assumed that a new product has to be cheaper than the product it is intended to replace in order to succeed [23]. But the price of a product tells to a customer also about its quality [23]. In that sense, a higher price could also be a benefit and a way to distinguish from the competitors. The price of a product is not the only factor which affects the success of a product on the market. According to a study of Hart and Tsokas [23], product advantages are the most significant factors to success in the market place. For biochemicals, sustainability is a major component of their added value.

However, forming partnerships can be complex and expensive since trust building requires time and efforts [18, 22, 24]. So, it is important to the P&P company to consider collaboration and networking issues when making decisions on biorefinery processes and products. In addition, for successful collaboration, coordinated decision making and communication are essential [15, 25].

Conclusions

The creation of a biorefinery cluster as possible path to biobased products is evaluated. The cluster, consisting of a P&P mill with a furfural plant on its site and a chemical making plant producing THF and PTMEG, is technically feasible. Biobased PTMEG, THF and also furfural have market potential in the future. The participants in this initiative gain the possibility to produce biobased products, share resources, access new markets and generate profits. However, several challenges have to be addressed to develop successful collaboration between a P&P mill and a chemical company.

References

1. Shen, L., Worrell, E., Patel, M. 2010. Present and future development in plastics from biomass. Biofuels, Bioprod. Biorefin. 4(2), pp. 25–40.

2. Dornberg, V., Hermann, B.G., Patel, M.K. 2008. Scenario projections for future market potentials of biobased bulk chemicals. Environ. Sci. Technol. 42(7), pp. 2261–2267.

3. Hämäläinen, S., Näyhä, A., Pesonen, H-L. 2011. Forest Biorefineries – Business opportunity for Finnish forest cluster. J. Cleaner Prod. 19(16), pp. 1884–1891.

4. Azzone, G., Dalla Pozza, I. 2003. An integrated strategy for launching a new product in the biotech industry. Manage. Decis. 41(9), pp. 832–843.

5. Bozell, J.J., Petersen, G.R. 2010. Technology development for the production of biobased products from biorefinery carbohydrates – the US Department of Energy's "Top 10" revisited. Green Chem. 12(4), pp. 539–554.

6. Mateos-Espejel, E., Marinova, M., Mostajeran-Goortani, B., Paris, J. 2009. Eco-industrial cluster centered on a Kraft mill in rural Canada. World Congress of Chemical Engineering. CD Rom no. 0845, Montreal, Québec.

7. Ajao, O., Senay, S., Radiotis, T., Jemaa, N., Marinova, M. 2012. The biorefinery cluster: Strategy for increased profitability of integrated forest biorefineries. Proceed. International Forest Biorefinery Symposium, PaperWeek Canada, Montréal, Québec. P. 687.

8. Hoydonckx, H.E., Van Rhijn, W.M., Van Rhijn, W., De Vos, D.E., Jacobs, P.A. 2012. Furfural and derivatives. Ullmann's Encyclopedia of Industrial Chemistry 16. Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim. P. 285.

9. A Global strategic business report. 2011. http://www.prweb.com/releases/tetrahydrofuran/PTMEG_solvents/prweb8281771.htm 16.3.2012.

10. Mamman, A.S., Lee, J.-M., Kim, Y-C., Hwang, I.T., Park, N.-J., Hwang, Y.K., Chang, J.-S., Hwang, J.-S. 2008. Furfural: Hemicellulose/xylose derived biochemical. Biofuels, Bioprod. Biorefin. 2(5), pp. 438–454.

11. Solventis. Tetrahydrofuran. 2012. http://www.solventis.net/others/tetrahydrofuran.

12. Müller, H. 2012. Tetrahydrofuran. Ullmann's Encyclopedia of Industrial Chemistry 36, p. 47. Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

13. Marcotullio, G. 2011. The chemistry and technology of furfural production in modern lignocellulose-feedstock biorefineries. PhD thesis, Delft University of Technology.

14. Conser S.p.a. consulting engineers. 2012. http://www.conserspa.com/frame_pr-de.htm.

15. Corbett, C.J., Blackburn, J.D., Van Wassenhove, L.N. 1999. Case Study: Partnerships to Improve Supply Chains. Sloan Manage. Rev., summer 1999, p. 71.

16. Coviello, N.E. 2006. The network dynamics of international new ventures. J. Int. Bus. Stud. 37(5), pp. 713–731.

17. Dwyer, F.R., Schurr, P.H., Oh, S. 1987. Developing Buyer-Seller Relationships. J. Marketing 51(2), pp. 11–27.

18. Gadde, L.-E., Snehota, I. 2000. Making the Most of Supplier Relationships. Ind. Marketing Manage. 29(4), pp. 305–316.

19. Gulati, R., Nohria, N., Zaheer, A. 2000. Strategic Networks. Strategic Manage. J. 21, pp. 203–215.

20. Janssen, M., Chambost, V., Stuart, P.R. 2008. Successful partnerships for the forest biorefinery. Ind. Biotechnol. 4(4), pp. 352–362.

21. Mohr, J., Spekman, R. 1994. Characteristics of partnership success: partnership attributes, communication behavior, and conflict resolution techniques. Strategic Manage. J. 15(2), pp. 135–152.

22. Kathuria, R., Joshi, M.P., Dellande, S. 2008. International growth strategies of services and manufacturing firms: the case of banking and chemical industries. Int. J. Oper. Prod. Manage. 28(10), pp. 968–990.

23. Hart, S., Tsokas, N. 2000. New product launch “mix” in growth and mature product markets. Benchmarking: An Int. J. 7(5), pp. 389–405.

24. Doney, P.M., Cannon, J.P. 1997. An Examination of the Nature of Trust in Buyer-Seller Relationships. J. Marketing 61(2), pp. 35–51.

25. Ashton, W. 2008. Understanding the organization of industrial ecosystems. A social network approach. J. Ind. Ecol. 12(1), pp. 34–51.

Production of surface active agents from hemicelluloses extracted from wood chips

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Abstract

This research project aims at converting a Kraft pulp mill into a biorefinery, by extracting hemicelluloses from wood chips and valorise them into alkyl polyglycosides which are surface active agents, in parallel to the production of cellulose fibres.

After the extraction of the hemicelluloses in the pre-hydrolysate the mixture of sugars (the bulk of which are xylose) can be reacted with *n*-butanol and H_2SO_4 to produce alkyl polyglycosides. However it was discovered that impurities in the pre-hydrolysate prevented the direct conversion to surface active agents. We then set out to investigate which impurities were interfering with the reaction and methods of processing the pre-hydrolysate so that the reaction could occur.

Introduction

The concept of turning a Kraft pulp mill into a biorefinery is a simple one. In a traditional mill the cellulose is efficiently extracted and converted into value-added products. The remaining black liquor is then burnt to produce energy. However the hemicelluloses within the black liquor have a much lower energy content than the lignin so this represents a poor use for them. Since it is very difficult to remove the hemicelluloses from the black liquor another method is required. Autohydrolysis of the wood before Kraft pulping is one solution.

There are many reports in the literature about the extraction of xylans from wood, by either autohydrolysis or acid hydrolysis, with up to 90% of the hemicelluloses able to be extracted [1–7]. While the pre-hydrolysates contain sugars (of which xylose is the major component), they also have a large variety of impurities, including dissolved lignin, organic acids (acetic acid and formic acid), sugar dehydration products (furfural and hydroxymethylfurfural) and salts [3–5].

Surface active agents are widely used in modern society. In an effort for more sustainable products, surface active agents from renewable sources have been developed [8]. One widely used class of surface active agents are alkyl polyglycosides, where the sugar acts as the hydrophilic head, while a fatty alcohol is the hydrophobic tail. Glucose is a very common feedstock for this, and the products are often used in products like cosmetics since they cause less irritation of the skin. If the sugars in the pre-hydrolysate could be directly converted into surface active agents without a large number of purification steps needed, this would represent a very useful value-added product able to be derived from the extracted hemicelluloses.

The process for producing alkyl polyglycosides is simple, as shown with xylose and *n*-butanol in Figure 1. The sugar is refluxed in the fatty alcohol along with an acid; the water which is produced can be removed via a Dean-Stark type apparatus which drives the equilibrium to the right. As the reaction is proceeding it is also possible that instead of the hydroxyl group of the alcohol condensing with the sugar, a hydroxyl group from another sugar in the mixture will condense instead. This leads to the formation of alkyl polyglycosides with multiple sugars in the head group. This is termed the degree of polymerisation (DP), with an alkyl polyglycoside with one sugar called DP 1 and two sugars DP 2 and so on. When analysing the resulting product, one of the important properties is the average DP of the alkyl polyglycoside formed.

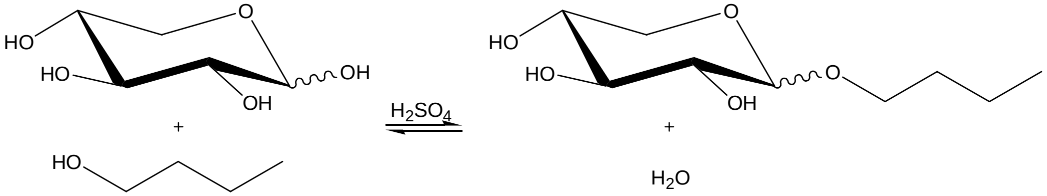

Figure 1. The production of alkyl polyxyloside showing the DP 1 product.

Experimental

Production of surface active agents

The reaction was done in a 250 mL jacketed glass reactor equipped with a condenser with a Dean-Stark apparatus and a mechanical stirrer. A 2.8 excess of *n*-butanol and 2% of 96% H_2SO_4 were added (both compared to xylose) and heated to 120°C under atmospheric pressure. A syrup containing xylose (50 g) at a concentration of 65% was added drop wise under stirring. In the case of adding impurities to the syrup, the amount water added was adjusted so that the concentration of the syrup remained at 65% xylose. Water was removed from the reactor by distillation using the water/butanol azeotrope. After the reaction mixture had reached a water content of approximately 8%, the reactor was allowed to cool to room temperature and the product removed. The resulting product was a homogenous syrup.

Analysis of surface active agents by GC-FID

Samples were first silylated using hexamethyldisilazane (HMDS), trimethylchlorosilane (TMCS) and pyridine with tridecanol or nonanol added as an internal standard. The analysis was carried out on a metal SIMDIST HT-CB column (10 m × 0.53 mm, film thickness 0.5 µm) with helium carrier gas. One µL of sample is injected, the injector is at 300°C while the detector is at 350°C. The temperature program starts at 60°C for 3 minutes and ramps to 350°C at 8°C per minute and holds for 12 minutes.

Results and discussion

The pre-hydrolysates were first concentrated to syrups of 65% xylose content. When the reaction was carried out on this pre-hydrolysate the reaction failed to work with only very minor traces of alkyl polyglycoside observed. In order to determine what impurity if any in the pre-hydrolysate was causing the problem, a series of experiments were carried out on xylose syrups with added impurities. Firstly a pure xylose syrup was reacted as a control. The next step was to take a xylose syrup and add different impurities at the same concentration as was found in the pre-hydrolysates. These model syrups were reacted under the same conditions and the product was analysed by GC-FID to determine the amount of remaining xylose as well as how much alkyl polyxyloside had been produced. The impurities tested included acetic acid, formic acid, furfural, hydroxymethylfurfural, lignosulfonate, sodium chloride, magnesium chloride, calcium chloride and D-glucuronic acid. The results are summarised in Table 1. Figure 2 shows the spectrum for the 65% xylose syrup. There are two peaks found for both xylose and the DP 1 alkyl polyxyloside since mutarotation causes both the α and β anomer to form. This produces a very large number of different isomers for the higher DP values meaning that individual isomers cannot be isolated and only the overall peak area for each higher DP value can be determined.

The analysis showed no major differences between the pure xylose syrup and the syrups with the impurities in either the amount of residual xylose or the produced alkyl polyxyloside. The only observable difference was that some impurities produced darker products than others. This colour difference was not considered a major issue since under industrial conditions the resulting surface active agents are bleached to remove colour.

Table 1. Results of the different trials in the production of alkyl polyxylosides, showing the amount of residual xylose left, the percentage of each DP fraction and the average DP.

Reaction conditions	**% xylose unreacted**	**Percentage of APX as:**				**Average DP**
		DP 1	DP 2	DP 3	DP 4	
65 % Xylose	10	74	17	7	2	1.4
65 % Xylose + Furfural	14	74	17	6	3	1.4
65 % Xylose + HMF	12	74	17	7	2	1.4
65 % Xylose + Acetic acid	11	72	18	7	3	1.4
65 % Xylose + Formic acid	9	68	19	9	4	1.5
65 % Xylose + D-Glucuronic acid	11	74	18	8	0	1.3
65 % Xylose + lignosulfonates (5 g)	15	75	17	6	2	1.3
65 % Xylose + lignosulfonates (11.5 g)	14	80	15	5	0	1.3
65 % Xylose + Phenol	11	78	15	7	0	1.3
65 % Xylose + Na^+ as NaCl	14	74	16	7	3	1.4
65 % Xylose + Mg^{2+} as $MgCl_2$	12	81	15	5	0	1.2
65 % Xylose + Ca^{2+} as $CaCl_2$	11	83	13	5	0	1.2

Since there was some difficulty in finding a good model compound for the lignin in the pre-hydrolysates it was thought that the lignin might be causing the difficulties with the reaction. To test this, the pre-hydrolysate was treated with activated charcoal by stirring overnight and filtering the resulting suspension. When the resulting pre-hydrolysate was reacted the analysis showed that alkyl polyxyloside had been formed as well alkyl polyglycosides derived from the other sugars present (glucose, mannose, arabinose and galactose), although in much lower quantities. This can be seen in Figure 2 which shows the spectrum, with many more peaks found between 12–20 minutes. This much larger amount of different products in the resulting mixture led to issues with quantification because of overlapping peaks. It is impossible with this method to separate the DP 2 and higher fractions into the different alkyl polyglycosides group. This meant that an average DP value could not be calculated. The peak area of the DP 1 alkyl polyxyloside was compared to that of the control groups and showed that a similar proportion of DP 1 alkyl polyxyloside had been formed. The amount of residual xylose was 16%. This was at the higher end of the range seen in the pure xylose experiments but still a similar result.

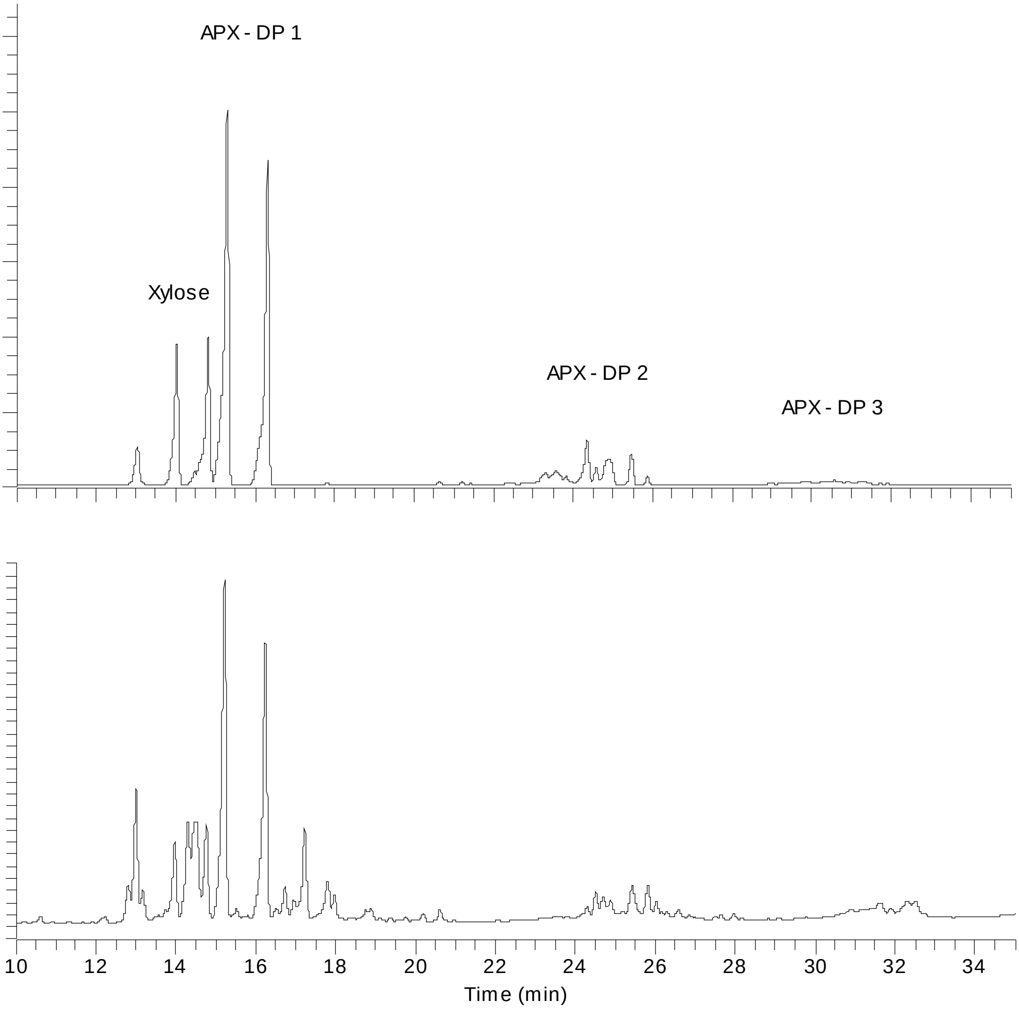

Figure 2. Portion of some GC-FID spectra, the upper spectrum shows the 65% xylose syrup, while the lower spectrum is for the pre-hydrolysate that has been treated with activated charcoal.

Conclusion

It was found that the raw pre-hydrolysate could not be directly reacted to produce the desired surface active agents. However it was shown that filtration of the pre-hydrolysate with activated charcoal to remove lignin produced a product that could be used directly to form alkyl polyglycosides. The other products found in the hydrolysate did not seem to have any significant effect on the production of APX. Further work needs to be carried out to better analyse the resulting complex mixtures of alkyl polyglycosides formed when using pre-hydrolysates.

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References

1. Garrote, G., Parajó, J.C. 2002. Non-isothermal autohydrolysis of Eucalyptus wood. Wood Science and Technology 36(2), pp. 111–123.

2. Chirat, C., Lachenal, D., Sanglard, M. 2012. Extraction of xylans from hardwood chips prior to Kraft cooking. Process Biochemistry 47(3), pp. 381–385.

3. Leschinsky, M., Sixta, H., Patt, R. 2009. Detailed mass balance of the autohydrolysis of Eucalyptus Globulus at 170°C. Bioresources 4(2), pp. 687–703.

4. Garrote, G., Domínguez, H., Parajó, J.C. 1999. Mild autohydrolysis: an environmentally friendly technology for xylooligosaccharide production from wood. Journal of Chemical Technology & Biotechnology 74(11), pp. 1101–1109.

5. Tunc, S.M., Van Heiningen, A.R.P. 2008. Hydrothermal dissolution of mixed southern hardwoods. Holzforschung 62(5), pp. 539–545.

6. Wafa Al-Dajani, W., Tschirner, U., Jensen, T. 2009. Pre-extraction of hemicelluloses and subsequent kraft pulping. Part II: acid- and autohydrolysis. Tappi Journal 8(9), pp. 30–37.

7. Bose, S., Barber, V., Alves, E., Kiemle, D., Stipanovic, A., Francis, R. 2009. An improved method for the hydrolysis of hardwood carbohydrates to monomers. Carbohydrates Polymers 78(3), pp. 396–401. Doi: 10.1016/j.carbopol.2009.04.015.

8. Kervedo, S., Brancq, B. 2008. Tensioactifs basés sur des sucres. L'Actualité Chimique, Oct–Nov 2008. p. 35.

The Forest Biorefinery: Canadian drivers and ongoing activities

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Abstract

The Canadian forest sector is in need of transformation as the demand for several of its traditional products is in decline. A uniquely Canadian approach has been developed over the last several years, driven by unique circumstances. This approach has been defined by:

- A collaborative model, built on a coordinated approach by industry, academia, research centres and governments;
- The concept of maximizing the use of existing assets and infrastructure, in order to minimize the cost of initial transformative steps;
- Large initiatives focused on a small number of well-defined objectives, based on the concept of innovation (i.e. R&D plus deployment); this implies concurrent R&D, engineering and market development, and close collaboration with downstream users and customers;
- A national approach, supported by industry and the federal government, with regional-level implementation carried out in collaboration with the provinces.

A range of programs have supported this approach and have led to early successes.

The Canadian context

Much has been written recently about the bio-refinery in general and the forest bio-refinery in particular. This concept must be considered in terms of regional differences: biomass is bulky and wet, and is therefore expensive to ship; its use must be local. This paper explores the Canadian context and the unique set of responses necessary to develop and implement the forest bio-refinery there.

Energy prices

Following a decade of high prices, North American natural gas prices are now at historic lows. Driven by the development of cheap technologies for exploiting abundant shale gas beds, natural gas prices at the wellhead have been well below $2.50/GJ for the last several years [1]. (All prices assume parity between US and Canadian currencies.) Natural gas liquids, such as ethane, pentane and butane, are more valuable than the natural gas itself, and provide incentives that encourage exploration and drilling even in the presence of historically low gas prices. In response, large scale gas-to-ethylene plants are being built in the US South; LNG terminals to export gas to Asia are in planning for the Canadian West Coast; and operators of major trucking fleets are converting their intercity fleets to operate on compressed or liquefied natural gas. These drivers will conspire to drive up gas prices in the medium term; public concern around the environmental impact of hydraulic fracturing processes may also have an impact. However, it is still likely that gas prices will stay below historical averages for some time to come.

Traditionally, West Texas Intermediate (WTI) oil has traded at a discount of $10 to $15/bbl below Brent crude; the discount is now at historically high levels, with WTI in the $85-$95/bbl range (about $15/GJ), and Brent in the range $110–$120/bbl (about $19/GJ). At the same time, spot market prices for Alberta heavy crude (Western Canadian Select, WCS) have been at least $15/bbl below WTI [2]; at these prices, several oil sands projects have been put on hold. Low WCS prices are driven by a lack of refinery capacity designed to take heavier crude, compounded by shortages in pipeline capacity linking Alberta and US Gulf Coast refineries. As with gas from shale, the volumes of oil available are large, and while the environmental concerns cannot be neglected, the likelihood is that WCS prices will remain lower than WTI prices for the foreseeable future.

Electrical power prices are also low across Canada. Rates are a provincial responsibility, but large industrial users can generally negotiate purchase contracts in the \$0.05/kWh to \$0.07/kWh range (\$14/GJ to \$19/GJ), while producers of biomass power can expect to sell their power into the grid for prices in the \$0.10/kWh range (\$28/GJ).

Gasoline prices at the pump are currently around \$1.30 per litre (\$37/GJ) in Canada, and around \$1.00 per litre (\$28.50/GJ) in the US. These numbers are historically high, but still do not compare with prices of €1.30 per litre or more (almost \$60/GJ) in typical European contexts.

Finally, while some local efforts have been made in North America, there is an absence of any coordinated effort to impose a cost on carbon emissions (whether by carbon tax, renewable fuel standard or other policy measure). Renewable fuel standards have led to a glut of conventional ethanol as fuel demand has dropped. Furthermore, many investors are reluctant to invest where the business case rests too heavily on government action.

The low cost of energy and of carbon emissions in North America conspire to produce an environment where stand-alone bio-fuel processes are unlikely to be commercially viable in the short term. A few exceptions, such as exports of wood pellets from Canada’s West Coast to EU ports, are driven in part by large differences in carbon policies, and would not be economically sensible given consistent carbon prices in the EU and NAFTA. Energy costs in Canada will have to be significantly higher than they are today before bio-fuels, especially wood-based bio-fuels produced using slow-growing northern species, are economically viable on their own – high value co-products are an absolutely critical component of the forest bio-refinery in Canada, at least for the medium term.

On the other hand, there are opportunities to be found even in the context of low energy prices. For instance, the shift to natural gas-based ethylene plants, and away from the traditional naphtha-based plants, means that there is a looming shortage of by-products from the naphtha-based process, for example butylene and other petrochemicals used in the manufacture of synthetic rubbers and elastomers. There are other such opportunities, where shifting processes in the petrochemicals industry leave windows of opportunity for bio-based chemicals. The recent focus on succinic acid and lactic acid from bio-based sources [3] is a further indication that bio-chemicals provide opportunities that are not available to un-integrated bio-energy plants.

Wood supply, product portfolio and infrastructure ecology

Canada’s forests cover multiple ecological zones across 85 degrees of longitude [4], and are characterized by a wide range of wood species and large regional differences between forest type and age. The boreal forests represent the largest single eco-system, but even in the boreal forest, differences in properties, both between and within species, are large. Given the costs of shipping biomass, one solution will not fit the entire country.

As with energy resources, managing forestry resources is a provincial responsibility. There exists a wide range of forestry ownership and tenure programs across the country. Nova Scotia is unique in that approximately half the forests are in private hands; elsewhere the forests are largely on Crown lands where forest management agreements must be negotiated with the individual provincial government. So costs and regulations around forest use also vary across the country.

There is a broad range of infrastructure assets. In the East, many pulp and paper mills are built on sites that were initially developed over 100 years ago. Initially, many of these mills were not connected to a road network or power grid, but relied on river power to run the mill, supply raw materials, and ship goods to market. While all have been upgraded over the decades, the average age of assets is higher, and the average production rate per line lower, than in newer western mills.

There is also a regional difference in pulping processes. Mechanical pulp mills predominate in Eastern areas where the availability of cheap hydro-electric power makes them more cost effective than a kraft mill when wood prices are high. Western mills, built more recently, tend to be larger, single-line kraft mills without the legacy of older assets.

In many cases, there is a symbiotic relationship with sawmills, especially in the case of mills using softwood species. Few pulp mills can afford whole logs; sawmills can make more money from a given log by converting it into dimensional lumber. Residues are converted to chips and sold to pulp mills or used for fabricated panels of various sorts. Bark and sawdust are burned for heat and power. The implication here is that a slump in the sawmill industry will lead to chip shortages (and higher prices) for pulp mill operators; in the reverse case, sawmill operators can't sell their chips.

Shipping opportunities are also highly variable. Coastal mills in British Columbia have deep sea ports and easy access to Asian markets, while eastern coastal mills are closer to Rotterdam than Chicago. Mills in the centre of the continent rely largely on rail or truck to supply central US customers. The end-user for any novel value-added products will need to be identified in this context.

Historically, the Canadian industry has relied heavily on US sales. With the simultaneous collapse of the US housing market and US newsprint demand, the chip supply remains relatively balanced over most of the country, although there are locations where the decline in newsprint is hurting sawmills as well. If the sawmilling industry recovers, there will be a huge need for new outlets for chips, especially softwood chips. Exports of pellets to the EU will only be profitable as long as carbon pricing policies permit, and as long as sawmills can afford to sell chips for energy rather than for pulp. New, high-value products to consume these chips need to be identified quickly.

So the ecology in which the Canadian forest industry operates is complex and regional. There is a critical need to identify regional solutions that fit the various constraints across the country.

The Canadian approach to industry renewal

Response to the range of drivers

We have seen how the Canadian context requires a unique approach. The solution has been characterised by:

- Collaboration between industry, academia, research centres and governments;
- A focus on a small number of well-defined objectives, driven by solid economic, engineering and market analysis early in the process;
- A pan-Canadian technology development approach, supported by industry and the federal government, with regional implementation in collaboration with the provinces;
- Maximizing the use of existing assets and infrastructure, in order to minimize the cost of initial steps towards a transformed industry.

The last point, in particular, reflects the concept of the refinery, where a feedstock is transformed into successively lower-value products. A residue remains, from which no higher value can be extracted and which is therefore best converted to an energy product, Figure 1. Sawdust to pellets, bark to combined heat and power (CHP) plants, and gasification of municipal solid wastes leading to synthetic fuels are three such outcomes. This model, of conversion of residues to energy products, necessarily implies the existence of a healthy primary industry to generate these residues.

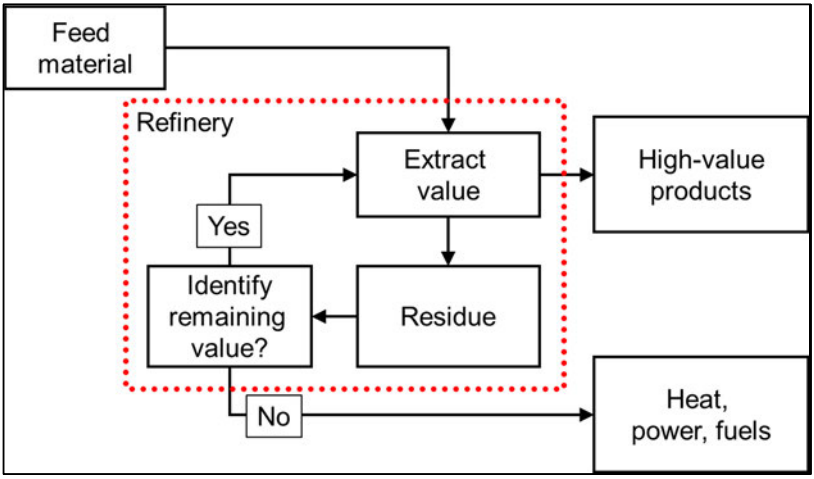

Figure 1. A conceptual model of a refinery designed to extract maximum value from the resource.

A range of programs have helped to build this model. The Pulp and Paper Green Transformation Program (PPGTP, [5]) provided incentives for Canadian pulp and paper mills to enhance energy efficiency and environmental performance. Projects undertaken included boiler and turbine upgrades, and installation of emission-control equipment. One major impact was to improve the ability of Canadian industry to effectively integrate novel processes into existing sites and infrastructure.

The Transformative Technologies Program (TTP, [6]) continues to map out novel pathways to new products from wood. This collaboration between Natural Resources Canada (NRCan) and FPInnovations has supported fundamental research work in a wide range of non-traditional areas.

The Transformative Technologies Pilot Demonstration Program (TTPDP, [7]) has helped move several of these new technologies to the demonstration scale, where they can be evaluated on a larger scale than the laboratory-scale work possible under the TTP. The Investments in Forest Industry Transformation (IFIT, [8]) funded a series of near-commercial scale plants. While aimed at larger scale installations than the TTPDP program, these are still demonstration plants and are not expected to be commercially viable on their own due to poor economies of scale, even though they are meant to prove concepts by making and selling product.

NSERC, Canada's National Science and Engineering Research Council, directs funds to university researchers. Its Forest Sector Research and Development Initiative [9] provided $34M over 5 years to create a series of 8 world-class R&D networks, involving over 100 senior academic staff across the country in research of relevance to the development of novel products from wood. In many cases, these researchers and their teams are new to forestry, bringing new viewpoints and knowledge of industries not usually associated with forestry. The networks are linked by FIBRE, an overarching organisation designed to build synergies in partnership with FPInnovations, NRCan, NSERC and the Forest Products Association of Canada (FPAC).

The Bio-Pathways project [10] set up an economic framework for evaluating novel processes and products early in the development stage. Managed by NRCan, FPAC and FPInnovations, the tools use a common approach; results allow research managers to quickly identify winning pathways and focus resources on solving critical problems that might limit or impair implementation [11].

The R&D and implementation processes described above have generated a large number of potential pathways to new products. Some projects are further along than others; one common thread is that implementation requires support from provincial governments. A range of provincial government initiatives, such as the Centre for Research and Innovation in the Bio-Economy (CRIBE) in Ontario [12], have assisted implementation of technologies that are most relevant given circumstances specific to the region. As an example, CRIBE is a partner, with Resolute Forest Products, NRCan, FPInnovations and NORAM Engineering and Constructors in the Bio-Economy Technical Centre, a facility designed to evaluate promising technologies on a semi-industrial scale. Located within the Resolute Forest Products mill in Thunder Bay, ON, the Centre has evaluated a methanol purification process for stripping TRS compounds from stripper condensate off-gasses, and is presently evaluating novel pathways to extract and modify lignin from black liquor at a 100 kg/d scale.

An example

The various programs described above have begun to show results, in terms of new life for forestry towns and industries where traditional products are no longer profitable. The list of projects supported by these programs is long and will not be repeated here; most are described in the references. Most follow the made-in-Canada approach described above: a collaborative approach across industry, academia, governments and research institutes; bolt-on additions to existing infrastructure; a focus on value-added products first with residues converted to energy products; national-level coordination, but with a focus on regional implementation.

CelluForce is one notable example of how the system has worked. An initial patent obtained by researchers at McGill University showed how to extract a purely crystalline cellulose chain from kraft pulp fibres by selectively dissolving the amorphous regions in cellulose. This nano-scale product, dubbed nano-crystalline cellulose (NCC), proved to have a wide range of exciting characteristics, including high tensile strength and a tendency to self-align into structures with unique optical properties. However, it remained a laboratory curiosity for a number of years as the processes to make the product had not been scaled up beyond the milligram scale.

Collaboration between FPInnovations and NRCan soon led to a pilot plant capable of producing kilogram-scale quantities, which allowed potential end-users to obtain and test samples in the search for novel products. As end-uses became clear, designs for a tonne-scale facility were prepared with NORAM. Finally, CelluForce, an independent joint venture between Domtar and FPInnovations, was formed [13] to build such a plant and market the product. Funding came from Domtar, the TTPDP and Québec’s Ministère des ressources naturelles et de la faune; FPInnovations contributed its intellectual property portfolio in the field. The plant has now been built next to the Domtar mill in Windsor, QC and operations are underway. As a component of a bio-refinery, it relies on the host mill for steam, power and effluent treatment services; sugar-rich residues from the process are currently converted to a biogas in an anaerobic digestor; the biogas is burned in the host mill’s CHP plant. Future, higher value uses of the residue stream are under development.

Conclusions

Unique contexts will require a unique approach to implementation of the forest bio-refinery. In Canada, this implies:

- Regional solutions;
- Solutions that are highly integrated into the existing industrial landscape (both forestry and non-traditional partners);
- Solutions which have a large focus on value-added products;
- Bio-energy products (heat, power, solid or liquid fuels) will come from the residues generated by these healthy primary industries, and are necessary but not sufficient for success;
- In the short term, bolt-on additions will dominate in order to save capital and reduce risk during initial implementation phases;
- Coordinated efforts across academia, research organisations, industry, and federal and provincial governments on both policy and joint activities with government-run laboratories.

The unique approach described here has proven to generate useful solutions, at a reasonable cost.

References

1. http://www.eia.gov/dnav/ng/hist/n9190us3m.htm, visited 31 July 2012.

2. http://www.theglobeandmail.com/report-on-business/industry-news/energy-and-resources/crude-glut-price-plunge-put-oil-sands-projects-at-risk/article4230759/, visited 30 July 2012.

3. http://www.bio-amber.com/bioamber/en/products/succinic_acid, visited 31 July 2012.

4. http://atlas.nrcan.gc.ca/site/english/maps/environment/forest/forestcanada/forestedecozones, visited 30 July 2012.

5. PPGTP: http://cfs.nrcan.gc.ca/pages/231, visited 30 July 2012.

6. TTP: http://cfs.nrcan.gc.ca/pages/166, visited 30 July 2012.

7. TTPSD: http://cfs.nrcan.gc.ca/pages/182/2, visited 30 July 2012.

8. IFIT: http://cfs.nrcan.gc.ca/pages/232?lang=en_CA, visited 30 July 2012.

9. NSERC's Forest Sector Research and Development Initiative: http://forest-foret.nserc-crsng.gc.ca/index_eng.asp, visited 30 July 2012.

10. BioPathways process overviews may be found here: http://cfs.nrcan.gc.ca/pages/171?lang=en_CA and here: http://www.fpac.ca/index.php/en/bio-pathways, visited 30 \July 2012.

11. Browne, T.C., Singbeil, D. et al. 2010. Bio-energy and Bio-chemicals Synthesis Report. Prepared for the Forest Products Association of Canada and FPInnovations, November 2010. http://www.fpac.ca/publications/biopathways/Bio%20Energy%20Final_En.pdf.

12. CRIBE: http://www.cribe.ca/, visited 31 July 2012.

13. CelluForce: http://www.celluforce.com/en/index.php, visited 31 July 2012.

Economic and ecological assessment of biorefineries – findings of the German biorefinery roadmap process

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Abstract

Biorefineries are assumed to become important material and energy users of biomass. Greenhouse gas mitigation, resource efficient and sustainable biomass utilization as well as positive economic effects along the value chains are drivers for biorefinery concepts but these potential benefits have to be achieved and proven. In doing so, economic and ecological assessments play an important role. Biorefineries are a heterogeneous research and development field. Initiated by the German Federal Ministries for Agriculture, Food and Consumer Protection as well as Education and Research (BMELV) and organized by the German Agency for Renewable Resources (FNR) members from politics, industry and research elaborated the German biorefinery roadmap. This roadmap aims at systematically determining the state of development of biorefineries in Germany and at analyzing strengths and weaknesses, as well as opportunities and threats (SWOT) of promising future biorefinery concepts in order to identify a strategy of research and policy measures for decision makers. Within this roadmap process a subgroup dealt with the issues of economic and ecological analyses and assessments. This paper summarizes the key findings of this subgroup. General aspects for analysis and assessment of biorefineries are sketched. Challenges with regard to data and methodologies are identified and conclusions are drawn.

Introduction

The ‘Biobased Economy’ first emerged as a policy concept linking renewable resources and (bio-)processes through industrial scale bio- and chemical technologies to produce sustainable products, jobs and income. A successful transition to a Biobased Economy will depend on a number of technological, economic, environmental and social factors. However, in the course of this process, it is important to understand the full environmental and economic implications of the changes that this transition will entail. Biorefineries promise in the best case to contribute to greenhouse gas mitigation, achieve a high level of resource efficiency and a nearly residue-free and sustainable utilization of renewable raw materials. Additionally, positive economic effects along the value chain such as a strengthening of agriculture and forestry, development of regional economies, business opportunities for process technologies and cost reductions are expected.

Initiated by the German Federal Ministry of Food, Agriculture and Consumer Protection and the German Federal Ministry of Education and Research and supported by further ministries a working group consisting of members from politics, industry and research elaborated the German biorefinery roadmap [1]. This group led by DECHEMA e.V. and organized by the German Agency for Renewable Resources (FNR) systematically determined the state of development of biorefineries in Germany and analyzed strengths and weaknesses, as well as opportunities and threats (SWOT) of promising future biorefinery concepts in order to identify a strategy of research and policy measures for decision makers.

Sustainability assessment can be used to steer the biorefinery development at an early stage and to provide urgently needed information for industry and politics to identify the most promising sustainable concepts and to support investment decisions. To find broad societal acceptance the expected advantages have to be proven and explained. Within this context economic and ecological analysis and assessment of biorefineries play an important role. Further, a sound data basis for communication and discussion of biorefinery concepts with the public can be built. For this purpose a subgroup was formed within the German biorefinery roadmap process that dealt with the above mentioned topics. The works within the economic and ecological assessment subgroup of the German roadmap biorefinery process provide a first evaluation and semi-quantitative discussion of essential assessment aspects.

The presentation covers key findings of this subgroup. The focus lies on issues of particular relevance for the economic and ecological assessment along the whole value chain. Considered are sugar and starch biorefineries, plant oil and algae lipid biorefineries, lignocelluloses and green biorefineries as well as synthesis gas biorefineries. For a definition of these types the reader is referred to [1]. Based on these analyses challenges for the economic and ecological assessment are identified. These cover both, the need for provision of data as well as the need for methodological improvement in dealing with multiple output systems, and dynamic markets.

General aspects

The assessment of biorefinery concepts has to cover all stages of the value chain. This comprises growing and harvesting of the feedstock, the conversion processes as well as the use and the end-of-life phase as well as storage and transport along the value chain. A comparison of different biorefinery concepts is difficult due to the large number of possible variations in terms of feedstock, logistical configurations, applied technologies, products and markets, capacities, development stages and the dependencies on regional conditions. Nevertheless, such assessments can be carried out with methods from material and energy flow balancing, material and energy flow analysis, economic and life cycle assessment (LCA). It is necessary to address the particularities of biorefineries leading to gaps with regard to data and methods.

Raw material provision

The sustainable provision of the necessary amounts of feedstock in proper quality at reasonable cost is a crucial factor for most biorefineries as it is for other biomass conversions. The possibilities for this depend inter alia on feedstock competition with existing but also further (future) biomass utilizations. The discussion about biorefineries and securing their raw material basis leads therefore to discussions on the efficient allocation of available land in agriculture and forestry under consideration of the precedence of food and fodder production.

The picture for the different feedstocks of the investigated biorefinery types, i.e. sugar and starch plants, oil seeds, green biomass, straw and wood from forests and short rotation plantations is different. Details concerning the feedstock analyses can be found in [1]. In comparison to fossil raw materials the accrual of renewable raw materials is mainly determined not by technical but by natural factors such as climate, weather, seasons, soil, and spatial distribution of the growing areas. These have to be considered in growing, harvesting, transport and storage. Particularly relevant factors are often the length of the harvesting season, the dispersed nature of the biomass supply, high water contents and low bulk densities. These are problematic because of limited storability of many agricultural feedstocks and unfavorable long distance transports in terms of costs and emissions.

To enhance storability and transportability conditioning steps such as pelletizing, torrefaction, pyrolysis, hydrothermal conversions also in combination with logistical network design measures such as a spatial or temporal decoupling of parts of the value chain are discussed.

Provision of raw materials for biorefineries has to achieve at least (i) a positive greenhouse gas emission balance over the whole life cycle from feedstock growing to residue utilization, (ii) an avoidance of soil degradation, (iii) tolerable material inputs and outputs and (iv) closed material cycles for the residues (cf. [2]).

Biorefineries

In total 13 different possible configurations of the investigated general biorefinery types are discussed on the basis of existing literature and studies from a technological subgroup of the German biorefinery roadmap group from an economic and ecological point of view. For a detailed definition of the investigated configurations the reader is referred to [1]. The semi-quantitative, i.e. a mostly qualitative analysis, comprising first quantitative considerations for lignocelluloses and synthesis gas biorefineries, covers aspects of development stage, suitable locations, capacity in terms of raw material demand, possible product types and amounts, orders of magnitude of investments and further major economic and ecological success factors. The investigated concepts differ to a large extent in these criteria. Comparably small biorefineries such as green biorefineries are assumed to be built in close vicinity to the raw material source. They are estimated to convert approx. 90 000 metric tons of grass (20% dry matter) and are estimated to require total capital investments in the order of magnitude of approx. 15 million Euro. Large biorefinery systems such as synthesis gas biorefineries are discussed up to feedstock capacities of 500 000 to 2 000 000 metric tons and are assumed to require total capital investments in the order of magnitude of 250 to 1 000 million Euro. The development stages vary between lab scale, e.g. for algae lipid biorefineries to demonstration plants for e.g. lignocelluloses biorefineries, synthesis gas biorefineries or bottom-up further developments of existing biomass conversion plants e.g. in the case of starch and sugar biorefineries.

Depending on the biorefinery concept, aspects of the integration into existing (chemical) production sites (economies of scope), energy costs, utility costs, especially for enzymes and catalysts can play a crucial role, both regarding economic as well as ecological assessments. For the latter two it is hard to determine their influence in advance. Additionally, the envisaged process efficiencies in terms of product yields but also e.g. enzyme and solvent recovery have to be achieved when the concepts are upscaled to an industrial plant. In general, the first of its kind industrial plant shows disadvantages with regard to the total capital investment but also operational costs in comparison to succeeding installations. Several installations are needed in order to realize learning and experience curve effects to reduce specific investments and costs and enhance efficiencies. High value material utilization of all product streams are essential in many cases to achieve profitability of the often more complex biorefinery conversion processes. To aim at bulk chemicals such as alcohols provides the advantage of existing markets at the costs of existing and often more mature value chains. Fine chemicals production offers the possibility of yielding higher prices through product differentiation. Nevertheless, associated markets are generally smaller. This will demand for the development of suitable new product family trees and portfolios.

Challenges for the economic and ecological assessment

The presented semi-quantitative analysis provides first orientation for further development and optimization strategies. For a quantitative assessment of the investigated biorefinery concepts and their variants several challenges exist. First of all, the large differences between the general concepts hinder a valid and just comparison between them. A direct comparison of different concepts is because of incompatibility of the investigated systems often not goal orientated. Nevertheless, a detailed investigation of the single concepts and their variants over the whole life cycle under consideration of location dependent factors possible.

With regard to the data basis for such detailed assessments gaps occur. Regionally and seasonally disaggregated material flow analyses for raw materials, especially organic residues, are missing so far. Further, for some of the named biorefinery concepts only first rough estimates for material and energy balances exist. Here a further elaboration of plant concepts and specifications, of processes and an experimental validation of material and energy flows in pilot and demonstration plants are necessary to come to meaningful disaggregated data on conditioning and conversion processes.

Besides this missing data methodological challenges exist, demanding for further comprehensive studies. Here especially common balancing standards for ecological indicators are needed. Further the accounting for humus formation, nitrous oxide and ammonia emissions from residues, impacts on (local) water quality and availability, direct and indirect land use change and land use efficiency, biodiversity and ecosystem services, temporal assessment, and regional specific impact assessments are necessary when assessing the environmental impacts of feedstock provision thoroughly. The combination of life cycle assessment with life cycle costing (LCC) and social life cycle assessments (SLCA) can lead towards a more comprehensive assessment regarding all pillars of sustainability. The number of different objective criteria, influencing factors, concepts and variants is large. Despite the complexity of the factors to consider the regarded systems have to be kept as simple as possible to allow meaningful conclusions. Expectations and needs of the different stakeholders should be taken into account. This requires suitable approaches for multi-criteria decision making. In general, suitable approaches to account for data uncertainties and approximations are needed.

For conclusions about the advantages of biorefineries in comparison to existing utilizations of biomass but also fossil resp. mineral-based value chains the definition of suitable reference systems and according data determinations, especially for material products are necessary. An estimation of the contribution of biorefineries to climate change mitigation, raw material security and economic development within the context of limited raw material and land availability and resulting competition requires a consideration of the dynamic development of these reference systems within the time frame for the biorefinery development, i.e. 2020–2030, as well as regional, national and international aspects.

Conclusions

A detailed analysis of biorefinery concepts under consideration of location-related factors can enable a quantitative assessment of these, even in early development stages. Thus, key figures for sustainability of these concepts and directions for the further development can be identified. The comparison with reference systems, other biomass utilizations and fossil-based value chains allows for drawing conclusions about the advantages and prospects of biorefinery concepts. In a semi-quantitative study 13 promising different biorefinery concepts are analyzed under economic and ecological aspects. Thus a first semi-quantitative characterization and discussion of these concepts is undertaken. A detailed analysis would require covering the whole value chain. Therefore detailed data is needed with regard to raw material provision, conditioning and conversion processes, logistics and reference systems. The size of the knowledge gaps varies to a large extent between the concepts. Methodological challenges exist with regard to aspects of life cycle assessment, multi-criteria analyses and the treatment of uncertain data.

An approach to resolve the named issues is the exemplary detailed assessment of selected biorefinery concepts in further studies with harmonized methods and data. This can enable a further evaluation of the advantages of the envisaged concepts in comparison to existing biomass utilizations and value chains based on fossil respective mineral raw materials. Additional reference data for further studies would be provided. To carry out such an assessment for all investigated biorefinery concepts is laborious but necessary to draw the intended conclusions. A two-step approach could reduce the efforts and direct the research. In a first step, a hot spot analysis, aggregated indicators are selected to identify economic key figures and map environmental impacts, e.g. carbon, water or nitrogen footprints. In a second step, detailed case studies are carried out for selected biorefinery concepts with regard to the key figures identified in the hot spot analysis. Thus, exemplarily the questions on the relevance and influence of different factors such as enzyme and catalyst usage, water usage and land use change can be dealt with and solution approaches can be developed and discussed. This would also contribute to harmonization of methodologies. The elaborated data could serve as a basis for regional, national and international system studies concerning economic and ecological contributions of biorefineries but also other biomass utilizations. Such studies could be based on results from other research projects, e.g. [3], [4], [5], [6], [7]. A valid data basis for fossil and mineral reference systems is to be developed. Besides one single assessment, a monitoring of the socio-economic and ecological effects on the different stages in the development process can identify problems and initiate corrections. Due to the immanent uncertainties assessments of biorefinery concepts will always lead to bandwidths. Nevertheless, they can accompany the discussion and development of biorefinery concepts and other biomass utilizations and contribute to achieving the goals connected with these.

References

1. Roadmap Bioraffinerien. 2012. German Federal Government (ed.). Berlin. URL: http://www.bmelv.de/SharedDocs/Downloads/Broschueren/RoadmapBioraffinerien.pdf.

2. Bodenschutz beim Anbau nachwachsender Rohstoffe, Recommendations of the commission soil protection at the German Federal Environmental Agency. 2008. Dessau URL: http://www.umweltdaten.de/publikationen/fpdf-l/3472.pdf.

3. BioCouple – Kopplung der stofflich/energetischen Nutzung von Biomasse. 2011. Wuppertal Institut, Fraunhofer Umsicht, Öko-Institut, Wuppertal, Oberhausen, Darmstadt. URL: http://www.energetische-biomassenutzung.de/fileadmin/user_upload/Downloads/Endberichte/Endbericht_BioCouple.pdf.

4. Bioraffinerie2021: Energie aus Biomasse – Neue Wege zur integrierten Bioraffinerie“, URL: http://bioraffinerie2021.de/.

5. Pilotprojekt “Lignocellulose-Bioraffinerie”. 2010. DECHEMA e.V. (ed.). Frankfurt. URL: http://www.fnr-server.de/ftp/pdf/berichte/22014306.pdf.

6. Star-COLIBRI: Strategic Targets for 2020 Collaboration Initiative on Biorefineries. URL: http://www.star-colibri.eu.

7. Kalundborg Cellulosic Ethanol Project (KACELLE). URL: http://www.inbicon.com/Projects/KACELLE/Pages/KACELLE_Project.aspx.

New pilot-plant facility of the “German Lignocellulose Feedstock Biorefinery Project” in Leuna – experiences with first time operations

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Abstract

The Fraunhofer-Center for Chemical-Biotechnological Processes opened on 2nd of October 2012. This new research center located at the chemical site of Leuna focusses on the scale-up of biorefinery technologies and the development of platform chemicals from biomass. Several new processes are transferred into the pilot scale and different pilot plants are going to start operation in 2012. One of these pilot plants is part of the “German Lignocellulose Biorefinery Feedstock Project”. The objective of this project is to establish an economical and sustainably integrated process for the complete usage of all the components of lignocellulose on a large industrial scale and to produce bio-based building blocks and polymers for the industrial biotechnology and the chemical industry. The pilot plant is designed to fractionate one ton of beech wood per week using an Organosolv process with the aim to provide all major fractions (lignin and sugars) in sufficient amounts for the development of new value chains.[1]. The design of the pilot plant is modular to allow optimisation of pulping and downstream processing. The lignocellulose is fractionated using ethanol-water pulping. The cellulose is enzymatically hydrolysed to glucose which is used for various fermentations in the project. The lignin fraction is used by the project partners for the development of duro-and thermoplastic applications.

Introduction

The Fraunhofer-Center for Chemical-Biotechnological Processes located at the chemical site of Leuna results from the cooperation of two mother-institutes: the Fraunhofer Institute for Chemical Technology ICT in Pfinztal and the Fraunhofer Institute for Interfacial Engineering and Biotechnology in Stuttgart. It is the main task and business field of the new center to accelerate the industrial implementation of processes for the production of biobased chemical products. Therefore, the CBP offers a broad range of pilot-scale facilities which are suited for the scale-up of chemical and biotechnological processes.

The total investment sum of 46 million € for the whole CBP is financed together by the federal state of Saxony-Anhalt, the Federal Ministry of Education and Research (BMBF), the Federal Ministry of Food, Agriculture and Consumer Protection (BMELV), the Federal Ministry for the Environment, Nature Conservation and Nuclear Safety (BMU) as well as by the Fraunhofer Society and the chemical site Leuna. The official inauguration on 2nd of October has terminated the construction period of less than two years.

Development and construction of the Lignocellulose Biorefinery pilot plant

One important constituent of the CBP is the pilot facility for the fractionation of wood, which is constructed and will be operated in the national joint research project “Lignocellulose Feedstock Biorefinery”. The aim of the project is the development of platform chemicals serving as key-components for biobased products. The project consortium consisting of 13 partners from academia and industry is coordinated by DECHEMA. In 2007 the BMELV started funding the development of a lignocellulose-biorefinery based on beech and aspen wood. During the first project phase, the systematic comparison of different processes resulted in the selection of ethanol-water-pulping as the most beneficial fractionation technology for the complete utilization and maximum valorisation of German hardwood species. The delignifying effect of ethanol-water mixtures had been discovered in Germany in the 1930ies by KLEINERT and TAYENTHAL [1]. The process was optimized up to a batch digester volume of 10 L and a variety of potential applications for the sugar and lignin fractions were identified and tested. In parallel, an economic (and socio-economic) evaluation confirmed the feasibility to run a production plant with an annual wood consumption of 400 000 t in Germany [2].

For industrial implementation of the process, the construction and operation of a pilot plant is an integral part of the second project term from 2010 to 2013 with the aims, on the one hand, to optimize the pulping and fractionation process and, on the other hand, to gain sufficient amounts of lignocellulose fractions (sugars and organosolv-lignin) for the development of biobased value chains.

The pilot plant is designed to produce 80 kg of pure organosolv lignin, 120 kg of glucose and 35 kg of xylose from 315 kg dry wood per week. If required, the wood processing capacity may be increased to one ton dry wood per week. A simplified process scheme is depicted in Figure 1.

The ethanol-water pulping is carried out discontinuously in a digester that can be operated with a maximum pressure of 40 bar at 200 C. Two additional pressure vessels and one atmospheric tank allow the preparation, preheating and storage of the cooking and washing liquors. The precipitation of the lignin from the pulping liquor after separation of the fibre fraction is carried out either by means of distillation of the solvent or by adding water. Thereafter the lignin is filtered, washed and dried. The hemicelluloses present in solution after filtrating of the lignin are purified and concentrated.

The cellulose fraction is disintegrated and washed. After dewatering, the enzymatic hydrolysis of cellulose is carried out in a stirred tank reactor. The glucose solution obtained can finally be concentrated for preservation by means of evaporation. The pulping solvents are recovered by means of rectification. The optimum operation conditions for pulping, lignin precipitation and enzymatic hydrolysis were determined by the project partners in parallel to the construction of the pilot plant. Completion of the pilot plant was achieved in September 2012, followed by the cold commissioning phase. First time operation with wood is planned in November.

With the start of operation the project partners will be supplied with the fractionated wood constituents to be able to scale up their product developments. The sugars (C5 and C6 sugars) are either chemically converted to polyalcohols serving as a basis for e.g. polyurethanes, or they are tested for a range of different fermentations:

- Acetone, butanol, ethanol
- Succinic acid
- Lactic acid
- Acetic acid.

The lignin is used for the development and testing of phenol-resins, polyurethane foams and thermoplastic compounds. Lignin residues are degraded into valuable phenolic mono- and oligomers by pyrolysis or hydrothermal cracking processes.

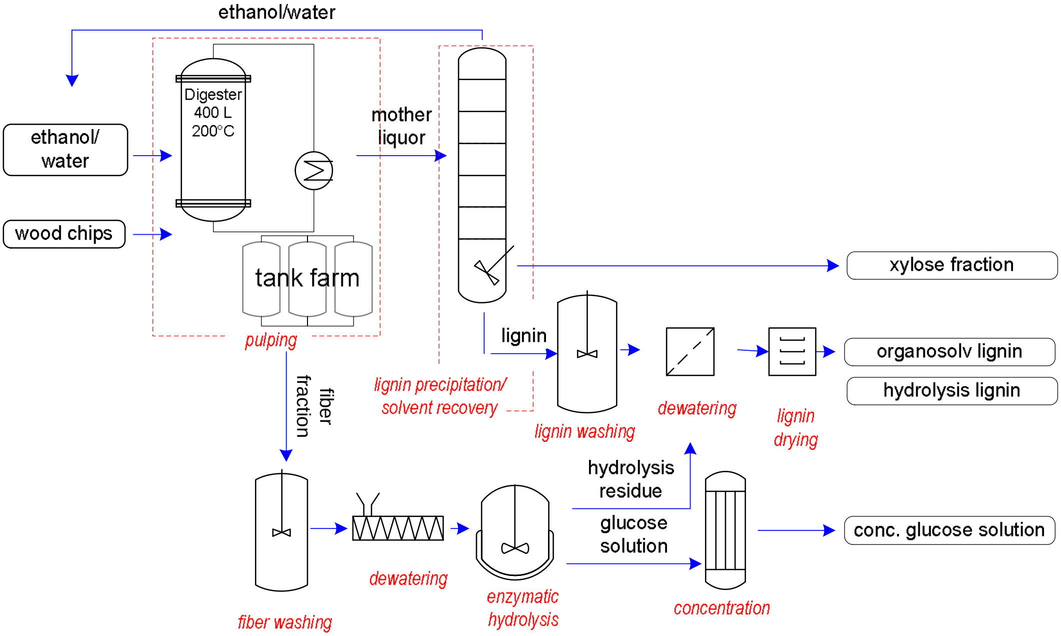

Figure 1. Simplified process scheme of the “Lignocellulose Biorefinery” pilot plant in Leuna.

In the pilot plant, the scale-up of all the different process steps on scalable unit operations is performed. This is the basis for the further scale-up of the process into the demonstration scale.
The main focus of the process optimization at the pilot scale is on the improvement of the energy balances and the closure of water loops.

Based on the results of the optimized process, the economic viability of the process is evaluated as well as the sustainability of the products.

Acknowledgement

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References

1. Kleinert, Th., v. Tayenthal, K. 1931. Über neuere Versuche zur Trennung von Cellulose und Inkrusten verschiedener Hölzer. Angew. Chem. 44, pp. 788–791. Doi: 10.1002/ange.19310443903.

2. Michels, J., Wagemann, K. 2011. The German lignocellulose feedstock biorefinery project. 3rd Nordic Wood Biorefinery Conference, Stockholm, Sweden. P. 70.

The LignoRef project: A national research initiative to enhance biorefinery process developments in Norway

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Abstract

The LignoRef project ("Lignocellulosics as a basis for second generation biofuels and the future biorefinery") gathers central Norwegian players (R&D and industry) along the value chain from lignocellulosic biomass to biofuels/biochemical products (Figure 1). The overall objective of this R&D project is to establish fundamental knowledge about central processes involved in the conversion of lignocellulosic biomass to second generation biofuels and value-added products. Central processes studied in this work include biomass pretreatment and separation, enzymatic hydrolysis, fermentation and thermochemical conversion of biomass and process by-products. A further objective of the project has been to join central national players in the biorefinery area in order to promote national progress in this field.

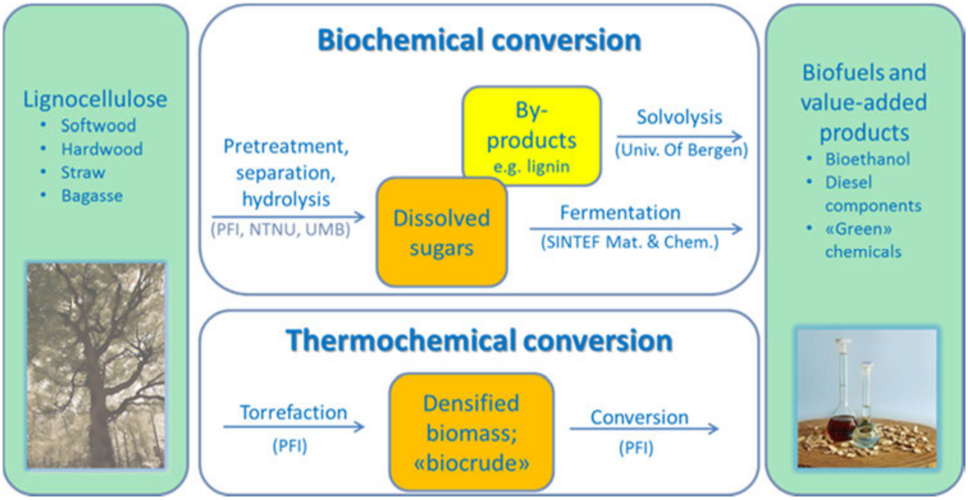

Figure 1. Lay-out of the LignoRef project. (PFI = Paper and Fibre Research Institute, NTNU = Norwegian University of Science and Technology, UMB = Norwegian University of Life Sciences).

Introduction

LignoRef (2009–2012) is a competence building project funded by the Research Council of Norway and industry. The project consortium consists of R&D and industry partners, with the Paper and Fibre Research Institute (PFI) as project owner. The R&D partners span the value chain from fundamental knowledge of the fibre raw material via the enzymatic breakdown of sugar polymers to the conversion of biomass monosugars and lignin to fuels and chemicals.

Biomass pretreatment (sulfite based, organosolv, steam explosion) and separation (lignin, hemicellulose) studies are performed by PFI in cooperation with the Norwegian University of Science and Technology (NTNU). Steam explosion pretreatment is performed by the Norwegian University of Life Sciences (UMB). Focus of the pretreatment studies is on designing pretreatment and separation schemes that will suit the raw material properties of different biomass inputs, aiming at high sugar yields, high separation efficiency and minimal formation of degradation products.

Enzymatic carbohydrate hydrolysis is studied by UMB. The focus is on development of novel enzymes and helper protein systems that make the hydrolysis of cellulose and hemicelluloses more effective. The work aims at understanding and exploiting the enzymes involved as well as on designing enzyme cocktails that ensure effective hydrolysis.

Microbial conversion of the lignocellulosic sugars, focusing on the development of novel microorganisms that ensure effective conversion of both C6 and C5 sugars to biofuels/biochemicals is performed by SINTEF Materials and Chemistry. Focus is on the development of novel genetic tools suitable for engineering robust industrial yeast strains for efficient conversion of all lignocellulose derived carbohydrates to fuels and chemicals.

Thermochemical conversion of lignin to a liquid bio-oil comprised of valuable components (e.g. fuel components, “green” chemicals) by solvolysis is studied by the University of Bergen. The work is performed in close cooperation with Statoil Research Centre which has a high competence on characterisation of oils.

Energy densification of biomass by torrefaction is studied by PFI.

The research is performed in close collaboration with industry partners, ranging from forest owners (Allskog) via biomass converters (Cambi, Borregaard, Weyland, Xynergo/Norske Skog) to fuel/energy producers (Statoil, Hafslund).

Experimental

Materials, methods

Lignocellulosic raw materials were collected, dried and characterised prior to use, including Norway spruce, wheat straw, bagasse and bark (spruce).

Initially, considerable efforts were undertaken to establish reliable analytical methods for chemical characterisation of raw material inputs, as well as process intermediates. This was especially important as we included raw materials that were new to us (e.g. bagasse). To be able to compare results obtained by the different partners, Round Robin tests were undertaken. Chemical analyses were based mainly on standardized methods, e.g. dry matter (ISO 638), lignin and structural carbohydrates (NREL/TP-510-42618), carbohydrate composition (HPAEC; Dionex ICS-5000), saccharification potential (NREL/TP-510-42629).

Imaging methods aimed at visualizing morphological fibre changes (e.g. fibre surface and cross sections) resulting from different treatments were developed, using scanning electron microscopy (SEM) and Field emission SEM in combination with advanced image analyses (Image Java).

Pretreatment processes

Pretreatment trials were undertaken using sulfite, organic solvents (ethanol/water) or steam. The work has focused on obtaining high sugar yields, good separation efficiency and low inhibitor formation. Hemicellulose pre-extractions were performed using conventional hot water or microwave setups. Pretreatment for thermochemical conversion of the biomass was based on torrefaction.

Enzymatic hydrolysis

Enzymatic hydrolysis of carbohydrate polymers has been focused in part on fundamental studies of the hydrolysis process, in particular studies of the favourable effects of the recently discovered lytic polysaccharide monooxygenases that promote breakdown of crystalline cellulose. Furthermore, the work has included applied testing of enzymes/enzyme mixtures (aiming at realistic conditions, e.g. high DM concentrations) as well as a targeted search for novel lignocellulose degrading enzymes.

Microbial conversion of C5 and C6 sugars

Metabolic engineering approaches are based on industrial *S. cerevisiae* wild type ATCC96581 as host strain. Key enzymes for conversion of C5 sugars (xylose reductase and xylitol dehydrogenase) from *Pichia stipitis* and xylulose kinase from *S. cerevisiae* have been integrated into the genome of *S. cerevisiae ATCC96581*, to make this strain capable of efficient pentose and hexose utilization.

Lignin conversion and bio-oil characterisation

Thermochemical lignin conversion to bio-oil is performed using a solvolytic approach (base case 380°C, 24 h, formic acid/ethanol solvent). A “test-battery” of methods suitable for both petro- and bio-oils is established. This involves “fingerprinting” techniques like mass spectrometry (ESI-MS), gas chromatography (GC-MS) and FTIR. The data are interpreted using chemometrics in order to evaluate similarities between samples and to characterize homologous series.

Results and discussion

Pretreatment processes

Sulfite pretreatment: A sulfite pretreatment method termed “low temperature sulphonation” has been developed, giving a highly sulphonated lignin, effective lignin dissolution and high enzymatic saccharification of the carbohydrates. The method which has been demonstrated for softwood provides good control of hemicellulose degradation (low inhibitor formation). The pretreated chips need no further refining prior to enzymatic hydrolysis. Water soluble lignosulfonates with high degree of sulfonation can be obtained as a by-product. The method is described in the poster; “Low temperature sulfonation of lignocellulose for effective biomass deconstruction and conversion”.

Organosolv pretreatment: Up to 70% of spruce lignin could be removed (ethanol/water solvent), resulting in a yield after enzymatic hydrolysis of 80%. More effective lignin dissolution was found for bagasse than for spruce at lower temperatures in the process setup used.

Steam pretreatment: Steam pretreatment of wheat straw has demonstrated high glucose yields. However, furfural formation remains a problem, causing adverse effects on the fermenting organism. Results are published in i.a. Horn et al., 2011 and in Chacha et al., 2011.

Hemicellulose extraction: Hemicellulose pre-extraction prior to pretreatment aimed at low depolymerisation. Conventional hot water extraction and microwave-assisted extraction gave similar results. Both extraction time and temperature were important. A higher degree of polymerization (DP) was obtained for hemicelluloses extracted from bagasse than from spruce. Further, less pronounced depolymerization was found with time for bagasse than for spruce. This is further described in the poster; “Hot water extraction of hemicelluloses from softwood and sugarcane bagasse using microwave heating technology”.

Torrefaction pretreatments have demonstrated that milled, torrefied spruce (approx. 0.25 mm particles), may be suited for use in entrained flow gasifiers (thermochemical conversion).

As expected, the pretreatment studies have shown that different raw materials behave very differently in the various pretreatment processes.

Enzymatic hydrolysis

Studies are focused on addressing how the recently discovered lytic polysaccharide monooxygenases from bacteria and fungi, currently referred to as CBM33s and GH61s (see Vaaje-Kolstad et al., 2010) can be utilized to better degrade biomass into biofuel precursors. The studies have shown that the accessory enzymes act synergistically with cellulases to improve the cellulose hydrolysis of pre-treated biomass (results in Forsberg et al., 2011; Westereng et al., 2011). Other classes of specific enzymes, such as mannanases, are also being tested for the same purpose.

Additionally, a search for novel biomass degrading enzymes is undertaken in collaboration with other projects at UMB. Results are published in Pope et al., 2012 and MacKenzie et al., 2012. A cluster of genes which appears important for biomass degradation in the gut of Svalbard reindeer has been identified and the characteristics and potential use of these enzymes in biomass conversion are being explored. Novel clusters of bacterial genes (Polysaccharide Utilization Loci, PUL) which appear to be important in degrading dietary biomass, have been identified and characterized. The results suggest that these enzymes and proteins are adapted to the degradation of β-glycans, xyloglucans, as well as glucomannans and galactomannans, indicating the potential of these enzymes for hydrolysis of e.g. spruce hemicelluloses.

The fundamental enzyme discovery and characterization work is combined with process-development studies aimed at developing effective enzymatic conversion protocols for LignoRef substrates, in particular pretreated spruce and bagasse.

Microbial conversion of C5 and C6 sugars

S. cerevisiae is the most promising candidate for production of ethanol from lignocellulose (excellent glucose fermentation capability, high ethanol tolerance, resistant to inhibitors). However, as native *S. cerevisiae* strains cannot utilize xylose neither for growth nor for ethanol production, metabolic engineering is used to develop *S. cerevisiae* mutant strains able to utilize xylose. Genes for xylose utilization from the yeast *Pichia stipitis* have been introduced into the chromosome of an industrial *S. cerevisiae* strain by using a combination of genetic engineering and random mutagenesis in an iterative way. Resulting mutant strains are shown to convert xylose efficiently to cell biomass (growth). In addition, novel genetic tools for cloning and recombinant protein expression in *S. cerevisiae* strains are constructed, facilitating the development of high potential yeast strains for cost-efficient conversion of lignocellulose to bio-ethanol and value-added fine chemicals.

The xylose utilizing industrial *S. cerevisiae* mutant constructed can serve as host strain for further genetic engineering. A new *S. cerevisiae* vector system has been constructed for cloning and inducible gene expression. New vectors with different promoter systems for recombinant gene expression in industrial *S. cerevisiae* strains are under construction.

Lignin conversion and bio-oil characterisation

Thermochemical conversion of lignin to bio-oil using a solvolytic approach is studied. The previously developed lignin-to-liquid (LtL) process is further developed with respect to raw material and reaction conditions (results in Kleinert et al., 2011). Analysis of post solvolysis fragmentation patterns has shown that different lignins behave rather similar during solvolysis and that the LtL process is robust. However, differences in the detailed composition of products are observed. Furthermore, black liquor with high sulfur contents is not suitable due to the formation of H_2S.

Mechanistic studies aiming to describe the chemical reactions involved in the LtL process have given new knowledge of the processes involved and form a basis for the further optimizations. Using model compounds 5 central reaction pathways involved have been identified as described in Holmelid et al., 2012. Different solvent systems have been studied (e.g. formic acid, paraformaldehyde, water), showing that water is an alternative “green” solvent system for this conversion.

Catalyst screenings to improve reaction efficiencies are on-going, aiming to develop systems where the depolymerisation of lignin, removal of oxygen and incorporation of hydrogen in the products is effective at low temperatures (below 360°C), see Luguori et al., 2011.

Methods suited for analysis of both petro- and bio-oils were established, including standardized methods for analysing fuels, as well as new methods for analysing components not normally found in petro-based products. The methods are used to determine needs for upgrading of bio-oils to transport fuel quality. This includes the use of mass spectrometry based “fingerprinting” techniques and chemometrics (as described in Carlson et al., 2012 and Gellerstedt et al., 2008).

Conclusions

The LignoRef project gathers central Norwegian players involved at different stages along the value chain from lignocellulosic biomass to biofuels/chemicals. Fundamental knowledge about central processes involved in the development of cost-effective conversion of lignocelluloses has been established. These processes include pretreatment and separation, enzymatic hydrolysis, fermentation and thermochemical conversion of both biomass and process by-products. The project has been and is still promoting national collaboration and progress in the biorefinery area.

Acknowledgement

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References

1. Gellerstedt, G., Li, J., Eide, I., Kleinert, M., Barth, T. 2008. Chemical structures present in biofuel obtained from lignin. Energy & Fuels 22(6), pp. 4240–4244.

2. Carlson, J.E., Gasson, J.R., Barth, T., Eide, I. 2012. Extracting homologous series from mass spectrometry data by projection on predefined vectors. Chemometrics and Intelligent Laboratory Systems 114, pp. 36–43.

3. Chacha, N., Toven, K., Mtui, G., Katima, J., Mrema, G. 2011. Steam pretreatment of pine (Pinus patula) wood residue for the production of reducing sugars. Cellulose Chem. Technol. 45 (7–8), pp. 495–501.

4. Forsberg, Z., Vaaje-Kolstad, G., Westereng, B., Bunaes, A.C., Stenstrom, Y., MacKenzie, A., Sorlie, M., Horn, S.J., Eijsink, V.G.H. 2011. Cleavage of cellulose by a CBM33 protein. Protein Science 20(9), p. 1479–1483.

5. Holmelid, B., Kleinert, M., Barth, T. 2012. Reactivity and reaction pathways in thermochemical treatment of selected lignin-like model compounds under hydrogen rich conditions. Journal of Analytical and Applied Pyrolysis In Press, Available online 31 March 2012.

6. Horn, S.J., Nguyen, Q.D., Westereng, B., Nilsen, P.J., Eijsink, V.G.H. 2011. Screening of steam explosion conditions for glucose production from non-impregnated wheat straw. Biomass and Bioenergy 35(12), pp. 4879–4886.

7. Kleinert, M., Gasson, J.R., Eide, I., Hilmen, A.-M., Barth, T. 2011. Developing solvolytic conversion of lignin to liquid (LtL) fuel components: Optimisation of quality and process factors. Cellulose Chemistry and Technology 45(1–2), pp. 3–12.

8. Luguori, L., Barth, T. 2011. Palladium-Nafion SAC 13 catalysed depolymerisation of lignin to phenols in formic acid and water. Journal of Analytical and Applied Pyrolysis 92(2), pp. 477–484.

9. MacKenzie, A.K., Pope, P.B., Pedersen, H.L., Gupta, R., Morrison, M., Willats, W.G., Eijsink, V.G. 2012. Two SusD-Like Proteins Encoded within a Polysaccharide Utilization Locus of an Uncultured Ruminant Bacteroidetes Phylotype Bind Strongly to Cellulose. Appl Environ Microbiol 78(16), pp. 5935–5937.

10. Pope, P.B., Mackenzie, A.K., Gregor, I., Smith, W., Sundset, M.A., McHardy, A.C., Morrison, M., Eijsink, V.G. 2012. Metagenomics of the Svalbard reindeer rumen microbiome reveals abundance of polysaccharide utilization loci. PLoS One 7(6):e38571. Epub Jun 6.

11. Vaaje-Kolstad, G., Westereng, B., Horn, S.J., Liu, Z., Zhai, H., Sørlie, M., Eijsink, V.G. 2010. An oxidative enzyme boosting the enzymatic conversion of recalcitrant polysaccharides. Science 330(6001), pp. 219–222.

12. Westereng, B., Ishida, T., Vaaje-Kolstad, G., Wu, M., Eijsink, V.G., Igarashi, K., Samejima, M., Ståhlberg, J., Horn, S.J., Sandgren, M. 2011. The putative endoglucanase PcGH61D from Phanerochaete chrysosporium is a metal-dependent oxidative enzyme that cleaves cellulose. PLoS One 6(11), e27807. Epub Nov 23.

Finnish BioRefine – new biomass products programme – RD&D on biofuels and biorefineries in Finland

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Abstract

The BioRefine – New Biomass Products Programme of Tekes, Finnish Funding Agency for Technology and Innovation, for 2007–2012 has aimed to generate new and unique expertise in processing of biomass and to apply it to the creation of processes, products and services related to biorefineries. A further objective has been to promote the development and use of second-generation production technologies in biofuels for transport.

A broad Finnish effort to develop new biorefining competencies and technologies has been coordinated under the umbrella of the BioRefine programme. The BioRefine programme together with the FuBio programmes of Finnish Bioeconomy Cluster FIBIC Ltd (former Forestcluster Ltd) and the special pilot and demo funding of the Ministry of Employment and the Economy has formed an extensive network of national and international collaboration. This entity has harnessed an extensive network of national research institutes, universities and enterprises. The total volume of the projects funded by Tekes in the BioRefine programme has already reached €285 million.

The projects of the programme cover a spectrum of products – biofuels, chemicals, materials – utilising biomass in a variety of forms. One of the main focus areas has been forest-based biorefineries. In addition to forest-based raw materials also opportunities of agro biomass, waste fractions and new biomass sources, like algae and microbes, have been worked with.

The research, development and demonstration of production technologies of biofuels has had a large role, e.g. technologies for producing biofuels for transport via the synthesis-gas route and the fermentation route and new liquid biofuel concepts based on integrating a fluidized-bed boiler and fast pyrolysis have been developed and demonstrated. Also the use of biofuels has been demonstrated, e.g. in the field tests with a bus fleet in the Helsinki Metropolitan area. Also opportunities of algae production and utilization in biofuel and bioenergy production have been studied. Greenhouse gas and other environmental impacts of production and use of biofuels have been assessed.

Several novel routes to produce materials and chemicals from biomass have been developed. Projects of the programme have focused e.g. on new fractionation methods of biomass, cost-effective methods to produce sugars from biomass, production of biopolymer foams, and methods to modify lignin into materials applicable for composites, coating adhesives and barriers. The programme has also been a platform for small and medium-sized companies to carry out development projects together with research institutes and universities.

The programme has facilitated innovations on the bioeconomy, and hence it has intensively paved the way for bioeconomy in Finland.

More information about the programme can be found at www.tekes.fi/programmes/biorefine

The Domsjö biorefinery – how to make more from the tree

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Pulp and papermaking has, since the substitution of lump to cellulosic fibres, been focused on using the fibres from trees for manufacturing of paper, tissue or packaging grades. The different pulping methods that have been developed are all based on the quality requirements for the different end products which have led to several different processes in which varying shares of the constituents of the tree are converted into pulps of different properties.

The different pulping processes all have in common an ambition in achieving the best possible pulp quality at the lowest possible raw material consumption. This has led to that the constituents of the tree to the largest achievable extent should be maintained in the final product. In other words, the final product should consist of the highest possible amount of cellulose, hemicelluloses, lignin and extractives which is achievable without compromising the quality of the pulp and the product that is produced thereof.

Since the main focus of the pulping processes was to maintain as much as possible of the constituents of the wood in the final product, all of the material that has been removed from the tree was initially considered as waste material. This waste material was disposed of to the nearest recipient or deposited on landfills at lowest possible cost. With growing environmental concerns and increasing energy prices the waste streams were recycled into the process and also used to create value by recovering the energy content of the organic part and heat value of the waste stream as well as for recovery of chemicals for the pulping process. This is also the current status of the major part of the pulp and paper industry – a main product is being produced from the tree resource and excessive material from the process is being recycled in order to recover chemicals and energy in the production process.

In Domsjö we have taken another approach in our development from a pulp producer for the paper, tissue and board industries to becoming the globally first Biorefinery based on natural materials from the tree. From the 1930's the Domsjö Sulphite pulp mill has been producing specialty cellulose as a raw material for Viscose Staple Fibre (VSF), to varying extents and with varying success. Even though the main focus was the production of chemical pulp Domsjö already the 1940's developed several other supplementary products from the waste streams of the sulphite pulp production. This was the cradle of the organic chemical industry in Sweden that subsequently was further developed in Stenungsund to a currently prosperous complex. From this period the ethanol production remains on the industrial site in Domsjö as a separate company, SEKAB, which is supplied with bioethanol from Domsjö together with operations owned by Akzo Nobel that manufactures chemically modified cellulose products.

After a troublesome period from 1980 during which the mill was subject for decisions to be shut down several times it experienced a revival with new ownership during 2000 and with a renewed focus on specialty cellulose as well as increased focus on creating additional value added products from the secondary process streams from the cellulose production. This has led to refinement of the concept of producing organic chemicals from the waste streams which was initially established in the 1940's, into the current Biorefinery. Since 2000 the Domsjö Biorefinery has changed the manufacturing focus from being mainly a producer of chemical pulp for multi-purpose usage into becoming a major supplier of a wide variety of sustainable product such as specialty cellulose for different applications, bio-ethanol, bio-lignin, biogas, bio-CO_2 and bio-energy based on sustainable production processes with low environmental impact.

The conversion from being a chemical pulp supplier into a supplier with an wide assortment of sustainable products has been possible since the long tradition and experience of producing several different products from the wood resource, described earlier, has to a large extent been preserved within or close to the industrial site. This strong competence and knowledge in the currently different organisations DomInnova, MoRe Research as well as the Processum cluster has rendered valuable networks and leverage to the research performed internally as well as been a channel for introducing research competence and innovation from the Universities in the nearby regions. This is also an important foundation for the future development of the Domsjö Biorefinery.

The future development of the Biorefinery includes both improving the current product assortment and introduction of new sustainable bio-products. The wood constitutes a sustainable resource of raw material of growing future importance for manufacturing of valuable alternatives currently based on limited and unsustainable resources. Biorefineries based on trees as raw material will in the future become increasingly important substitutes for the production of alternative textiles, fuels and other organic compounds. In such way the further development of our and other Biorefineries will become the foundations for the prosperity and preservation of the natural environment of coming generations.

Since April 2011 Domsjö is also a part of the global Indian group Aditya Birla, which among others is a globally leading producer of VSF. This has led to renewed directions in maintaining as well as developing the position of Domsjö as the leading Biorefinery based on sustainable wood resources.

Hence, currently as well as in the future the Domsjö Biorefinery makes more of the tree and we make it better than others.

UPM – producing fuels of the future from wood-based raw materials

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Abstract

UPM aims to become a major player in Europe in the production of renewable, advanced biofuels. The company has made the first biofuel investment decision on a biorefinery to Lappeenranta, South-Eastern Finland. Other UPM biofuel projects are currently mainly in the development and piloting stage. Sustainability of operations has been one of the main criteria for the development of the UPM biofuels business and the production of biofuels will not be based on materials suitable for food.

UPM's first biofuel project, biorefinery to Lappeenranta, is based on hydrogenation process. The investment decision has been made in the beginning of February 2012 and building of the biorefinery has started in June 2012. The biorefinery's main product will be renewable, advanced biodiesel. The raw material will be crude tall oil, a wood based residue of pulp making process.

UPM's advanced biodiesel, UPM BioVerno, is an innovation which will decrease greenhouse gas emissions of transport up to 80% in comparison to fossil fuels. The product's characteristics correspond to those of the traditional oil-based fuels and highly complement today's vehicles and fuel distribution systems.

UPM plans to build a biomass-to-liquid (BTL) biorefinery either to Rauma, Finland or to Strasbourg, France. It will be using energy wood as the raw material and the main product would be renewable, advanced biodiesel.

UPM biorefineries will be located in connection of company's current pulp and paper mills. This way UPM will gain synergies in, for example, infrastructure, energy and logistics. In addition, UPM takes part in biofuel related joint development project in bio oil, which is also referred to as pyrolysis oil. UPM is also studying the possibility of using the pyrolysis oil for the production of transportation fuels.

Hydrogenation biorefinery

UPM has made an investment decision on a hydrogenation biorefinery producing biofuels from crude tall oil in Lappeenranta. The industrial scale investment is the first of its kind globally. The biorefinery will produce annually approximately 100 000 tonnes of advanced second generation biodiesel for transport, equating to 120 million litres of biodiesel. Construction of the biorefinery has begun in the summer of 2012 at UPM's Kaukas mill site and be completed in 2014. UPM's total investment will amount to approximately EUR 150 million and is completed without public investment grants.

Figure 1. The facility of the UPM biorefinery is located in Lappeenranta, Finland, and will produce biodiesel from crude tall oil at UPM's Kaukas mill site.

Lappeenranta is the first step on UPM's way in becoming a significant producer of advanced second generation biofuels. This is also a focal part in the realisation of UPM's Biofore strategy, combining bio and forest industries.

Raw material

The main raw material of UPM's first hydrotreatment biorefinery is crude tall oil, which is a residue of chemical pulp production, mainly generated in the production of sulphate cellulose from softwood. A significant part of the raw material comes from UPM's own pulp mills in Finland.

UPM's wood sourcing is based on the principles of sustainable forest management, chain of custody and forest certification. By further processing crude tall oil UPM is able to utilise the wood it uses for its pulp production in a more efficient way without increasing wood harvesting or land-use. UPM does not use raw materials suitable for food.

Biodiesel process

UPM has been developing an innovative production process in Lappeenranta Biorefinery Center, Finland. The whole process from crude tall oil to the final product, pure second generation biodiesel, is performed and controlled at the same biorefinery site. The main steps of the process are pretreatment of crude tall oil, hydrotreatment, recycle gas purification, and fractionation.

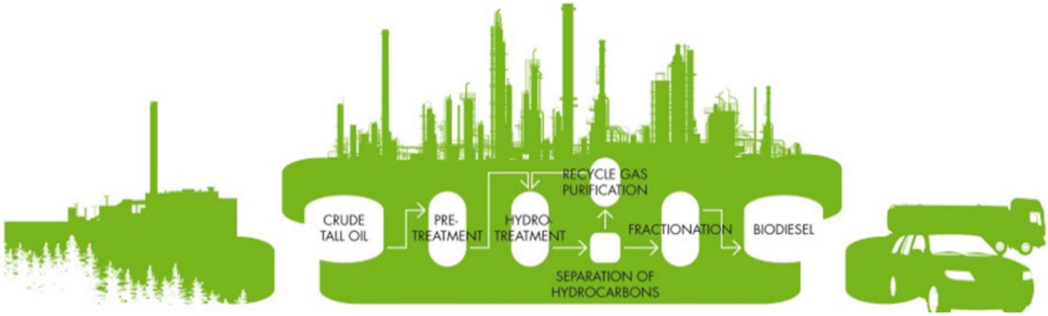

Figure 2. The biodiesel process in Lappeenranta biorefinery.

Product

UPM's advanced biodiesel, UPM BioVerno, is an innovation which will decrease greenhouse gas emissions of transport up to 80% in comparison to fossil fuels. The product's characteristics correspond to those of the traditional oil-based fuels and highly complement today's vehicles and fuel distribution systems.

UPM BioVerno has been tested for its properties, functionality, and effect on diesel engines in various laboratories such as VTT in Finland and in FEV (Forschungsgesellschaft für Energietechnik und Verbrennungsmotoren GmbH) in Germany. In addition, numerous vehicle tests with both blended and pure biodiesel proved that UPM BioVerno functioned as drop in fuel (direct replacement for fossil diesel) in all tested engines and vehicles, and reduced greenhouse gas emissions significantly.

Figure 3. UPM BioVerno is an innovation that serves as a non-food origin drop-in fuel for diesel with 80% reduction in greenhouse gas emissions.

Biomass-to-liquid (BTL) biorefinery

UPM is investigating the production of various advanced biofuels. One of the ongoing projects is biomass-to-liquid (BTL) biorefinery producing advanced biodiesel, UPM BioVerno, from energy wood.

Raw material

In BTL biorefinery, UPM is planning to produce high-quality, advanced biodiesel from forest energy wood. The raw materials to be used in the production of UPM's biodiesel would mainly consist of sustainably sourced energy wood: logging residues, woodchips, stumps and bark. UPM will not use raw materials suitable for food.

Gasification technology

UPM has been developing gasification technology for biodiesel production with Andritz/Carbona. The initial testing programme was completed at Gas Technology Institute in the United States as planned.

Location

Locating the BTL biorefinery adjacent to an existing UPM pulp and paper mill will enhance the ability to utilize wood-based raw materials efficiently and minimize the required capital investments. Energy integration will offer further benefits. The possible locations for a biorefinery producing advanced biodiesel are Rauma paper mill in the city of Rauma, Finland and Stracel paper mill site located in Strasbourg, France. The environmental impact assessment has been completed in Rauma and started in Strasbourg.

EU's NER300 grants

UPM has applied for EU's NER300 grants for BTL biorefinery from Finland (Rauma) and from France (Strasbourg). Both applications were passed on to next step to European Investment Bank and UPM has been shortlisted in their evaluation. UPM has announced that the BTL biorefinery investment decision will be made only after the EU's grants are decided. EU's NER300 grant decisions are expected on the second half of 2012. In addition to an investment grant, the investment decision will be significantly impacted by the long-term outlook for wood price and availability in the market.

The European Union's NER300 programme (New Entrants Reserve) is funded from the sale of emission allowances in Europe, i.e. the funding comes from the European companies who need to buy emission allowances for their businesses. The purpose of the programme is to finance and advance innovative new technology. The programme is also one of the political decisions targeted for reducing Europe's carbon footprint. The amount of funding available is expected to be around EUR 1.3 – EUR 1.5 billion.

EU 2020 targets create a demand for sustainable biofuels

The demand for biofuels is expected to grow by approximately 7% a year in the EU. The target of the EU is to increase the share of biofuels in transport fuels to 10% by the year 2020. In Finland, the corresponding target is even more challenging with an increase of 20%.

The EU's renewable energy directive (RED) favours advanced biofuels, which are produced from lignocellulose, waste and residue-based raw materials. According to the directive, these biofuels are double counted UPM's biofuels exceed the current and continuously tightening sustainability requirements set by both the EU and Finland. when calculating the renewable target. Thus 5% of UPM's advanced biofuels would be regarded as 10% when counting the share of biofuels in transport.

UPM utilises its own development work and sustainable wood-based raw materials. As a result UPM produces a cost-competitive high quality transport fuel that truly decreases emissions and is fully compatible with today's vehicles and fuel distribution systems. UPM biorefinery in Lappeenranta is the first significant investment in a new and innovative production facility in Finland during the ongoing transformation of forest industry.

UPM's biofuels exceed the current and continuously tightening sustainability requirements set by both the EU and Finland. The annual production of the Lappeenranta biorefinery will contribute approximately one fourth of Finland's biofuel target in transportation fuels if sold entirely on the domestic market.

Scaling up Borregaard’s BALI™ biorefinery concept

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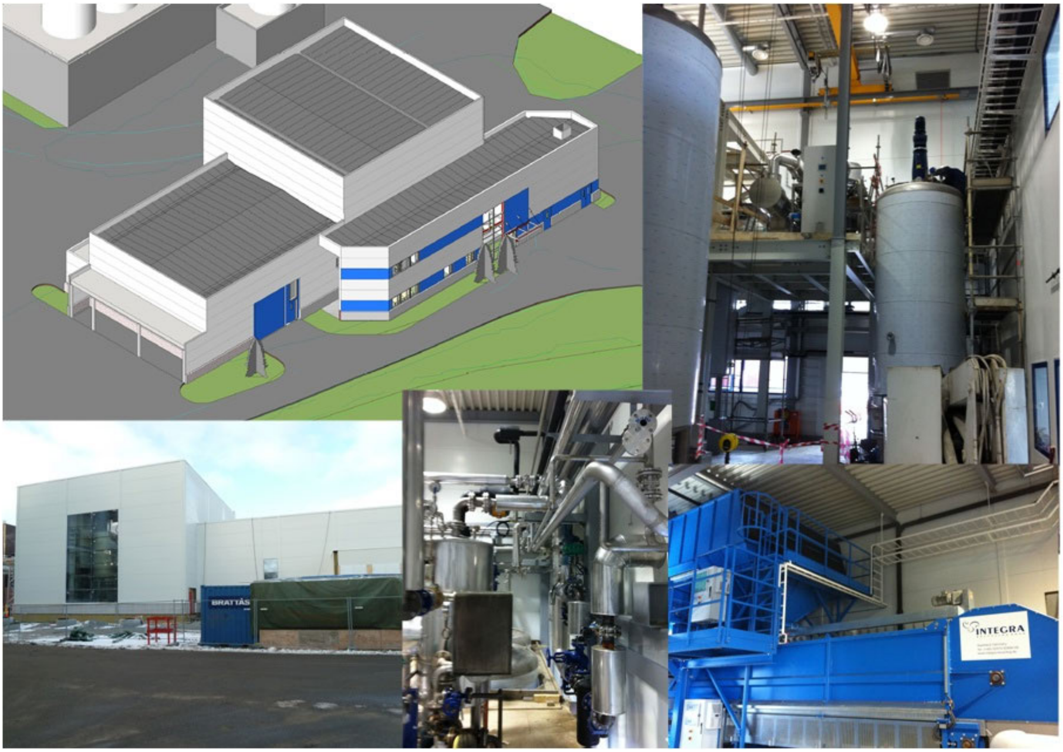
Abstract

Over the last few decades Borregaard has evolved into one of the world’s most advanced biorefineries in operation. In recent years Borregaard has directed substantial resources into developing the BALI™ biorefinery concept. The concept includes a sulfite pretreatment process and yields a water soluble lignin which can easily be separated from the cellulose pulp. The cellulose pulp is then enzymatically hydrolyzed in a novel process running at high total solids concentrations. The low viscosity achieved allows a high throughput and the use of conventional equipment. This in combination with identified applications for all streams makes for an attractive process economy. Borregaard has invested 130 million NOK to scale up the BALI™ concept to 1.2 t/day. The process runs continuously and is fully automated. Initial experiences from scale up of the feedstock handling, pretreatment and enzymatic hydrolysis will be presented.



New Swedish programme Ethanol Processes – status and challenges

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Introduction

The Swedish forest is a natural resource of great importance and has been so for several centuries. As much as 55 % of Sweden is covered with forests. They have given us raw material to build houses, ships, provide fuel to heat our homes, to make pulp and paper products, to produce tar and coke, the latter needed in iron and steel making. The forests have also provided us a landscape for recreation, wildlife and food. With increasing knowledge we have learnt to use the forest resource for more and different purposes.

We live in a time, when the challenges and threats our planet faces today are manifold and often related. Resource depletion is coming into focus more and more, be it oil, natural gas, clean water, minerals, fish, biodiversity and altogether a functioning ecosystem. The climate problem is global and complex and to put it simply, there is an urgent need to act now, if we seriously mean to assume responsibility for providing reasonable living conditions for living creatures, who are just about to enter this world.

In this context, renewable raw materials are agreed by many to be one cornerstone for the global development we see ahead of us. But this has to be combined with an efficient use of them and all other resources. The word efficient should be understood as efficient in a global context.

With these introductory words, I will now narrow down the perspective to the theme of this conference – bio refineries – and to the subject of my presentation, the new Swedish Ethanol programme.

Biorefineries and renewable raw materials

Even though the term bio refinery has appeared in the literature for a few decades, it is mainly during the last ten years that bio refining has attracted a great deal of attention. There are several reasons for that:

- Pulp and paper industry in Scandinavia and North America has met increased competition, due to cheaper, fast-growing wood in southern countries.
- There is less demand for certain paper products.
- Companies see a need to consider their product portfolio and to develop strategies and plans for a more profitable production mix, which can include new business areas.
- Due to the climate problem, governments and companies look at ways of substituting fossil raw materials to renewable.
- Fossil raw materials are finite and are becoming depleted, which is also a reason to introduce renewables as a substitute in manufacturing processes, in combination with efforts to improve efficiency in processing and to recover and reuse all kinds of materials.
- Bio refineries offer one way to address these challenges where a combination of different products can be made at one place.

There are numerous definitions of a bio refinery. Common to some of them is that they point out three categories of products, i.e. materials, energy carriers and chemicals.

Energy carriers like electricity, district heat, pellets and process steam are well established and motor fuels is a fairly new member in this group.

A perceived advantage of a bio refinery is that production of various products at one site could result in a more resource-efficient production in terms of raw material, energy and infrastructure.

Previous Swedish ethanol programmes

Looking back, Swedish ethanol research based on lignocellulosic raw materials started on a small scale in 1980. In the years 1993–2011 three ethanol programme periods were executed in Sweden. An important prerequisite for the achievements obtained has been the continuous governmental support to this research.

What were the major challenges and results during this period?

- Understanding the basics of hydrolysis regarding hemicellulose and cellulose. Initially the focus was on hardwoods since these materials are more easily attacked by the enzyme systems of wood-degrading org microorganisms.
- In the last two decades, Swedish ethanol research has focused on softwood, which is considered to be a more challenging and recalcitrant raw material.
- Ordinary small-scale laboratory studies need to be verified on a larger scale and the individual steps in the ethanol process line need to be studied together in various process configurations.
- Upscaling a batch-wise laboratory process a couple of hundred times to a continuous process line in the pilot plant has been a big undertaking. To develop the technology in pilot scale proved to be more difficult and time consuming than was anticipated in the beginning.
- In the end, pilot plant trials have to produce sufficiently good results, showing a performance, which is needed in a commercial process.

The outcome of these programmes includes various types of result:

- Technical progress regarding process chemistry, process technology and development of microorganisms
- Techno-economical: development of process models
- Creating academic competence in several research groups,
- Secure Intellectual property, such as patents
- Educating people to be employed by the industry
- Building a versatile research infrastructure, where the large laboratory-scale Process development unit, PDU, in Lund and the Pilot plant in Örnsköldsvik should be mentioned.

On the whole, the goals set up in the three ethanol research programmes have been accomplished. The ethanol pilot plant has become a well -functioning unit, where continuous operation for several weeks of the whole process line have been demonstrated.

Laboratory results have been verified in the PDU and in the pilot plant.

Using softwood, where the major part of the carbohydrates consists of 6-carbon sugars, hexoses, trials in the ethanol pilot have verified a yield of ethanol, based on incoming hexoses, at a level of 70 % of the theoretical. Ethanol yields of as much as 80 % have been demonstrated in the PDU.

Fermentations in cubic meter scale regularly give an ethanol concentration of 4 weight-% (and higher) which is needed to limit the steam demand in distillation to an acceptable level.

In later years, trials with other raw materials have successfully been run in the PDU and in the pilot, mainly agricultural-based lignocellulosic materials.

Techno-economical modeling based on results achieved in the PDU and pilot plant have produced input data for up-scaling to commercial plant size.

The new Swedish Ethanol programme “Ethanol processes”

In June 2011 the Swedish Energy Agency started a new four-year-long ethanol programme, which will go on to June 2015. The annual governmental funding has increased over the years. It is currently around 30 million SEK per year, with a total budget of 130 million Swedish kronor (SEK) for the whole programme period, roughly equivalent to 16 million Euro.

What are the present challenges?

- The results obtained in previous programmes have mainly been concerned with the ethanol process line. But ethanol is seldom the only product from a plant. The new ethanol programme has been given the name “Ethanol processes” in order to address questions related to a wider concept where ethanol from lignocellulose is just one output from a plant – for instance a bio refinery.
- This wider scope opens the programme for concept with other products as well. One aspect of this is System studies. How can a resource-efficient multiproduction plant (bio refinery)be organized?
- The programme is of course also open for improving the ethanol process line. How can better process efficiency be achieved when subject to higher dry matter concentration, less dosage of enzyme and yeast, while still fulfilling process goals like yield, productivity and concentration.
- Coupled to the previous point, techno-economic modeling can also have an important role to play in defining the lay-out of multiproduct plants.
- The economy of a process is of interest to researchers, developers, financers and market. However, calculations are highly uncertain as long as a process has not been implemented and run successfully for a couple of years in commercial scale. Will an ethanol process be able to compete with other uses of the raw material?

A constant challenge has been how to make companies and financers interested to engage in development and to invest in this field. This is still a major problem in Sweden and elsewhere, even though technology solutions have proven to be successful in pilot and demonstration plants and are considered ripe for implementation.

Biorefinery initiatives implemented by Nippon Paper – torrefaction of wood biomass for co-firing in a pulverized coal boiler

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Abstract

Nippon Paper Industries (NPI) has modified its carbonization plant for paper sludge into a pilot torrefaction plant for wood biomass. The carbonization plant was operated at 700–800°C and the torrefaction plant was operated at 200–300°C. NPI has operated the pilot torrefaction plant during the period from October 2011 to January 2012 and conducted co-firing tests of torrefied wood biomass in the pulverized coal boiler at Yatsushiro paper mill this March. In this paper, physical properties (especially for grindability) of the torrefied wood biomass prepared in the pilot torrefaction plant are discussed as well as the results of co-firing test of the torrefied wood biomass in the Yatsushiro paper mill.

Introduction

Torrefaction is a pre-treatment technology consisting of mild pyrolysis between 200–300°C to make biomass more suitable for co-firing in a pulverized coal boiler. In order to reduce carbon dioxide emission in a coal boiler, biomass is being co-fired in many places around the world. But the co-firing ratio is limited at a maximum of 3%. Torrefaction can improve grindability and hydrophobicity of wood biomass and increase the co-firing ratio. However, no commercial torrefaction plant exists so far. In this study, to proof the torrefaction concept, co-firing tests of torrefied biomass in a pulverized coal boiler were carried out. Especially the grindability of torrefied biomass has been investigated. This research was funded by New Energy Development Organization in Japan.

Experimental

Laboratory torrefaction

A laboratory kiln equipped with a thermocouple measuring the torrefaction temperature was used. The kiln size was about 5 L and 20 g of sample was torrefied. Japanese cedar bark ground using a hammer mill into sizes smaller than 50 mm was used for the torrefaction experiments. The sample was dried from 50% to 0% moisture content and then torrefied in the laboratory kiln. Torrefaction temperature was set to be in the range from 225 to 300°C and the residence time was 30 minutes. Nitrogen was purged into the kiln during torrefaction to ensure the absence of oxygen. Mass and energy yield were measured. Hardgrove Grindability Index (HGI) was evaluated.

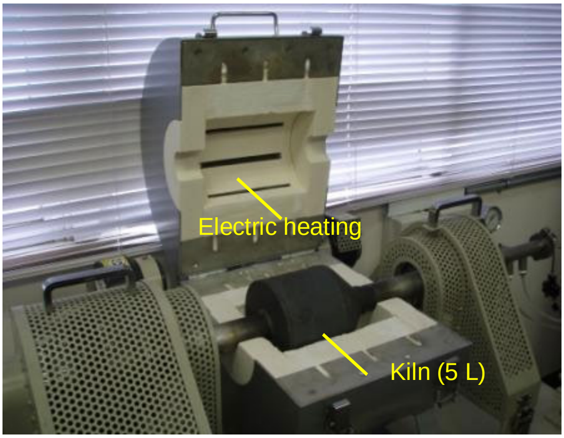


Figure 1. Laboratory kiln for torrefaction test.

Pilot torrefaction plant

A commercial carbonization plant for paper sludge was modified into a pilot torrefaction plant for wood biomass. The maximum input rate of the pilot torrefaction plant was 1 000 kg/h. The process diagram of the pilot torrefaction plant is shown in Figure 2. Japanese cedar bark pellets produced in the Forest Energy Kadokawa co. were used for torrefaction. Japanese cedar bark pellets were dried using a drum dryer and the moisture content of pellets became less than 10%. Dried pellets were torrefied through an Antler kiln (Hiroshima gas techno service co.) which has several exits of torrefaction gas which can combust with the fuel oil burner. Temperature inside the Antler kiln was decreased from 700–800°C for carbonization to 200–300°C for torrefaction. The residence time of drum dryer was 15 minutes and that of the kiln for torrefaction was 30 minutes. Torrefied Japanese cedar bark pellets were cooled through the cooling kiln for 10 minutes and temperature of the pellets was less than 50°C to prevent self-ignition. Mass and energy yield were calculated by input and output mass and calorie values. Properties of torrefied pellets such as tendency of cause dust explosion were evaluated.

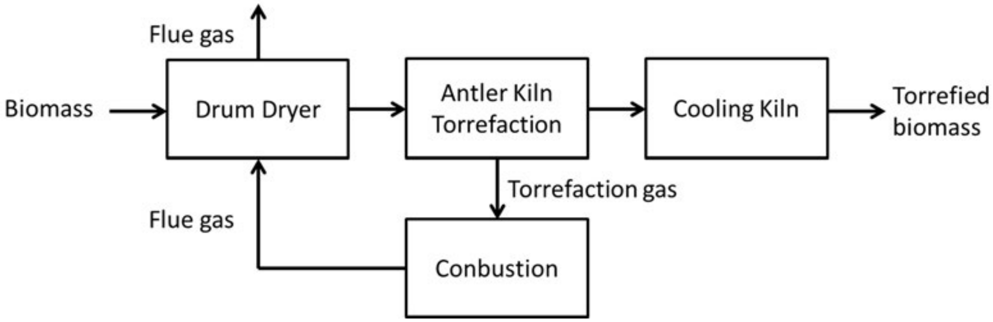


Figure 2. Process diagram of pilot torrefaction plant.

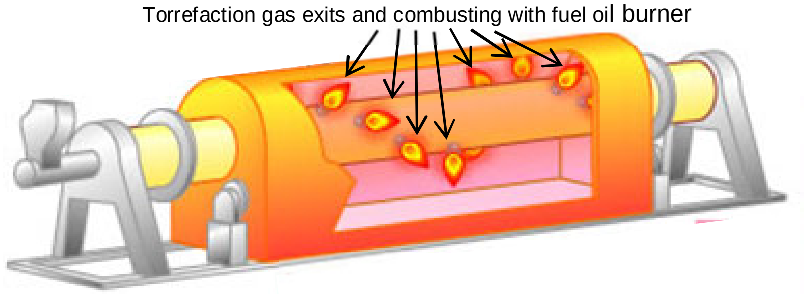
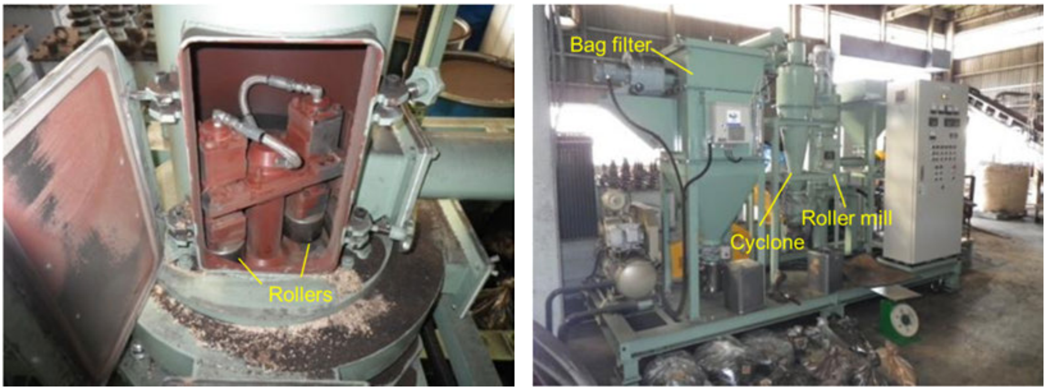


Figure 3. Schematics of antler kiln with several exits of torrefaction gas.

Pilot roller mill grindability of torrefied wood biomass

Grindability improvement after torrefaction of wood biomass is the most important property. Hardgrove Grindability Index (HGI), which is a well-known analysis technique to determine the grindability of coal, produces very conservative results for torrefied wood biomass compared to coal. The higher HGI value the better the grindability. Bergan *et al.* (2005) developed new way to determine the grindability of torrefied wood biomass using a heavy duty cutting mill and measuring the electric power consumption from coarse particles to 0.2 mm particle size. However, pulverized coal boiler power plant's installed roller mill for grinding coal is not a cutting mill and a cutting mill may get favourable grindability results for resistant fibrous wood biomass. In this study, a pilot roller mill (Kotobuki RM10) was prepared to measure the electric power consumption from coarse particles to 0.076 mm particle size (200 mesh screen) of torrefied wood biomass and coal.


a) Overview of pilot roller mill

b) Inside of roller mill

Figure 4. Pilot roller mill for grindability evaluation of torrefied biomass.

Co-firing test in a pulverized coal boiler

Yatsushiro paper mill has a pulverized coal boiler to produce electricity and steam for paper production, and sells surplus electricity to outside. Three roller mills (IHI co.), which have an average grinding rate of 11.1 t/h of coal for each, were in series with a pulverized coal boiler (Figure 5). In the coal stock yard, torrefied Japanese cedar bark pellets were mixed with Australian Wambo coal which had a HGI of 51, and were carried to Yatsushiro paper mill. The mixing percentage of torrefied Japanese cedar bark pellets to the coal were 5%, 10%, 15% and 20% for the co-firing test. Torrefied pellets and coal mixture was fed into one of three roller mills. The roller mill grindability such as electric power consumption was observed in the co-firing test.

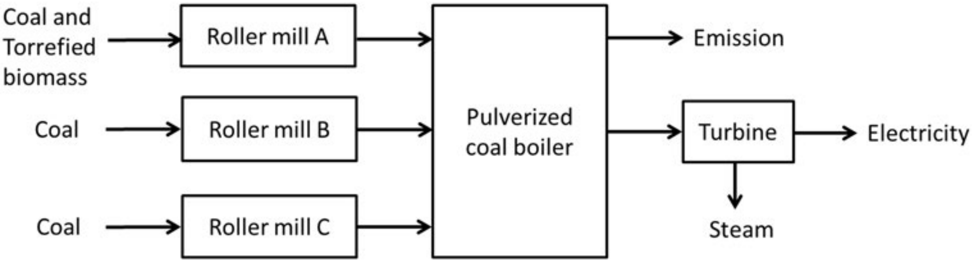


Figure 5. Process diagram of pulverized coal boiler in Yatsushiro paper mill.

Results

Laboratory torrefaction

The effect of torrefaction temperature on mass and energy yield of Japanese cedar bark are shown on the left hand side of Figure 6. Mass and energy yield of Japanese cedar bark decreased as the temperature increased. Energy yield was about 10 points higher than mass yield in the temperature range from 225°C to 300°C. HGI of torrefied Japanese cedar bark is shown in right hand side of Figure 6. HGI of Japanese cedar bark before torrefaction was 17. After torrefaction for 30 minutes, HGI of Japanese cedar bark became about 50 in the temperature range from 225°C to 300°C. In the pulverized coal boiler of NPI, the coal which HGI is from 40 to 60 and this is acceptable for grindability. In terms of grindability, torrefaction temperature at 225°C would be sufficient.

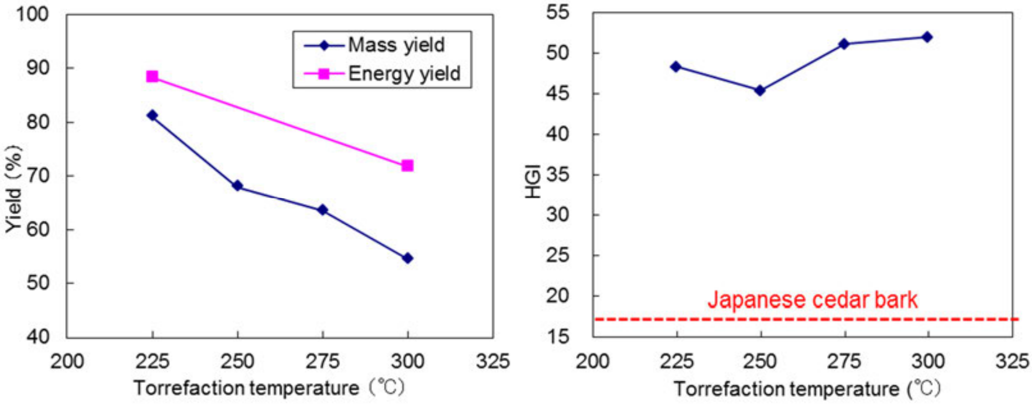


Figure 6. Mass and energy yield of Japanese cedar bark with torrefaction temperature.

Pilot torrefaction plant

In the pilot torrefaction plant, 900 kg/t of Japanese cedar bark pellets were fed into the torrefaction process which operated for 6 hours per day. Finally, 60 tons of torrefied Japanese cedar bark pellets were produced in an operation lasting 3 week. Torrefaction temperature was 260°C as measured by the thermocouple fitted inside of antler kiln.

Table 1. Properties of torrefied Japanese cedar bark pellets compared to a coal.

		Japanese cedar bark pellets	Torrefied Japanese cedar bark pellets	Coal
Bulk density	g/cm^3	0.60	0.55	0.80
HGI		25	35	40 - 60
Ignition temperarure[1)]	℃	465	456	480 - 530
Lower explosive limit[2)]	g/m^3	120	80	60
Self-exothermicity[3)]	℃	130	124	147

1) ASTM E 659

2) JIS Z 8818, SAP12-10

3) The temperature of 1 L sample, which was left at ambient temperature of 120 ℃ for 24 hours

Mass and energy yield were about 90% and 96%, respectively. HGI of Japanese cedar bark pellets was 25. After torrefaction, HGI of torrefied Japanese cedar bark pellets had increased to 35. Properties of torrefied Japanese cedar bark pellets are shown in Table 1. Except for bulk density, the properties of torrefied pellets were almost the same as a coal. HGI of torrefied pellets were slightly lower than that of coal.

Pilot roller mill grindability of torrefied biomass

Australian Wambo coal (HGI = 51) was fed into the pilot roller mill at the rate of 5 kg/min. After 10 minutes, the pilot roller mill reached a steady state and ground Wambo coal blown at the same rate as the feeding rate i.e. 5 kg/min. After 40 minutes, the feed of coal into roller mill was stopped and then the remaining coal was ground and blown out. In this experiment, the feeding rate of samples was fixed at 5 kg/min and electric power consumption at steady state was evaluated.

Indonesian Senakin coal (HGI = 40) consumed about 40% higher electric power on average than that of Wambo coal because of its lower HGI which means harder grindability. When Wambo coal containing untorrefied 10% Japanese cedar bark pellets was ground in a pilot roller mill, the electric power consumption of this material on average became about 30% higher than that of 100% Wambo coal. On the other hand, when Wambo coal containing 10% torrefied Japanese cedar bark pellets was ground in the pilot roller mill, the electric power consumption of this material became almost the same as that of 100% Wambo coal. The grindability of Japanese cedar bark pellets was improved dramatically by torrefaction. However, when the percentage of torrefied Japanese cedar bark pellets was increased to 20% in a mixture with Wambo coal, the electric power consumption in average became about 20% higher than that of 100% Wambo coal (Figure 7).

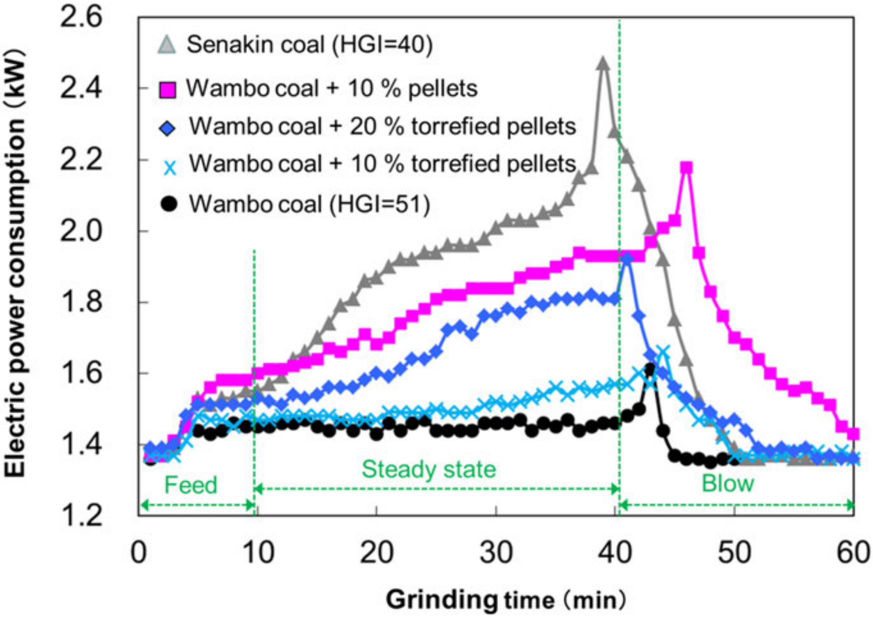
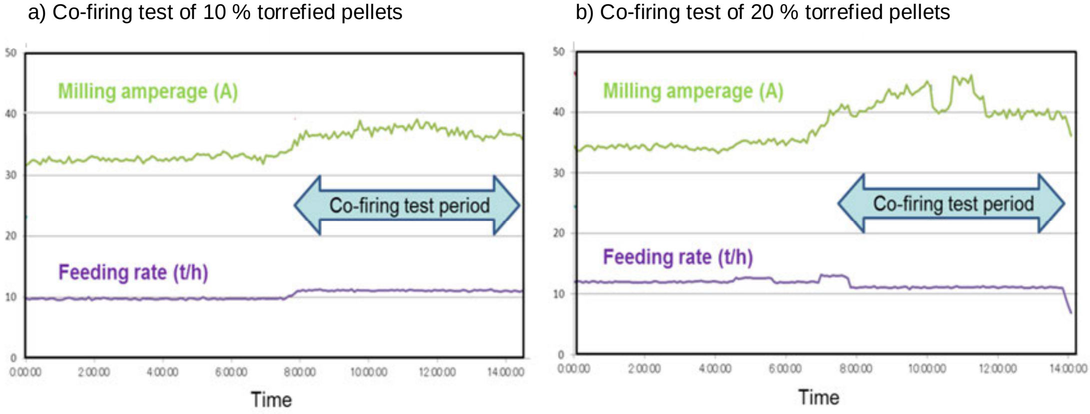


Figure 7. Power consumption of pilot roller mill grinding torrefied biomass and coal.

Co-firing test in a pulverized coal boiler

The milling amperage of co-firing tests is shown in Figure 8. When the Wambo coal (HGI = 51) containing 10% of torrefied Japanese cedar bark pellets (HGI = 35) was ground trouble-free in one mill, milling amperage was about 8% higher than that of 100% Wambo coal without any for 6 hours. On the other hand, when the Wambo coal containing 20% of Japanese cedar bark pellets was ground in one roller mill, milling amperage became about 30% higher than that of 100% Wambo coal. These results indicated that grindability of torrefied biomass has to be close to the coal for increasing co-firing ratio of torrefied biomass.


a) Co-firing test of 10 % torrefied pellets

b) Co-firing test of 20 % torrefied pellets

Figure 8. Power consumption of roller mill at co-firing test in Yatsushiro paper mill.

Conclusions

NPI has modified a carbonization plant for paper sludge into a pilot torrefaction plant for wood biomass and produced 60 tons of torrefied Japanese cedar bark pellets. In the Yatsushiro paper mill, Wambo coal containing 20% of Japanese cedar bark pellets was ground in one roller mill and co-fired in a pulverized coal boiler. In this test, electric power consumption in one roller mill increased about 30%. Therefore, improvement of grindability by torrefaction in higher temperature would be required for increasing percentage of co-grinding ratio of torrefied Japanese cedar bark pellets.

References

1. Bergman, P.C.A, Boersma, A.R., Zwart, R.W.R, Kiel, J.H.A. 2005. Torrefaction for biomass co-firing in existing coal-fired power stations, ECN-C-05-013.

2. Bergman, P.C.A, Kiel, J.H.A. 2005. Torrefaction for biomass upgrading, ECN-RX—05-180.

3. Koukious, E.G., Mavrokoukoulakis, J., Abatzoglou, N. 1982. Energy densification of biomass. Proc. 1st National Conf. On Soft Energy Forms, Thessaloniki.

4. Almeida, G., Brito, J.O., Perre, P. 2000. Alternations in energy properties of eucalyptus wood and bark subjected to torrefaction: The potential of mass loss as a synthetic indicator. Bioresource Technology 101(24), pp. 9778–9784.

Pressurized entrained flow gasification of biomass powder – initial results from pilot plant experiments

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Abstract

Direct gasification of wood residues based on a pressurized and oxygen blown entrained flow concept followed by catalytic conversion of the resulting syngas is an attractive alternative for production of renewable transportation fuel. In order to accelerate the technology development, a pilot plant (0.5 MWth at 6 bar) for oxygen blown Pressurized Entrained-flow Biomass Gasification (PEBG) has so far been operated for ~150 h at ETC in Piteå, Sweden. The technology concept is based on a high temperature entrained flow gasification process, which should gasify biomass powders to a syngas with low tar, soot and other general hydrocarbon contents. So far, relatively fine powders produced from stem wood and bark has been gasified with good results considering the resulting carbon conversion and gas composition. The reactor process temperatures have been varied in the interval 1 100–1 300°C at oxygen excess ratios up to 0.45, which resulted in relatively low H_2/CO molar ratios (around ~0.5) in the final syngas composition (with no steam added). Furthermore, the effect of using nitrogen or carbon dioxide as process inert gas was investigated. During the PEBG experiments, the plant was operated at 2 bar and a thermal fuel load of 0.2 MWth.

Introduction

It is estimated that the total world energy demand will increase by 40% over the next 20 years and one of the fastest growing sector is the transportation sector [1]. Oxygen blown high temperature entrained flow gasification is one alternative route for syngas generation and transportation fuel synthesis from biomass. Production of synthetic fuel or chemicals from coal gasification is a proven technology. However, commercial biomass gasification plants for transportation fuel production are still under development [2–3]. Pilot and demonstration scale Methanol- and BioDME production have been demonstrated from black liquor gasification [4–5].

To increase the knowledge regarding fuel synthesis from high-temperature gasification of woody biomass, several issues have to be investigated prior to process commercialization.

In the present study, an oxygen blown pilot scale Pressurized Entrained-flow Biomass Gasification plant (PEBG) was designed, constructed and operated. The main challenges for a long term success with this type of process involve efficient fuel preparation, robust fuel feeding, controlled ash/slag handling, durability of containment materials, safe plant operation and to obtain an optimal syngas composition with high cold gas efficiency. The objective was to provide valuable information to the understanding of auto-thermal entrained flow biomass gasification. The general aim with this project was to characterize the process and evaluate whether biomass residues can be utilized as raw material in the gasifier. This paper provides results from gasification experiments with spruce bark, bark mixture and stem wood biomass. The focus was to evaluate the syngas quality with respect to down-stream synthesis of motor fuels.

Experimental

Pilot plant

The PEBG plant was designed for high process temperature (1 200–1 500°C), oxygen blown, slagging gasification of biomass with a thermal throughput of maximum 1 MW_{th} and pressures up to 11 bar. A schematic process flow diagram is shown in Figure 1.

Fuel powder was prepared by milling in a hammer mill and the particle size distribution was controlled by the hammer mill sieve size before the fuel powder was transported to the lock hoppers. Fuel feeding was accomplished by a twin based mechanical lock hopper system where the twin hoppers (1 m^3) were sequentially filled and alternately operated in order to keep the pressurized process in continuous operation. An Auger screw feeder controlled the fuel feeding rate. A mixture of oxygen and inert gas was added through the oxidant register of the burner. Both gas streams were controlled by mass flow controllers. The gasifier consisted of a ceramic lined reactor (inner diameter 0.52 m and the length of vertical reactor wall 1.67 m) followed by a bubbling quench for syngas cooling and smelt/particle separation.

Prior to process start-up, the reactor ceramics was heated by an electrical heater mounted at the reactor centre line. The heater was removed before the gasification process was started. Thermocouples measured the process temperature at different locations inside the reactor.

A water cooled nitrogen purged camera probe, mounted on top of the reactor and slightly tilted towards the reactor axis, visualized the flame and the interior of the reactor. This was a qualitatively valuable tool for operation, especially at process start up. The generated syngas was cooled down below 100°C by water sprays at two different levels in the quench tube. Particles (i.e. ash and char) are collected either at the quench bottom or in the sedimentation vessel downstream the quench water outlet.

System pressure was controlled by a regulating valve on the syngas outlet after the quench. The main syngas stream was incinerated in the flare on top of the building. A LPG (Light Petroleum Gas) pilot flame was used as a continuous ignition source.

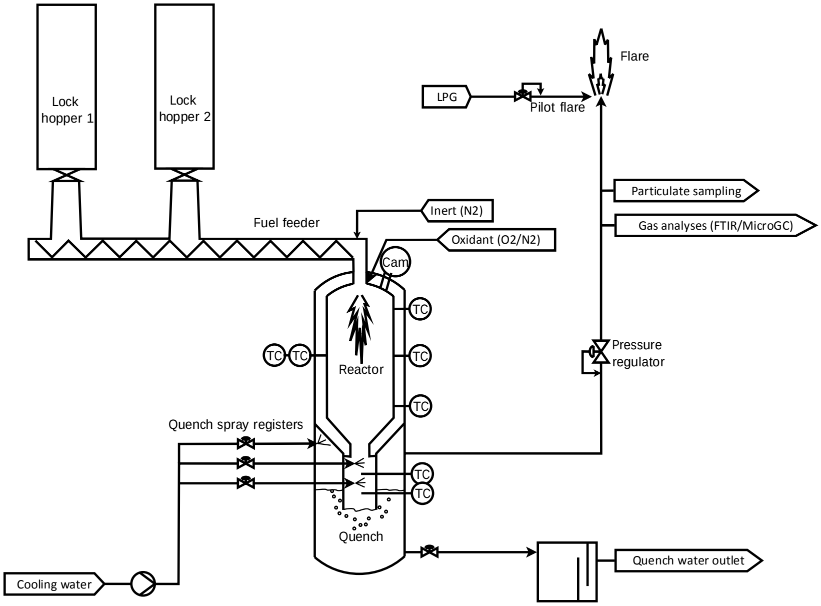

Figure 1. Schematic process flow diagram of the PEBG plant.

Operational conditions

The fuels used in this study were spruce bark, bark mixture from the Smurfit Kappa Kraftliner paper mill and pine stem wood. The fuels ultimate analyses are shown in Table 1.

Table 1. Ultimate analysis of the different fuels.

Ultimate analysis (wt% dry)	Ash	C	H	O	N	S
Spruce bark	4.2	52.2	5.6	37.5	0.41	0.037
Bark mix	2.2	52.6	6.4	38.3	0.38	0.026
Stem wood	0.4	50.9	6.3	42.4	0.10	<0.01

Table 2 summarizes the gasification conditions in this study. As can be found in Table 2, spruce bark powder was produced with 1.0 mm screen size installed in the hammer mill, whereas the other fuel powders were produced with 0.75 mm hammer mill screen size. This was done in order to achieve similar particle size distributions for the different fuels.

The oxygen excess ratio (lambda, λ) was defined as the ratio between the actually supplied oxygen and the stoichiometric oxygen demand (for complete combustion).

Syngas characterisation

Syngas sampling was performed by letting a small slip stream of the produced syngas flow from the syngas pipe, through particulate removal equipment followed by a water condenser. The dried syngas was then analyzed consecutively by a FTIR instrument and a µGC.

The concentration and size distribution of particulates in the syngas was measured by a Dekati® Low Pressure Impactor (DLPI).

Table 2. Experimental settings.

Parameter	Unit	Spruce Bark	Bark mix	Stem wood	Stem wood + CO_2
Fuel size[a)]	mm	1.0	0.75	0.75	0.75
Fuel feeding rate	kg/h	40	40	40	40
Total Nitrogen inlet	kg/h	13	16	14	0
Oxygen inlet	kg/h	24	27	25	27
Oxygen excess ratio (λ)	-	0.44	0.45	0.44	0.48
System pressure	bar	2	2	2	2
Quench water level[b)]	%	30	30	30	30

[a)] Fuel size figure corresponds to the sieve size used in the hammer mill.
[b)] Bubbling quench if the water level > 20%.

Results and discussion

Example of reactor process temperature profile over time from a typical experiment is presented in Figure 2. The graph show the average mid reactor process temperature (left ordinate) and CO, N_2 and H_2 dry product gas composition in mol-% (right ordinate). The reactor was electrically heated to approximately 1 020°C, after which the heater was removed and the gasifier nitrogen purged. After a first process start-up and approximately 30 minutes of operation, the process had to be shut-down and re-purged with nitrogen. After the second start-up the plant was continuously operated for 6 h 50 min. During the first 90 minutes after the second start-up, the operated λ was 0.50 in order to quickly reach a desired high process temperature (>1 200°C). A minor process temperature dip in an otherwise continuous temperature increase occurred when the operated λ was reduced to 0.44. Between process time 310 min and 470 min the temperature increase was approximately 20°C/h. The gas composition was stabilized at the new process conditions approximately 30 minutes after the λ-reduction. Hence, the gas composition seems unaffected of temperature within the range 1 190–1 250°C. The ragged part of the curves, i.e. from process time 470 min and forward in Figure 2, arose from irregular nitrogen addition to the fuel feeding system. Immediately after the experimental run a large volume of nitrogen gas was flushed through the reactor for purging the reactor system resulting in a sharp temperature drop and nitrogen peak in Figure 2.

The resulting reactor temperatures and dry gas compositions are presented in Table 3 for the different campaigns. For comparison, approximate gas composition from black liquor gasification (BLG) described by [6] is also presented in the table.

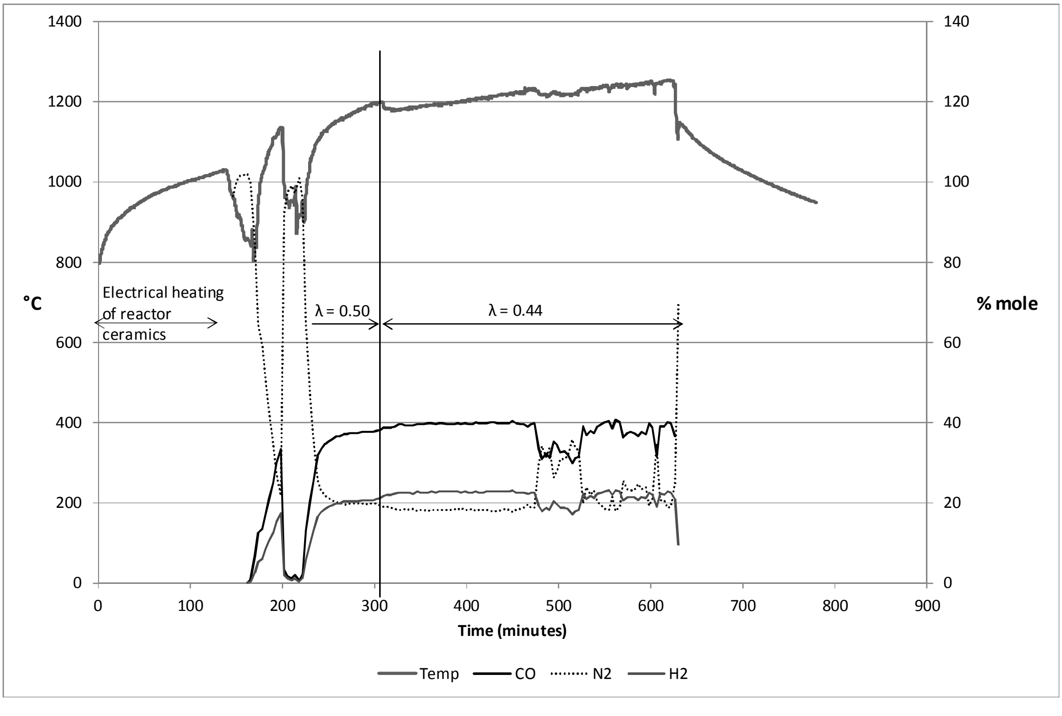

Figure 2. Process temperature profile (left ordinate) together with the resulting CO, N_2 and H_2 concentration profiles (right ordinate) from a typical experiment.

Table 3. Resulting reactor temperatures and gas compositions (dry gas) for the different campaigns. Black liquor gasification (BLG) gas composition added as a comparison.

	Unit	**Spruce bark**	**Bark mix**	**Stem wood**	**Stem wood + CO_2**	**BLG**
Reactor temperature	°C	1 100–1 145	1 190–1 230	1 190–1 250	1 200–1 220	~1 050
Dry gas composition						
H_2	mol%	22.7	23.6	22.7	21.5	~27
N_2	mol%	17.7	17.1	18.1	0.3	~21
CO	mol%	40.1	42.8	39.8	47.5	~21
CO_2	mol%	15.8	13.7	16.7	29.7	~28
CH_4	mol%	1.9	1.6	1.9	1.6	~1
C_2H_4	mol%	0.1	<0.1	0.1	0.1	n.a.
C_2H_2	mol%	0.1	0.1	0.2	0.2	n.a.
H_2S	mol%	-	-	-	-	~1
Syngas LHV	MJ/kg_{dry}	7.82	8.25	7.70	7.48	5.7
H_2/CO	mol%	0.57	0.55	0.57	0.45	1.3

Gasification of wet biomass fuels, e.g. black liquor, generates a syngas with higher H_2/CO ratio compared to dry biomass gasification. Simultaneously the process temperature becomes lower. Introducing steam directly to the PEBG gasifier would most probably have the same effect on the syngas quality and process temperature.

The CO_2 campaign resulted in increased CO and decreased H_2 content of the syngas, indicating that the increased amount of CO_2 promotes the formation of CO and H_2O by the reversed water-gas shift reaction.

Conclusions

- Oxygen blown entrained flow gasification of bark, bark mixture and stem wood powder was verified.
- Carbon dioxide (CO_2) was successfully used as inert gas to the process instead of nitrogen (N_2).
- The CO concentration in the syngas was relatively high which resulted in a H_2/CO ratio around 0.5. This implies that shifting the syngas towards higher H_2/CO ratio is necessary if the syngas is intended for catalytic synthesis of motor fuels such as DME or Fischer-Tropsch diesel.

Acknowledgement

The financial support from the Swedish Energy Agency, IVAB, Sveaskog, and Smurfit Kappa Kraftliner is thankfully acknowledged. Partial funding also came from the Bio4Energy collaboration and the Swedish Biomass Gasification Centre. Thanks also for the excellent collaboration with IVAB and Luleå University of Technology.

References

1. World Energy Council. Policies for the future – 2011 Assessment of country energy and climate policies [PDF]. http://www.worldenergy.org/documents/wec_2011_assessment_of_energy_and_climate_policies.pdf. (Accessed May 24, 2012.)

2. Swanson, R.M., Platon, A., Satrio, J.A., Brown, R.C. 2010. Techno-economic analysis of biomass-to-liquids production based on gasification. Fuel 89(Suppl. 1), pp. S11–S19.

3. Zhang, W. 2010. Automotive fuels from biomass via gasification. Fuel Process Technol 91(8), pp. 866–876.

4. Häggström, C., Öhrman, O., Rownaghi, A., Hedlund, J., Gebart, R. 2012. Catalytic methanol synthesis via black liquor gasification. Fuel Process Technol 94(1), pp. 10–15.

5. Granberg, F., Nelving, H., Landälv, I. 2010. Production of dimethyl ether (DME) from black liquor for use in heavy duty trucks.

6. Öhrman, O., Häggström, C., Wiinikka, H., Hedlund, J., Gebart, R. 2012. Analysis of trace components in synthesis gas generated by black liquor gasification. Fuel 102(7), pp. 173–179.

Green Fuel Nordic – The Smart Way: Utilising RTP™ technology to produce sustainable 2nd generation bio-oil from local feedstocks

Timo Saarelainen, *Jerkko Starck*
Green Fuel Nordic Oy

Abstract

Transitioning to a low-carbon economy is one of the major global megatrends of our time. This development trend unlocks new business opportunities for open-minded, responsible companies that have operations based on e.g. technology developments leveraging innovative, renewable raw materials or on the commercial implementation of these technologies.

Green Fuel Nordic Oy is a Finnish biorefining company. Company's business idea is to utilize the already commercially proven RTP™ technology for production of second-generation bio-oil from local, renewable forest-based biomass.

The Rapid Thermal Process (RTPTM) unit is at the core of the rapid pyrolysis-based biorefinery. Biomass is fed into the reactor and then gasified by a circulating fluidized bed of hot material (sand). The gas that is generated is led to a cyclone, where the bed material and char are mechanically separated from the gas stream. The gas moves from the cyclone into a condenser, where it is cooled and condensed into bio-oil. The off-take is a liquid, low-carbon and sulfur-free bio-oil that can directly replace light and heavy fuel oil in renewable energy applications.

Operating environment for renewable liquid biofuels

Dependence on exhaustible, non-renewable fossil natural resources and the climate change caused by their use are significant forces driving political, social and business development. Transitioning to a low-carbon economy is one of the major global megatrends of our time. Reducing energy consumption and replacing the use of fossil natural resources with renewable raw materials are important means for realizing this development process.

The aim to reduce energy consumption is very challenging. The energy need in developing economies will grow as industrialization increases and the consumption by populations with rising affluence grows. As population growth continues, a shortage of food will emerge and food prices will rise. The food shortage can be partially attributable to environmental disasters and the industrial utilization of the food chain's raw materials for non-food production.

Dependency on fossil oil is related to its utilization not only as an energy source and fuel for transportation, but also as a raw material for chemical industry products like plastics.

The scarcity of fossil oil that can be utilized cost-effectively increases its price. At the same time, the competitiveness of new bio-oils is improving, and progress is being made in the development efforts to utilize them in applications beyond energy production, e.g. in the chemical industry. The CO_2-neutrality of second-generation bio-based fuels, eliminating the need for CO_2 emissions allowances, also boosts competitiveness.

This development trend unlocks new business opportunities for open-minded, responsible companies that have operations based on e.g. technology developments leveraging innovative, renewable raw materials or on the commercial implementation of these technologies.

The EU's intention of mitigating climate change has led to several directives and incentives guiding the activities of member countries. These include the so-called 20-20-20 target and the related Renewable Energy Sources (RES) target of 38% for Finland. They unlock attractive business opportunities for renewable bio-oil in Finland and elsewhere in Europe.

The growing forest assets also favor Finland as a location for biorefineries. The growth of well managed forests significantly exceeds the industrial use of sustainably utilizable wood. The conventional forest industry's structural distress also releases more wood for new types of applications, e.g. for use as feedstock for biorefineries.

Green Fuel Nordic Oy

Green Fuel Nordic Oy is a Finnish biorefining company. Its business concept is based on utilizing commercially proven, innovative RTP™ technology to produce second-generation bio-oil.

Utilizing existing technology accelerates the start-up of refinery operations and the commissioning of commercial bio-oil production and it enables distributed energy production. In the near future, the company plans on building several biorefineries close to Finnish feedstock. In doing so, it is contributing to the achievement of the targets set for Finland's renewable energy production and supporting energy self-sufficiency.

The chosen technology can be used to produce liquid, low-carbon and sulfur-free bio-oil from local, renewable forest-based biomass. Bio-oil can be utilized directly in industrial and municipal electricity and heat production, replacing light and heavy fuel oil.

The Smart Way

The need to build an increasingly lower-carbon society that is less dependent on fossil energy sources will grow the demand for renewable biofuels, among other things. This strong development path is also one of the drivers of Green Fuel Nordic's bio-oil refining business. Another significant driver is the decision to utilize existing, commercially proven technology.

This RTPTM technology can be used to produce second-generation liquid, sulfur-free bio-oil from local, renewable forest-based biomass. Finland's sustainably managed and widely certified forests grow over 100 million cubic meters per year. Industrial wood use amounts to about 50 million cubic meters per year. However, sustainable use would allow the utilization of 70–75 million cubic meters of wood on a yearly level.

So there is no shortage of forest biomass suitable for bio-oil production, especially since the conventional forest industry is not increasing its use of wood in Finland. RTP™ technology also makes it possible to use sawmill and pulp industry by-products as feedstock.

Green Fuel Nordic's biorefinery investments support distributed energy production, which is strategically important for Finland, and strengthen energy self-sufficiency. Moreover, the company's operations support the achievement of Finland's RES target. At the same time, it offers employment opportunities for local communities affected by forest industry restructuring as well as a new, local refining path for forest biomass.

The storage and transportation properties of RTP™ Green Fuel bio-oil support flexible energy distribution.

Bio-oil can be utilized directly in industrial and municipal electricity and heat production, replacing light and heavy fuel oil. Emerging alongside of these applications is the use of bio-oil to power marine diesel engines.

In the near future, it will be possible to upgrade bio-oil also into products comparable to normal transportation fuels. Interesting applications in the longer term are found in the chemical industry.

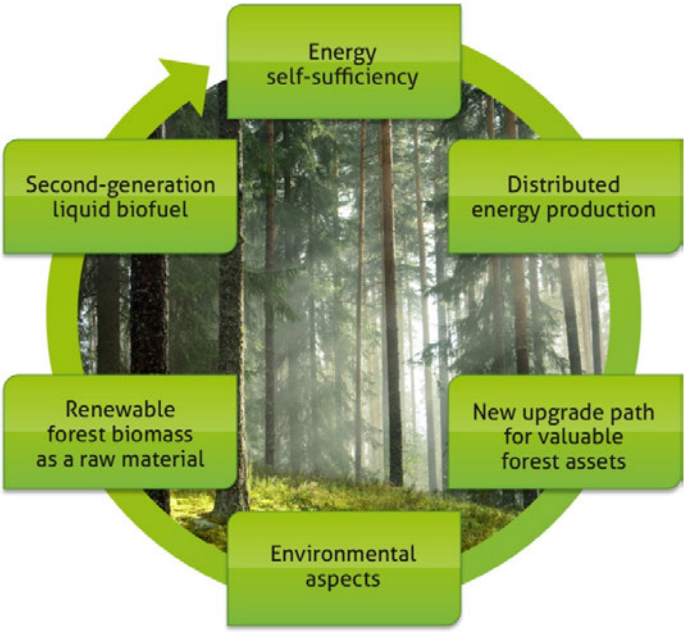

Figure 1. Some main steps of the Smart Way of Green Fuel Nordic Oy.

Renewable, local feedstock

Finland's sustainably managed and widely certified forests grow more than 100 million cubic meters per year. Industry uses about 50 million cubic meters of wood annually. Sustainable use would enable a significantly higher volume of wood to be used, i.e. industrial utilization of 70–75 million cubic meters annually.

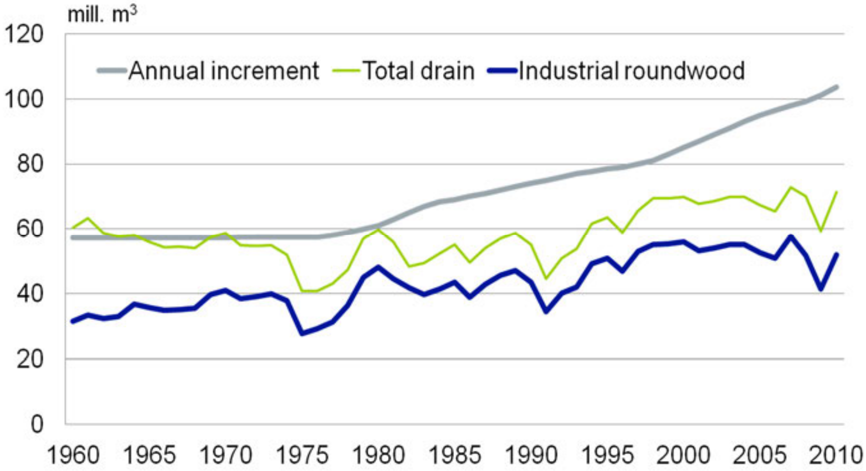

Figure 2. Forest balance in Finland 1960–2011. Sources: Metla, Finnish Forest Industries.

The raw material Green Fuel Nordic uses for bio-oil is renewable biomass directly from forests or in the form of wood-based by-products of sawmills and the pulp industry. Bio-oil refined using RTP™ technology is a second-generation liquid biofuel that doesn't use any raw materials from the food chain.

Bio-oil production is a new and sustainable refining path to put the yield of Finnish forests to good use. This is particularly significant in the communities hit by structural changes in the conventional forest industry and where the forest has always been a significant source of jobs and income.

RTP^{TM} Production Technology

Green Fuel Nordic Oy's bio-oil production process consists of several parts that together form a functioning biorefinery. In the biorefinery, renewable wood-based raw material is converted into second-generation bio-oil.

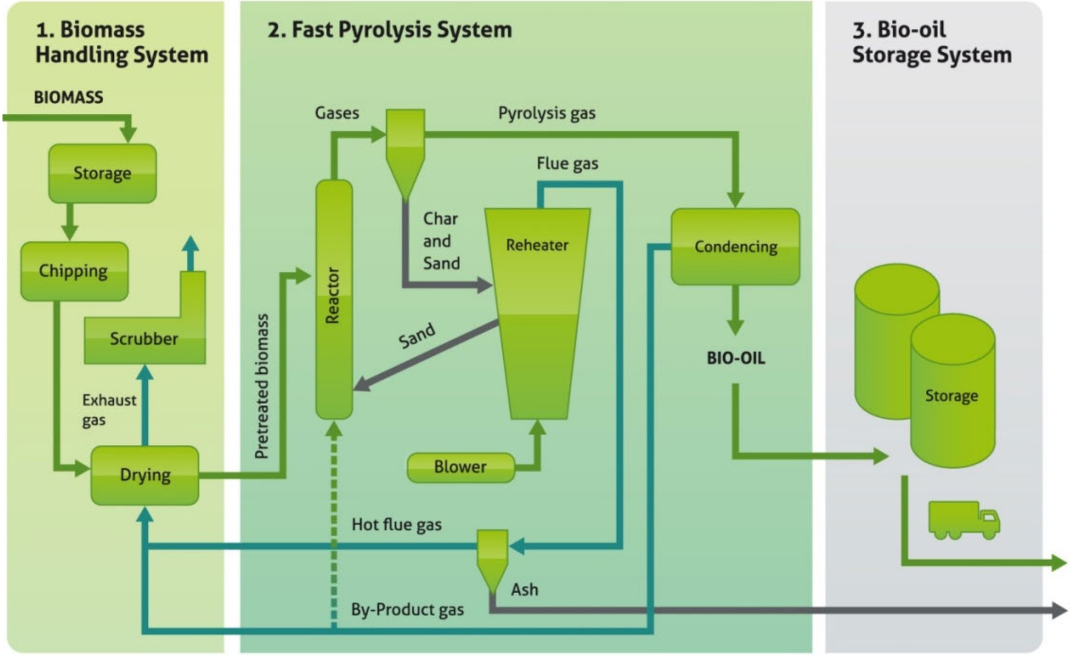

Figure 3. Green Fuel Nordic's RTP^{TM} production process.

The Rapid Thermal Process unit is at the core of the rapid pyrolysis-based biorefinery and is where the preprocessed biomass is converted into bio-oil. Bio-mass that has been preprocessed to the correct particle size and moisture content is fed into the reactor and then gasified by a circulating fluidized bed of hot material (sand). The gasification takes place in virtually oxygen-free conditions and thus no combustion occurs.

The gas that is generated is led to a cyclone, where the bed material and char are mechanically separated from the gas stream. The gas moves from the cyclone into a condenser, where it is cooled and condensed into bio-oil. Finally, the bio-oil produced is filtered before exiting the RTP unit.

The char (biocoal) that is produced as a by-product returns from the cyclone to the boiler to heat the reactor's bed material; this is where it is burned and generates the thermal energy required by the process. The product gas generated as a by-product in the condensing process is used in the drying of the biomass.

Before reaching the RTP unit, the biomass is processed into the correct particle size and moisture content. Feedstock processing requires numerous screens and grinding equipment. Drying takes place in a drying drum that uses the thermal energy of the RTP unit's hot flue gases. After drying, the moist flue gas is led to the flue-gas scrubber, where the majority of the environmentally harmful substances are separated from the flue gas.

The filtered bio-oil produced in the RTP unit is fed into day tanks and the quality is analyzed before being piped to storage tanks.

RTP™ Green Fuel Applications

The main applications for liquid biofuel are industrial boilers, district heating and lime kilns that can utilize bio-oil with only minor modifications to the existing systems. Other feasible applications are marine applications, particularly slow- and medium-speed diesel engines. Future applications can be found in upgrading bio-oil into transportation fuel and extraction of chemicals for the use in chemical industry, pharmaceuticals, cosmetics, and many more.

References

1. Bridgwater, A., Meier, D., Radlein, D. 1999. An overview of fast pyrolysis of biomass. Organic Geochemistry 30, pp. 1479–1493.

2. Bridgwater, A. 2004. Biomass Fast Pyrolysis. Review paper. BIBLID 0354-9836, 8, pp. 21–49.

3. Oasmaa, A., Kuoppala, E. 2003. Fast Pyrolysis of Forestry Residue. 3. Storage Stability of Liquid Fuel. Energy & Fuels 17, pp. 1075–1084.

Towards industrial production of microbial oil for high quality traffic fuels

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Abstract

Neste Oil is world-wide the largest producer of paraffinic hydrotreated vegetable oils (HVO) with annually 2 million tonnes NExBTL renewable fuel production capacity. A clear priority of the company's strategy is to expand the raw material base of its NExBTL refining process with sustainable and commercially feasible feedstock from residues and side streams. Waste and residue-based microbial oil has been in recent years the object of intensive research efforts in a close co-operation between Neste Oil and Aalto University, where feasibility of microbial oil as a feed for the NExBTL process has been demonstrated in laboratory and bench scale. Microbial oil technology allows efficient conversion of waste and residue materials, such as lignocellulosic materials, into oil. As a step towards industrial production of microbial oil the company decided in late 2011 to invest into a microbial oil pilot facility, which serves to generate necessary data for design of a commercial scale reference plant. This proceeding summarizes some key features of the microbial oil concept and gives an update from the path towards its industrialization.

Broadening the feedstock base

Materials classified as waste, residues, or by-products accounted for 41% of the renewable raw materials used by Neste Oil in 2011 for production of renewable HVO-type NExBTL diesel. Increasing the use of waste, residues and by-products for renewable fuel production beyond 50% is a strategic objective set by the company and striving for it requires strong R&D efforts.

Several prerequisites have to be fulfilled when selecting potential new raw materials for renewable diesel production. Availability of the raw material is an important requirement for large-scale industrial production. Sustainability criteria are of major importance and include carbon and water footprint, land use efficiency and nutrient use. Technical and commercial feasibility of the raw material are also key requirements for industrial use.

Microbial oil research

Lab and bench-scale demonstration

Interest towards developing microbial oil production from lignocellulosic raw materials rose remarkably when in a co-operation with the biochemistry group of Aalto University it was demonstrated that microbes convert lignocellulosic sugar into an oil which can be used to produce NExBTL diesel. Furthermore, the conversion process was found to be very effective as sugars from both cellulose and hemicellulose were equally effectively converted into microbial oil, which increases the overall utilization of a lignocellulose raw material.

Microbial oil technology utilizes special microorganisms that are able to produce and accumulate high amounts of oil when cultivated on waste and residue materials. Microbial oil production is performed in fermentor-type bioreactors and the process concepts are being developed for improved microbe and oil productivity. Figure 1 shows oil-rich fungal cells, which in a couple of days production cycle can produce oil in quantities up to 80% from their cell dry weight.

Microbial oil consists of triglycerides resembling thus vegetable oils. Comparison of the fatty acid distribution of microbial oil with rapeseed oil and especially with palm oil (Figure 2) shows that from refining point of view microbial oil is a drop-in solution for the NExBTL process. Fatty acids in microbial oil are highly saturated (low iodine number) making it highly suitable for production of paraffinic fuels such as NExBTL renewable fuels (Table 1).

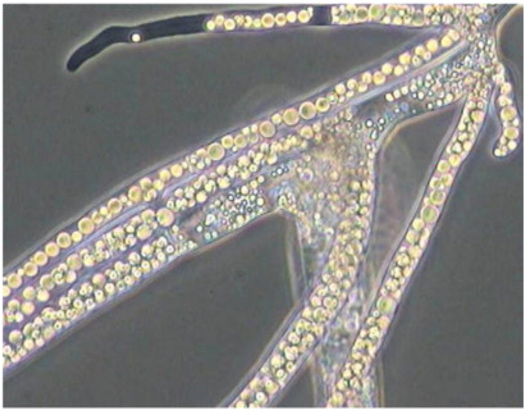

Figure 1. Oil-rich fungal cells; the white spots inside cell hyphae are oil (>50% oil from cell dry weight). Magnification 400x.

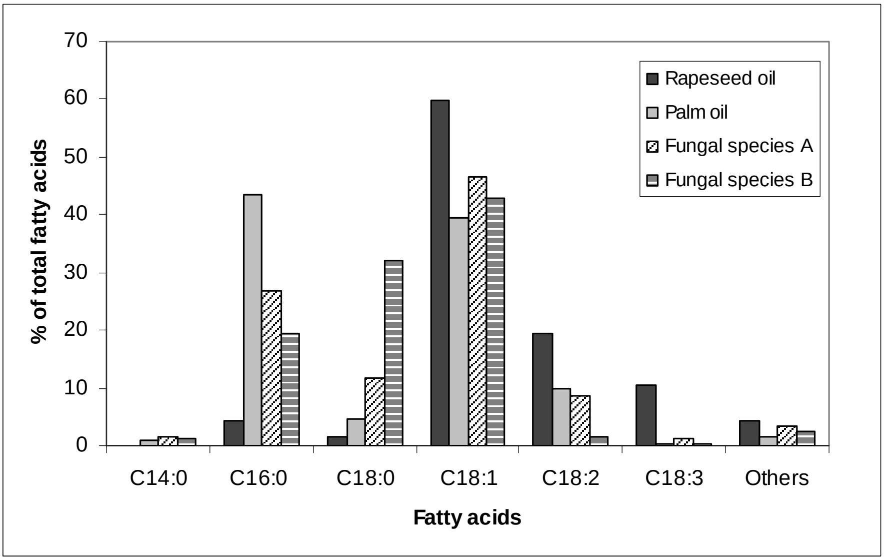

Figure 2. Fatty acid chain distribution makes microbial oil an excellent feed for the NExBTL process.

Table 1. Chemical composition of vegetable oils and microbial oils.

	Rapeseed oil	**Palm oil**	**Fungal species A**	**Fungal species B**
Oligomers	0	0	1	1
Triglycerides	96	89	95	88
Diglycerides	3	6	3	7
Monoglycerides	0	0	0	0
Carboxylic acids	1	4	2	4
Iodine number	115	53	54	66

Raw materials and oil production potential

Oil-producing microorganisms are very versatile in raw material utilization. Potential raw materials as feed for microbes include lignocellulosic materials such as agricultural residues straw, bagasse and stalk, pulp and paper industry residues and hemicellulose side streams. In addition, glycerol residues from traditional FAME-biodiesel production can be used. Depending on the raw material used the greenhouse gas reduction from dwell to wheel is typically higher than 75%, which is significantly higher than for currently used vegetable oils.

Global resources of agricultural residues are high as can be estimated from crop production statistics from FAO. Alone sustainably produced agricultural based residues are estimated to exceed one billion tonnes annually (Kim and Dale 2004; FAO 2012.), which could, potentially, be sufficient to cover all currently used biofuels.

Pilot scale

To further explore the possibility of industrial microbial oil production Neste Oil decided in late 2011 to invest into a microbial oil pilot facility to generate necessary data for estimating the feasibility of commercial scale production of microbial oil and create data for process scale-up. The pilot will serve to optimize microbial oil technology from waste and residue materials and generate microbial oil and side products for further studies. The pilot plant consists of raw material fractionation, microbial oil production and oil recovery units (Figure 3).

A benefit of the concept is that technology for fermentation is readily available and also the extraction of the oil from the microbial biomass is technically rather straightforward. After oil extraction the residue dry biomass can be used as animal feed or for other applications which adds to the overall value generation.

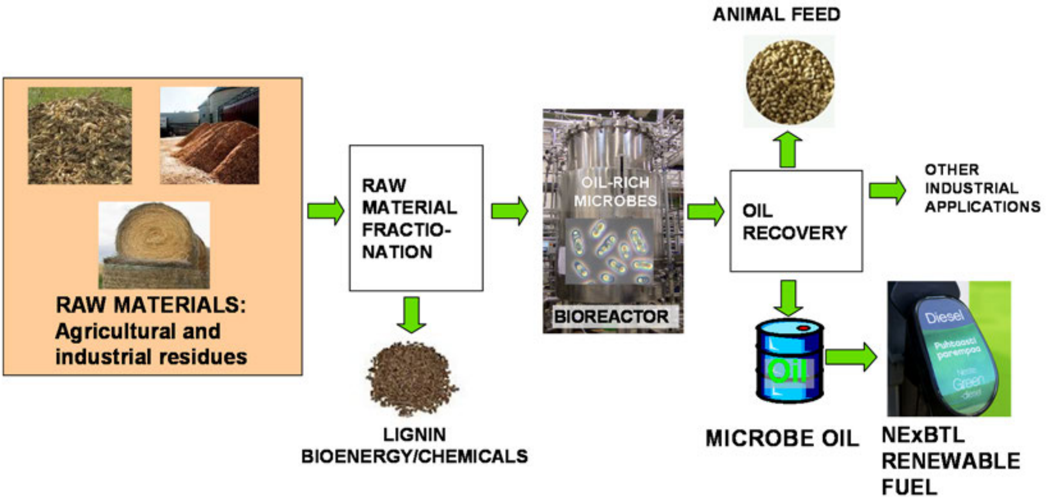

Figure 3. Microbial oil production concept.

High quality applications

Renewable NExBTL is a paraffinic HVO-type biofuel, which allows use of existing infrastructure, logistics and engine technology without need for any modifications. It is a drop in solution with no blend walls as it can be used even as 100% neat fuel in existing engines.

Due to its excellent properties, including cold properties, NExBTL enhances the overall quality of fuel and can be used in very demanding applications such as aviation. Neste Oil is very committed to be a forerunner in providing high-quality solutions for fuelling cleaner traffic in a sustainable way. The target of utilizing more than a million tonnes of residues, wastes and by-products for high-quality renewable fuel production is worth striving for.

References

1. Food and Agriculture Organization of the United Nations (FAO). http://faostat.fao.org/site/567/default.aspx#ancor.

2. Kim, S., Dale, B. 2004. Global potential bioethanol production from wasted crops and crop residues. Biomass and Bioenergy 26, pp. 361–375.

CHP-integrated bio-oil production demonstration plant, project development and current status

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[3]*Fortum Power and Heat*
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Abstract

The focus on fast pyrolysis research in Finland has been on fuel oil production from biomass for HFO-replacement applications. Experience has been gained by producing bio-oil from various feedstocks in bench and PDU scale units at VTT and lately in an integrated pilot scale unit Metso's R&D facility in Tampere, Finland. Characterisation methods and fuel oil analyses have been developed, various bio-oils analysed, and compared, and work has been done in order to obtain specifications and standards for this new type of bio-oil.

The consortium, Metso, Fortum, UPM, and VTT, has been operating a 7 tpd bio-oil production unit In Tampere in which a pyrolysis reactor is integrated to a conventional fluidized-bed boiler. The concept enables high overall efficiency and high bio-oil yields. All by-product streams are utilized to produce heat and electricity. Proof-of-concept has been carried out: over 100 tons of bio-oil has been produced and about 40 tonnes of bio-oil combusted in 1.5 MW district heating plant with high efficiency and low emissions.

Metso is currently building a 30 MW bio-oil demonstration unit at the existing Fortum combined heat and power (CHP) plant in Joensuu, Finland. The start-up for an integrated unit is scheduled for late 2013. Process optimization and quality control through the whole value-chain is critical when moving to commercial scale systems.

The focus of this paper is to discuss both on the challenges and the potential solutions for Fortum's bio-oil demonstration plant.

Background research

VTT has made, with the support of Finnish industry and Tekes, techno-economic assessments, market studies, and experimental research on fast pyrolysis for over 20 years and published quite a number of papers. Bio-oil is quite different from conventional liquid fuels, and many challenges remain to be overcome. VTT has systematically developed analytical methods by which the bio-oil quality can be followed both in laboratory and on-line during process. A stepwise market introduction is proposed: bio oil would first replace fuel oil in boilers, where its properties would not be prohibitive.

VTT has been developing an integrated concept, in which fast pyrolysis is integrated with a fluidized-bed boiler. In this concept hot sand from the boiler provides heat for the pyrolysis reactor. By-products from pyrolysis, such as char and non-condensable gases are used as fuel in the boiler. Using the pyrolysis by-product as fuel to replace boiler fuel improves the overall energy efficiency of the concept, because the by-products are used in the production of power and heat in fluidized bed boiler operating with high steam parameters.

Experimental work on fast pyrolysis has been targeted at supporting this concept. The integration is considered to offer the following technical and economic advantages:

(i) high overall efficiency
(ii) reduced investment costs because of utilization of existing infrastructure
(iii) low operating costs due to existing personnel and operations
(iv) good operating flexibility because of full exploitation of the byproduct in main boiler.

Industrial movements

Pilot plant

The consortium, Metso, Fortum, UPM, and VTT, has been operating a 7 tpd bio-oil production unit in which a pyrolysis reactor is integrated to a conventional fluidized-bed boiler. The concept enables high overall efficiency and high bio-oil yields. All by-product streams are utilized to produce heat and electricity. Proof-of-concept has been carried out: over 100 tons of bio-oil have been produced and about 40 tonnes of bio-oil combusted in 1.5 MW district heating plant with high efficiency and low emissions.

Demonstration plant

Metso is building a bio-oil production unit at the existing Fortum combined heat and power (CHP) plant in Joensuu, Finland (Figure 1). The nominal output of the plant will be 30 MW (oil production) and the planned annual production will be 50 000 tons. The annual production will equal to 210 GWh of energy, which corresponds to the yearly heating consumption of more than 10 000 private houses. The production plant will utilize in its process 225 000 solid-m^3 of forest residue and sawdust in a year. Integration of bio-oil production into the power plant process enables to utilize the side product from the production process in the generation of electricity and district heating. Utilization of bio-oil produced in the Joensuu plant helps reduce carbon dioxide emissions by 59 000 tons in a year.

The integrated technology has been developed into commercial scale in cooperation between Fortum, Metso, UPM and VTT as part of Tekes BioRefine research programme. In the integrated bio-oil production concept the heat for pyrolysis is transferred from hot sand of a fluidized-bed boiler. The integration of bio-oil production into the power plant process enables both high overall efficiency and high bio-oil yield. Pyrolysis by-products char and gases are used in the boiler to partially replace main fuel in the generation of electricity and district heating.

Metso will deliver the plant to Fortum as a turn-key delivery. The full scope delivery includes civil and construction works, fuel handling and pretreatment, bio-oil production and storage equipment, a Metso DNA automation system, and E&I. This demonstration venture will test and further develop integrated pyrolysis technology, and the control solutions of the Metso DNA system, which will be utilized in the pyrolysis processes of larger-scale power plants in the future. The new bio-oil production plant is scheduled for start-up in the autumn of 2013.

Figure 1. Industrial-scale integrated bio-oil plant in Joensuu, Finland.

Challenges for commercialization

The most important challenge is to make pyrolysis oil as a fuel competitive for combustion applications. The whole value-chain from the fuel procurement to the end-use should be capable of operating in the margin between the price of the fossil fuel to be replaced and the price of the feedstock. Process optimization and quality control through the whole value-chain is critical. Demands for pyrolysis process inputs, such as the requirement of low moisture content of feed with very small particle size are very challenging and energy consuming. For example, utilization of secondary process heats for drying and pyrolysis process integration to the fluidized bed boiler whenever possible should be considered. A belt dryer using low-grade process heat is economic and efficient for drying purposes. On-line analyses provide up to date information on process and save time and money. On-line moisture analyser based on Metso's invention has been successfully used in pilot and a solids analyser is under testing at VTT. Standards and specifications both for pyrolysis oil and combustion systems have been pushed forward. Comprehensive guidelines for transportation and MSDS are provided, standardisation under CEN has been initiated, as well as data for REACH registration gathered.

Properties of fast pyrolysis bio-oil

Fast pyrolysis bio-oils are highly polar and hence completely miscible with polar fuels like methanol or ethanol. About 80 wt-% of the bio-oil is water-soluble. They contain about 25 wt-% water which cannot be separated by physical means, like centrifugation. Another major fraction is composed of lignin-derived material, which is around 20 wt-% of the bio-oil (pyrolytic lignin).

Main single compounds are acetic acid (3–5 wt-%) and levoglucosan (4–10 wt-%). The rest of the bio-oil is composed of hundreds of various oxygen-containing compounds, most of them are present at low concentrations (below 1 wt-%). Fast pyrolysis bio-oils are acidic TAN being around

100 (pH 2.5–3), which means that careful selection of proper contact materials is needed. Heating value is roughly half from that of mineral oils and **density is higher (1.2 kg/dm^3).**

Standardisation

Guidelines for transportation, handling and use of fast pyrolysis bio-oils

At the moment it seems that the product should be classified as Class 8 (Corrosive) product. To make a final classification, all required tests should be done according to relevant transport regulations, referring to UN Manual of Tests and Criteria, OECD test, and others as applicable. It also appears that the variations between different products could lead to different classifications. It is the duty of each bio-oil producer to prove that the classification suggested in this paper is valid also for their product. For bio-oils there is no UN number assigned at the moment. If further testing shows that the properties for bio-oils are mostly the same, it may be possible to suggest a new UN number for the product. This suggestion should be made to UN, normally by a competent authority, or an association. A suggestion for transport classification is (Material Safety Data Sheet, Section 14 Transport Information):

> UN NUMBER: 3265, PROPER SHIPPING NAME: CORROSIVE LIQUID, ACIDIC, ORGANIC, N.O.S. (contains x, y*), CLASS: 8, PACKING GROUP: III, ENVIRONMENTAL HAZARDS: NO.

It is the oil producers responsibility to show that their bio-oil meets the same classification as shown here. More research is needed on material testing using a standard or well proven method at relevant test conditions.

Table 1. Summary table of transportation guidelines.

Property	Transportation classification	Existing test methods	Limit values	Fast pyrolysis bio-oils	Conclusion
Flammable	**Class 3, flammable liquids**	**Flashpoint** **Sustained combustibility**	**≤60ºC (closed cup test)** **Does not sustain combustion**	**Does not apply to bio-oil** **Does not sustain combustion**	**If the product does not sustain combustion, it is not needed to be classified as flammable liquid**
Corrosivity corrosive	**Class 8, corrosive substance**	**Full destruction of skin tissue** **Metal corrosion of steel / Al**	**OECD tests** **UN test manual**	**Slightly corrosive for rabbit, pH>2,5** **Not corrosive for steel, corrosive for aluminium**	**Probably corrosive (PG III)**
Toxic	**Class 6.1, toxic substances**	**Rat testing**	**LD_{50}≤ 300 mg/kg (oral)**	**>2000 mg/kg (oral, rat)**	**Not classified as toxic substance**
Environmentally hazardous	**Class 9, misc. dangerous goods**	**Aquatic toxicity** **Bioaccumulation** **Degradation**	**10 mg/L** **10 mg/L** **OECD tests**	**Algae 72h:100 mg/L** **Daphnia 48h: 100mg/L** **Aerobic biodegradability 28 days: 42%**	**Not env. hazardous** **Not class. as env. hazardous**

Reach registration

In the EU a new chemical regulation system REACH (Registration, Evaluation and Authorisation of Chemicals) is being applied. Registration under REACH has to be made if bio-oil is produced or imported to the EU. This paper describes fast pyrolysis bio-oil in details and highlights the major differences to other bio-oils. It also provides information on analytical methods suitable for fast pyrolysis bio-oil and data needed for REACH registration of fast pyrolysis bio-oil.

References

1. Solantausta, Y. 2000. Cost and performance analysis of new wood-fuelled power plant concepts. Doctoral dissertation: University of Aston in Birmingham. 364 p. + app. 91 p.

2. McKeough, P., Solantausta, Y., Kyllönen, H., Faaij, A., Hamelinck, C., Wagener, M., Beckman, D., Kjellström, B. 2005. Techno-economic analysis of biotrade chains. Upgraded biofuels from Russia and from Canada to the Netherlands (Techno-economic analysis of biotrade chains. Upgraded biofuels from Russia and from Canada to the Netherlands). Espoo: VTT Processes. 40 p. + app. 25 p. (VTT Tiedotteita - Research Notes 2312) ISBN 951-38-6745-5, 951-38-6746-3. http://www.vtt.fi/inf/pdf/tiedotteet/2005/T2312.pdf.

3. Solantausta, Y., Podesser, E., Beckman, D., Östman, A., Overend, R.P. 2000. IEA Bioenergy Task 22: Techno-economic assessments for bioenergy applications 1998–1999. Final report. Espoo: VTT Energy. 241 p. (VTT Tiedotteita - Meddelanden - Research Notes 2024) ISBN 951-38-5655-0, 951-38-5656-9 http://www.vtt.fi/inf/pdf/tiedotteet/2000/T2024.pdf.

4. Sipilä, E., Vasara, P., Sipilä, K., Solantausta, Y. 2007. Feasibility and market potential of pyrolysis oils in the European pulp and paper industry. Proceedings of the 15th European Biomass Conference and Exhibition; Berlin, Germany, May 7–11, 2007.

5. Pöyry Management Consulting Oy. Market Potential of Bio-oil Production in North American Forest Industry; Pöyry Management Consulting Oy: Vantaa, Finland, Nov 11, 2010.

6. Review from Iva Tews: Potential of fast pyrolysis applications within North American forest industries IEA. PyNe Newsletter, Issue 30, December 2011, pp. 34–35.

7. Oasmaa, A., Kuoppala, E., Selin, J.-F., Gust, S., Solantausta, Y. 2004. Fast Pyrolysis of Forestry Residue and Pine. 4. Improvement of the Product Quality by Solvent Addition. Energy & Fuels 188(5), pp. 1578–1583.

8. Oasmaa, A., Kuoppala, E., Solantausta, Y. 2003. Fast Pyrolysis of Forestry Residue. 2. Physicochemical Composition of Product Liquid. Energy & Fuels 17(2), pp. 433–443.

9. Oasmaa, A., Kuoppala, E. 2003. Fast Pyrolysis of Forestry Residue. 3. Storage Stability of Liquid Fuel. Energy & Fuels 17(4), pp. 1075–1084.

10. Oasmaa, A., Kuoppala, E., Solantausta, Y., Gust, S. 2003. Fast Pyrolysis of Forestry Residue. 1. Effect of Extractives on Phase Separation of Pyrolysis Liquids. Energy & Fuels 17(1), pp. 1–12.

11. Oasmaa, A., Solantausta, Y., Arpiainen, V., Kuoppala, E., Sipilä, K. 2010. Fast pyrolysis bio-oils from wood and agricultural residues. Energy & Fuels 24(2), pp. 1380–1388.

12. Oasmaa, A., Peacocke, C. 2010. A Guide to Physical Property Characterisation of Biomass-Derived Fast Pyrolysis Liquids. VTT, Espoo. VTT Publications 731. P. 79. ISBN 978-951-38-7384-4. http://www.vtt.fi/inf/pdf/publications/2010/P731.pdf.

13. Oasmaa, A., Kuoppala, E. 2008. Solvent fractionation method with brix for rapid characterization of wood fast pyrolysis liquids. Energy & Fuels 22(6), pp. 4245–4248.

14. Oasmaa, A., Kuoppala, E., Elliott, D.C. 2012. Development of the basis for an analytical protocol for feeds and products of bio-oil hydrotreatment: ACS. Energy & Fuels 26(4), pp. 2454–2460. Doi: 10.1021/ef300252y.

15. Oasmaa, A. 2003. Fuel oil quality properties of wood-based pyrolysis liquids. Academic dissertation. Jyväskylä, Department of Chemistry, University of Jyväskylä. Research Report Series, Report 99. 32 p. + app. 251 p. SBN 951-39-1572-7.

16. Elliott, D.C., Oasmaa, A., Preto, F., Meier, D., Bridgwater, A.V. 2012. Results of the IEA round robin on viscosity and stability of fast pyrolysis bio-oils. Energy & Fuels 26(6), pp. 3769–3776.

17. Oasmaa, A., Korhonen, J., Kuoppala, E. 2011. An approach for stability measurement of wood-based fast pyrolysis bio-oils: ACS Publications. Energy & Fuels 25(7), pp. 3307–3313.

18. Oasmaa, A., Elliott, D.C., Korhonen, J. 2010. Acidity of Biomass Fast Pyrolysis Bio-oils: American Chemical Society. Energy & Fuels 24(12), pp. 6548–6554.

19. Oasmaa, A., Kuoppala, E., Ardiyanti, A., Venderbosch, R.H., Heeres, H.J. 2010. Characterization of Hydrotreated Fast Pyrolysis Liquids: American Chemical Society. Energy & Fuels 24(9), pp. 5264–5272.

20. Lehto, J., Jokela, P., Alin, J., Solantausta, Y., Oasmaa, A. 2010. Bio-oil production integrated with a fluidized bed boiler—Experiences from a pilot project. PEI Power Engineering; PennWell: Tulsa, OK. Pp. 182–187. http://www.powerscenarios.wartsila.com/upload/articles/BestPaperAwards_2010.pdf.

21. Solantausta, Y., Oasmaa, A., Sipilä, K., Lindfors, C., Lehto, J., Autio, J., Jokela, P., Alin, J., Heiskanen, J. 2012. Bio-oil production from biomass: Steps toward demonstration: ACS. Energy & Fuels 26(1), pp. 233–240. Doi: 10.1021/ef201109t.

22. Oasmaa, A., Källi, A., Lindfors, C., Elliott, D.C., Springer, D., Peacocke, C., Chiaramonti, D. 2012. Guidelines for transportation, handling, and use of fast pyrolysis bio-oil. 1. Flammability and toxicity. Energy & Fuels 26(6), pp. 3864–3873. Doi: 10.1021/ef300418d.

23. Solantausta, Y. 2009. BIOCOUP: renewable energy from forest industry to conventional refineries. The 2nd Nordic Wood Biorefinery Conference, NWBC-2009. Helsinki, Finland, 2–4 Sept. 2009. Proceedings, Oral Presentations. Pp. 136–137.

24. Oasmaa, A., Solantausta, Y., Arpiainen, V., Kuoppala, E., Sipilä, Kai. 2010. Fast Pyrolysis Bio-Oils from Wood and Agricultural Residues. Energy & Fuels 24(2), pp. 1380–1388. Doi: 10.1021/ef901107f.

25. Sipilä, E., Vasara, P., Sipilä, K., Solantausta, Y. 2007. Feasibility and market potential of pyrolysis oils in European pulp and paper industry. 15th European Biomass Conference & Exhibition. Berlin, Germany, 7–11 May, 2007. ETA-WIP.

26. http://www.biocoup.com/.

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R&D highlights

Utilization of hydrolysis lignin in the Soviet Union and Russia: What is applicable in the wood biorefinery era?

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> **"We should focus on lignin applications in the areas inaccessible for the oil "firedrake". Perhaps a time will come when oil and natural gas become so expensive that we will be able to compete with this dragon in its own land. However we should patiently wait for this at least several decades"**
> Michael I. Chudakov. Industrial lignin utilization. In: Wood chemistry: Lignin and its utilization. Zinatne, Riga, 1968

Abstract

Since its establishment in the mid 1930s and till the collapse by the end of 1990s, Soviet hydrolysis industry produced enormous amounts of the so called hydrolysis lignin as a major by-product (>40% of the total consumption of plant raw material), which has never been exactly accounted. In the mid 1980s its annual production in the former USSR reached roughly 1.5 mio. metric tons. Only 30–40% of this amount was in fact utilized, whereas the major part was usually placed on the local dumps. The review is focused on the composition of hydrolysis lignin produced by Soviet industry and its industrial utilization. The following areas of lignin application are briefly outlined: lignin as a domestic industrial and household fuel, lignin carbonization, lignin humification and utilization in various fertilizers, lignin derivatives as viscosity reducers by oil drilling, adsorbents from lignin, lignin as a filling agent, lignin as a binder, lignin in compositions for rust removal. Current state of hydrolysis lignin utilization in the former Soviet republics and the environmental problems caused by hydrolysis lignin dumps are also briefly addressed.

Lignin as a by-product and "the headache" of Soviet hydrolysis plants

Most of the Soviet hydrolysis plants, which have been built after the World War II, specialized on the production of furfural and/or fodder yeast rather than ethanol. So called hydrolysis yeast plants were projected to almost completely utilize the polysaccharide fraction of a feedstock, producing hydrolysis lignin similar to that of the older ethanol plants. Large and relatively modern enterprises, e.g., Kirov biochemical plant, produced both furfural from the pre-hydrolysates of wood chips or sawdust and the fodder yeast from the acid hydrolysates of residual lignocellulose. In contrast with that, smaller furfural- or xylitol-producing hydrolysis plants in Karelia, Siberia, White Russia, Ukraine and the former Soviet Central Asian republics have consumed mostly hemicellulose fraction of the renewable feedstock (hardwood or agricultural residues), whereas the residue, a so-called "cellolignin" constituting 60–65% of the initial raw material, was often not utilized at all. For example, acid-free production of furfural from tan waste by Rechitsa hydrolysis plant or Shumerlya chemical plant resulted in rapid accumulation of cellolignin dumps around these plants.

In 1950–1970s, dried softwood cellolignin was considered a promising feedstock for glucose production by low-temperature hydrolysis with small amounts of 75% H_2SO_4 (so called Rizhsky process tested in the end 1950s – beginning of 1960s) or an excess of partially recycled 41% HCl. The latter, an analog of Noguchi Institute and Udic-Rheinau processes, was developed by "VNII gidroliz" and has been operational for about 16 years (1958–1974) in the Kansk plant, producing annually about 600 t of crystalline glucose [1]. The residual lignins after low-temperature hydrolysis retained more native structure than highly condensed lignin after percolation hydrolysis with diluted H_2SO_4. They could be converted into some valuable chemicals by hydrogenolysis with higher yields and revealed good properties by molding. However, after closing of the demonstration plants in Japan and Germany, production of glucose from wood with concentrated acids was also stopped in the USSR. At low prices for wood and agricultural residues, cellolignin, the by-product of furfural plants, was no more considered a valuable feedstock, although, alike that of steam-exploded wood, its cellulosic fraction could be enzymatically converted into glucose with high yield after neutralization of the intrinsic acetic acid to pH 4, without substantial inhibition of cellulolytic enzymes with residual furfural or HMF.

Even if hydrolysis plants produced both furfural from hemicellulosic fraction and hexoses for subsequent fodder yeast manufacturing by a two-stage percolation hydrolysis of a feedstock, furfural as a “strategic” chemical was usually a priority product of the plants. It could be obtained more easily and quickly than fodder yeast. Because of that large biochemical plants, e.g., now abandoned Manturovo plant, could simultaneously deposit in their dumps both hydrolysis lignin and cellolignin. Although hydrolysis lignin and cellolignin substantially differ from each other in the content of polysaccharides (<20 or >50% respectively), the presence of sulfuric acid, particle size distribution, degree of lignin condensation, heat capacity, carbonization behavior, they were deposited together and were never precisely accounted. Therefore, speaking about lignin residues produced by the former Soviet hydrolysis industry we can not usually strictly define whether it was hydrolysis lignin or cellolignin. In this communication the applications of hydrolysis lignin rather than cellolignin will be mainly addressed. However, the potential reader should realize that as a secondary resource, the real lignin residues of Soviet hydrolysis plants may contain both lignin and cellolignin in different ratios. The content of lignin itself in (cello)lignin dumps may vary from 40 to 88%, resins and lignohumic substances constitute from 5 to 19% and ash contributes from 0.5 to 10% odm depending on storage conditions.

Characteristics of hydrolysis lignin

The amount of lignin residues, produced by the Soviet hydrolysis industry, increased from 0.5 to 1.5 mio. t/yr since 1960s till the end of 1980s [2, 3]. Although this lignin was always a minor fraction of total Soviet lignin production, which grew from ca. 4 to ca. 10 mio. t/yr in only 10 years since 1960s till 1970s, this was the most condensed and difficult for utilization lignin by-product. It contained substantially less functional groups (excluding -OCH_3) and can not be easily dissolved in alkali or polar solvents. In contrast with native lignins, it contained polynuclear aromatics, which formed benzenepolycarbonic acids by alkaline MnO_4^- oxidation [4, 5].

Lignin accumulated in the former Soviet Central Asian Republics was mostly of the cotton plant origin (cotton hulls, stalks, etc.). Hydrolysis lignin of South Russian and Ukrainian plants was mainly of agricultural origin, whereas that produced by White Russian, the North-European Russian, Ural, Siberian and Far Eastern plants originated from soft- and hardwood.

Current amounts of lignin wastes in the Ukraine and White Russia are estimated as 5 to 15 mio.t, whereas Russian Federation has accumulated an order of magnitude greater amounts of residual lignin. For example, lignin waste stocks in Irkutsk oblast, where Tulunsky, Biryusinsky, Ziminsky and Ust-Ilimsky hydrolysis plants are situated, are estimated as >20 mio. t.

Hydrolysis lignins of different producers may strongly differ from each other by the amount of residual reducing substances and nonhydrolyzed polysaccharides, methoxyls, ash, and acid content. Their composition depends on the type and granulometric composition of the feedstock, total amount and concentration of H_2SO_4 at the hydrolysis stage, solid/liquid ratio in the hydrolysis apparatus, its construction material, temperature and duration of hydrolysis.

Table 1. Yields and content of different hydrolysis lignins [1–5].

Feedstock	Yield (% odm)	Major Contaminants	% ODM
Softwood	38	Polysaccharides	15–30
Hardwood	32	Residual monosaccharides	2–10
Cotton hulls	37	Lignohumates (alkali-soluble)	5–15
Corncobs	24	Sulfuric acid	0.5–2
Sunflower seed hulls	32	Ash	2–10

Table 2. Average composition of softwood hydrolysis lignin (left) and ash of various lignins.

Components (softwood lignin)	% ODM	***Ash component***	CaO,%	1.5–32.8
Sulfuric acid	0.6–1.5		MgO,%	0.3–0.65
Reducing substances	1.5–3.0		Fe_2O_3,%	0–16.5
Nonhydrolysed polysaccharides	15–20		Al_2O_3,%	0–1.11
Ash	<3		SiO_2,%	49.5–93.4
OCH3-groups	10–11		P_2O_5,%	0–1.5
Phenolic OH-groups	<3		TiO_2,%	0–0.1
Resins (dichloroethane-soluble)	7–12		Na_2O+K_2O,%	0.33–0.6
			SO_2,%	0–7.95

Variations of ash composition are attributed to the presence of contaminants rather than the nature of utilized plant feedstock.

Organic acids in the hydrolysis lignin are represented mainly by formic and acetic acid. About one half (ca. 10%) of 20% tightly bound sugars (glucose) may be released by a treatment of hydrolysis lignin (moisture 68%, H_2SO_4 1.3%) at 300°C in an autoclave.

Granulometric composition of lignin is far from uniform because of simultaneous utilization of different ratios of wood chips and sawdust in the hydrolysis reactors. Size distribution of hydrolysis lignin particles may vary in a wide range from 1 mm to >1 cm. The so called commercial hydrolysis lignin for further industrial utilization should in principle contain moisture <65%, ash <4.5%, H_2SO_4 <1,5%. The bulk density of lignin with the moisture content <40% vary in the range 200–300 kg/m^3, whereas that of lignin containing 65% moisture is about 700 kg/m^3, 2/3 of which contributes acidic moisture. Angle of repose of the moist lignin falls within 40–43o. All this makes the transportation of hydrolysis lignin expensive. A commercial cellolignin should in principle contain moisture <52%, ash <2.5%, organic acids (accounted as acetic acid) <3.5%. However, these standards were usually controlled by further production of granulated lignin (particle size 20 mm for >90% granules, moisture <20%, ash<7%, bulk density >550 kg/m^3), which was used for crystalline Si and Al-Si alloys production, or lignin flour (moisture 10–20%, specific surface area 200–300 m^2/g), which was consumed as a filler in glues, plastics, or linoleum. The parameters of the major part of lignin or cellolignin, which was placed on local dumps within 10–20 km around the production facility were usually not controlled at all.

Hydrolysis lignin as a fuel

Although burning of produced lignin could cover >25% of the overall energy consumption by a hydrolysis plant, the use of unprocessed lignin as a fuel in the usual boilers was limited because of high (50–70%) moisture content and the presence of H_2SO_4. Average heat capacity of the hydrolysis lignin strongly depends on its moisture content, decreasing from 23–27 MJ for 1 kg of the oven dry matter to 20; 7.8; 6.2–6.9; or 5.7 MJ/kg of lignin containing 18–25; 60; 65; or 68% of moisture, respectively [2–4]. For the environmental reasons it was originally projected that the new hydrolysis yeast plants burn >50% of lignin in their boilers and yeasts dryers. However, only the demo Leningrad plant at "VNII gidroliz" burned ~70% of lignin in its boilers. The other plants burned much less lignin, because its moisture content should be initially reduced to <45% for a stable burning without black oil or natural gas co-firing. This increased the expenses, making lignin fuel non-competitive with the cheap Siberian opencast coal, particularly in the East of Russia.

Onezhsky, Kirishsky, Kedainiaisky, Bratsky and some other hydrolysis plants have used non-milled lignin of 60–65% moisture in the low-temperature vortex combustion boilers E-50-24K NTV or E-75-40K NTV equipped with black-oil torch. The boilers were designed by the chair of steam generators at the St. Petersburg Polytechnic University [6]. The largest one consumed 32 t/h of moist lignin and produced 65–75 t/h of steam at 440°C and the pressure of 4MPa with the energy conversion efficiency of 85–88%. It could also stably work without the use of black-oil torch. However, after closing of the hydrolysis plants these boilers do not burn lignin anymore. Attempts of the use of three large NTV furnaces at the Bratsky plant for combustion of non-milled bark and sawdust without the use of black oil failed and the wood residues are now incinerated in the fluidized-bed furnaces, whereas the old lignin boilers are not in use.

Swirling-type low-temperature furnaces for stable lignin burning without substantial feeding with black oil were designed by "Biyskenergomash" for relatively small-scale boilers. The larger boilers with the capacity from 30 to 100 MWt for lignin, peat, or sawdust incineration, e.g. boiler E-75-3,9-440DFT, are produced by Belgorodsky plant for boilers manufacturing (OAO ZKO) and utilize fluidized-bed combustion principle. Authors of [7] also propose a stabilized suspension of coal dust and moist hydrolysis lignin (1:1) as a liquid fuel. However, whether hydrolysis lignin is actually used within the country for incineration at the current internal prices for fossil fuel in Russia, is not clear.

In contrast with Russian Federation, White Russia strongly depends on exported fuel. This motivates local authorities for lignin utilization. Current annual production of hydrolysis lignin in White Russia is equivalent to ca. 25 000 TOE or about 4.4% of the total secondary energy resources produced in the country. Commercial hydrolysis lignin for energy production in the White Russia should contain moisture <60%, ash <23% odm, ^{137}Cs<18 Bq/kg at the elemental composition: 0.9% S, 20.14% C, 2.31% H, 0.05% N, 13.88% O. Heat capacity should be within 8.51–11.76 MJ/kg at the lowest value >6.2 MJ/kg.

Established in 1936, Bobruisky hydrolysis plant (White Russia) has placed ~2,5–3 mio. t of hydrolysis lignin in the dumps, depositing up to 150–230 t daily. Since 2004 Bobruisky plant produces fuel briquettes from lignin. The plant has acquired abandoned turf briquette manufacture "Redkij Rog" in the suburb Tugolitsa together with 8 ha land for lignin deposition. In the summer time the specialists of plant prepare lignin of 40% moisture content by a standard turf drying and storage technology for the whole-year briquette production. To avoid undesirable effects of H_2SO_4, freshly obtained lignin is neutralized directly in the hydrolysis apparatus before its unloading. In 2005–2006 the state power generation company "Mogilevenergo" has ordered a project of a special boiler for lignin incineration in the Bobruisk heat power station TEC-1. According to the project prepared by BelNIItopproject, 17 ha of the local 34-ha lignin dump were adapted for lignin processing. The plant together with the national Ministry of natural resources has invested $3.2 mio. in the necessary machines used in peatery and garbage separation. The other $15 mio. were invested by the local power station and the Ministry in the equipment, including boiler E-30-3,9-440DF of the Beloozersky energomechanical plant for lignin incineration. The boiler produces 30–35 t/h of steam at a pressure of 3.9 MPa, consuming 14 t/h of lignin (moisture 55–60%) with the energy conversion efficiency of 87–88%. In 2009, 68 000 t of lignin were consumed by this boiler of TEC-1, whereas the other 40 000 t were used in the briquette production for household. Heat and electricity produced by this boiler were twice as cheap as those from Russian natural gas. However, the existing lignin dump in Titovka (7 km from Bobruisk) can continuously supply the cheap fuel (<20 $/t) for the whole exploitation period (30 years) of only one lignin-fueled boiler, therefore no more such boilers will be installed.

Unfortunately, this successful project seems to be unique. Indeed, deposited in Kazazaevka (Gomel oblast, White Russia) (cello)lignin residues from Rechitsky furfural semi-industrial plant are no more used as a local fuel source since the plant bankruptcy, although the plant was equipped with a special lignin-combustion for-chamber DE 24/25 with a capacity of 10 MWt (Axis Industries, Lithuania). A modern fully automated mini-heat power station of Rechitsa consumes only peat and sawdust but not lignin.

In 1980s, four Soviet plants have produced ~17 000 t/yr of lignin briquettes as a domestic fuel or reductant for ferroalloys, using press-machines BPD-2 at a productivity of 0.5–2 t/h [3, 8]. At present >20 manufacturers, mostly from Ukrainian regions Zaporozhye (Teplosintez, PeKo and 5 others), Kharkov (Alfa Tech, Svet Shakhtera), Lvov (Ecotec), Donetsk (Fart PR, Energeticheskiy briquette), Novaya Kakhovka, Lugansk (Grandlug), Vinnitsa (Kamiral); as well as at least 6 from Russian regions Sverdlovsk (Uak Chistaya energiya), Vladimir (Triks), Yaroslavl (Yarinterles), Kropotkin Krasnodar krai, Elabuga Perm krai, Gulkevichi Krasnodar krai (Girei plant); and one from White Russia (Bobruysk plant, Mogilev oblast) produce and sell lignin briquettes or pellets (Table 3).

Table 3. Manufacturers of hydrolysis lignin pellets and briquettes.

manufacturer	t/month	$/t	MJ/kg	Ash, %	H_2O,%	S,%
Gulkevichi, Krasnodar krai	1 000, briquettes		18	19	6	0.4
Bobruysk plant Mogilev oblast	1 200, briquettes >25 mm	50–60	>13 (13.6)	<20 (11.8)	<22 (15.7)	0.4
Teplosintez Zaporozhye	>500, briquettes		24.7	20	8.7	0.45
Zaporozhye	2 500, briquettes 30 x 70 mm	120	22–23	10–15	10–12	
Zaporozhye	1 000–5000 briquettes TBR-1		19	<15	<10	<0.56
Zaporozhye	pellets		18.9–25.6	20	20	0.6
Zaporozhye	300–500, pellets 6–8 mm	75–80 FCA	24.2	6.1	4.9	0.69

Some enterprises also offer unprocessed hydrolysis lignin/cellolignin as a fuel for local heat power stations and for export into Poland. Ukrainian businessmen from Zaporozhye offer 1 500–20 000 t/month for 30 €/t FCA or 60 €/t DAF (Izov – Khrubeshov). Linas Agro Group (Lithuania) planned to supply ~50 000 t of lignin (standard EN 14961-1:2010) from the former Kedainiai hydrolysis yeast plant for €2.1 mio. in 2010. Local authorities (Rechitsky Raizhilkomkhoz) in Gomel oblast offer a tender for 50–225 thousand t of a lignin-cellolignin mixture (moisture <70%, ash <10%, H_2SO_4<1.5%) from the abandoned Rechitsa furfural plant on the condition of an establishment of a lignin-processing enterprise, creation of at least 5 new jobs, investment of $200–500 thousand at place, and providing a fire-protecting measures for the rest of lignin dump. Starting price is defined as 3.4 €/t of moist lignin-cellolignin mixture.

Lignin as a fertilizer and absorbent

Lignin has obvious advantages over petroleum products in at least two features: as an absorbent and a potential source of humus. Swollen hydrolysis lignin has highly developed internal surface area (760–790 m^2/g), although after drying it decreases almost 100 times. Large internal surface area has stimulated utilization of the insoluble residue of hydrolysis lignin after alkaline extraction as oil-collecting absorbent [9] or as a matrix for preparation of ion-exchange absorbents of heavy, noble or rare metals. Charcoal from hydrolysis lignin has also found various applications as the absorbent (Table 4).

Numerous studies have been devoted to the utilization of lignin as a component of fertilizers, potential source of humus, and soil-structuring agent. Hydrolysis lignin is also a good carrier, stimulating prolonged sustainable release of inorganic nutrients or plant growth hormones [3–5]. A lignin-stimulating fertilizer (LSU) was produced and used as growth stimulator of various agricultural cultures in Uzbekistan (Table 4). However, hydrolysis lignin should be neutralized for agricultural applications. For example, complex organic-mineral fertilizer for sandy or clay soils (90% of hydrolysis lignin, NH_4NO_3, superphosphate, KCl) contains 5% of lime [10, 11]. Residual H_2SO_4 can also be neutralized with phosphorite flour $Ca_3(PO_4)_2$ which forms gypsum and Precipitate ($CaHPO_4$) fertilizer. In Sverdlovskaya oblast three hydrolysis plants (Lobva, Ivdel, Tavda) have placed a lot of lignin in the dumps. At present, an absorbent-fertilizer Agrimus C (probably an analog of Agrimus fertilizer manufactured by Agrifuran in France from a cellolignin-like residue) is produced from lignin (ca. 800 t in 2009) in this region.

Hydrolysis lignin in chemistry and other areas

The most important drawbacks of lignin as a feedstock for chemistry remained relatively low yields of the desired products and competition with petrochemistry. Following lignin hydrogenolysis studies of Noguchi Institute in 1940–1960s, which has succeeded in obtaining ~50% of monophenolic (o- and p-cresols, ethyl- and propylphenols) from HCl-lignin alike that produced by Kansk hydrolysis plant, similar studies were performed in the USSR. The main objective was an attempt of o-, m- and p-cresols preparation, which were not supplied by Soviet petrochemistry. Some attempts of hydrogenolysis of residual lignin after high-temperature hydrolysis of wood or agricultural residues with diluted H_2SO_4 were made in Tashkent Institute of Cellulose Chemistry and Technology, but cheap and efficient hydrogenolysis catalyst that could provide high yields of cresols was not found. Hydrolysis lignin of cotton hulls was used for thermal production of cresols with the total yield up to 5%, including >3% of m-cresol, whereas lignin of sunflower husks produced 4.5 and 2.5% respectively. Contrary to that, lignin of corncobs produced almost exclusively o- and p-cresols (total yield 3.2%). Total yield of raw phenolic fractions from agricultural hydrolysis lignin reached 12%. The other chemicals obtained from hydrolysis lignin with low yields were DMS, DMSO (<10%) and pyromellitic dianhydride PMDA (<5%).

Novel exciting results of biomass into diesel conversion by thermo-catalytic low temperature hydrogenation in liquid medium (KDV) have also inspired Siberian specialists in developing new routes of hydrolysis lignin hydrogenation. Liquefaction and gasification of 70–96% of hydrolysis lignin by Pt- or Pd-catalysts-driven hydrogenolysis was shown to proceed in supercritical MeOH, EtOH, or n-BuOH, resulting in demethoxylation and de-oxygenation of lignin. As the final products, “ligno-oil” of an empirical formula $C_{10\text{-}14}H_{13\text{-}20}O$ containing three times less oxygen than lignin, as well as gaseous C_1-C_4 hydrocarbons and CO_2 were obtained. Final solid residue consisted of a reduced catalyst, ash (70–86%), which, according to the new KDV technology can also be used as a hydrogenation catalyst, and a product containing 11–21% C; 1.5–2.3% H and 0.4–1.0% S [12]. Another interesting approach was a co-pyrolysis-hydrogenation of hydrolysis lignin with molten polyethylene or polypropylene wastes. Hydrogen-rich (>14% H) cracking fragments of polyolefines saturate lignin structures making them more reactive. Hydrogenation of liquid products of co-pyrolysis results in the enrichment of liquid fractions (b.p. 180–350°C) with aliphatic rather than aromatic, heterocyclic compounds or cycloalkanes [13, 14].

Lignin has long been considered promising for the application in the building industry [15–19]. Broceni cemex (Latvia) and Vorovsky cement plant (Leningrad oblast) used 0.3–0.4% lignin in cement mill, which increased the productivity of milling up to 20% [3–5]. Utilization of 22 000 t/yr of unprocessed (cello)lignin (15–30% of its production by a hydrolysis plant), as a burning clay filler by ceramic bricks production would be sufficient for a production of 50 mio. bricks/yr [20]. This was tested by Leningrad bricks plant, which utilized 9–12% moist lignin in clay for production of bricks.

Recently, based on thermoplastic properties of hydrolysis lignin, a new waterproof lignoplastic was obtained from lignin flour and 20–40% of polyethylene [21]. This can be an interesting alternative to “liquid wood” polymeric composition Arboform proposed in FRG.

Table 4. Industrial hydrolysis lignin applications tested in the USSR and CIS [1–5, 22–32].

Plant location	**Product**	**Technology**	**Yield,%**	**Scale, t/yr**	**Applications**
Andijan 1985 Krasnodar	Nitrolignin Igetan Sunil Lioxid Chlorolignin	8–50% HNO_3 Nitrolignin saponification Nitrolignin sulforeduction H_2O_2-oxidation Chlorine water	95–98 97–98	15 000 3 000 products	Surfactants, clay liquefiers by oil wells drilling Tannin substitutes Ore flotation, rare metal precipitant
Andijan 1985 Krasnodar, Fergana1968	Collactivite (charcoal absorbent)	20%-oleum treatment (carbonization)	70	5 000 prod. 1 500 1 500	Discoloration of xylitol solutions
Nikolaev Zaporozhye 2005	Lignin rust remover PRL-2	Mixing with H_3PO_4 vegetable oil, fat, ethyl silicate, etc.	80–90	<1 000 product	Protection from corrosion without cleaning
Krasnoyarsk 1972	Granulated coal	Pyrolysis	35–40 coal, 10–20 settled tar, 15–20 fuel gas	plan12 670 product 117 000 lignin use	CS_2 production (coal), fuel
Krasnoyarsk 1972	Alkali-soluble lignin	Alkaline cooking, 200°C, 40% alkali	70–80	plan10 000 product	Filler by rubber vulcanization (soot substitute)
Biryusinsk 2010	Granulated charcoal	pyrolysis		10 000 product	Absorbent
Khakasiya 1968	pitch oil, coke	Fluidized bed pyrolysis	12 pitch oil, 30 coke, fuel gas	plan25 300 dry lignin use	Herbicide (pitch oil), fuel
Manutrovo St. Petersburg 2005	Polyphepan entero-absorbent	Removal of mild alkali-soluble fraction	70–80	300 60	Medicine, veterinary
Andijan1972 Chimkent 1972	quinone-nitropolycarbonic acids	diluted HNO_3, 6h, 100^oC, neutralized with NH_4OH	30 product, 7–10 oxalate	300, with lignin 1:10 plan50 000	Lignin-stimulating fertilizer, plant growth hormone
St. Petersburg 1972	lignophenolformaldehyde resin	Condensation of phenollignin and formaldehyde		pilot	Press-powders
Fergana 1972	Ligno-fiberboard	$1.9 m^3$ wood chips + 1 t moist lignin	1 t (330 m^2) fiberboard	plan20000 product	Building material heat-insulator
Andijan 1972	formic, acetic, succinic, malic, glycolic acid	air oxidation in alkali or ammonia	25–35 org. acids, 25 ammonia lignin	?	Yeast biomass 0.1 t/t lignin, fertilizer (20%N) 0.25 t/t lignin

Environmental issues and conservation of lignin dumps

The abandoned Ziminsky hydrolysis plant (Irkutsk oblast) has placed >11 mio t of hydrolysis lignin in a 25-ha dump currently under management of the local authorities. In 2003 local division of the Russian Ministry of Emergency Situations has extinguished with water the smoldering lignin till the depth of 2 m on 13.3 ha with 18 firefighting cars and 305 firefighters for 1.5 months. However in a short time the extinguished fires appeared again, since the lignin layer depth exceeds 15–18 m.

In 2005–2006 the Limnology Institute (Irkutsk) has tested for the recultivation of Ziminsky lignin dump its conservation technology [33], which was earlier successfully used for the preservation of the lignin dumps at Selenginsky cellulose and cardboard plant on Baykal. For this purpose, 10 000 t of the fly ash from the abandoned coal heat station TEC-3 in Zima were spread on 1 ha of the lignin dump till its depth from 30 cm to 1–1.5 m (on the smoldering areas). This has protected the recultivated area from further smoldering fires. Local authorities together with the A/S Irkutskenergo (owner of the abandoned coal station) have planned to cover all the dump area with 262 000 t of the fly ash stored on the coal station and invest about 1 mio. USD in the gardening of the dump area, where later a golf course or tennis courts can be arranged. The local authorities believe, when a time will come, the upper 1.5-m layer of the dump can still be utilized for the production of porous bricks or cement, or by building of roads, whereas the major thick bottom layer will be used as a new source of peat.

In June-October 2010, following personal request of Vladimir Putin, a similar technology was also used to extinguish the smoldering lignin of the Kansk hydrolysis plant (Krasnoyarsk krai) near the Trans-Siberian Highway, route M-53: Krasnoyarsk-Irkutsk. The local dump containing 3 mio. t of hydrolysis lignin on 23 ha was covered with a 30-cm layer of a 2:1 mixture from clay (200 000 t) and the fly ash (100 000 t) of the Kansk coal power station. To provide gardening, the dung from local chicken farm was then additionally spread on the surface. Total investment exceeded $1.5 mio. [http://www.allrussia.ru/new/100720132130.html].

An alternative solution of lignin dump problem was proposed by the management of Kirov biochemical plant located in the North-East of European Russia. This plant remains the only hydrolysis enterprise still producing on a relatively regular basis ethanol and dried fodder yeast (ca. 10 000 t in 2010) from wood residues in Russia. In its almost 40-years history this largest plant has utilized ca. 100 mio m^3 of solid wood residues. Its currently available capacities can consume up to 2 mio. m^3/yr of solid wood (sawdust and non-utilized wood). In the recent years the plant also produces fuel pellets from sawdust using corresponding equipment of the German company Münch-Edelstahl GmbH, whereas hydrolysis lignin is not utilized. The lignin dump near the plant occupies by various evaluations from 30 to 60 ha, where about 50 mio. t of hydrolysis lignin and cellolignin were placed in the last 39 years. Soon after its opening, the plant has built a water pumping station with a 800 mm pipeline to pump 150–400 m^3/h of water from Vyatka river to the lignin dump. However, in 2000s the pump failed, and the lignin smoldering has become a nightmare for the population of the city. In 2010 water supply was recovered and the smoldering lignin was converted into a marsh. The expenses exceeded 0.4 mio. USD in 2010, total water consumption in the recent few years reached 0.6 mio. t. However, utilization of the fly ash from the local heat power station was not planned by the governments of Kirov city and oblast responsible for the lignin dump. Currently hundreds of seagulls occupy in summer the marsh surface. Hopefully, their dung will also convert with time this acidic marsh into a fertile soil.

Conclusion

In the long history of Soviet hydrolysis industry many different applications of hydrolysis lignin were proposed and successfully tested on the large- (lignin as a fuel, absorbent, fertilizer, filler) and small-scale industrial applications (oxidized alkaline extract of hydrolysis lignin as an immunostimulator of a broad spectrum [34, 35]). However, lignin after biomass hydrolysis with diluted H_2SO_4 is apparently the worse type of lignin for further utilization compared to other industrial lignins. Utilization of hydrolysis lignin requires in every case a specially equipped facility and substantial capital investments at the production or storage place. Unfortunately, in all applications, lignin is not a unique and currently not the cheapest feedstock compared to biomass or fossil resources. Therefore, **if we are not sure that we can utilize or prepare lignin for further utilization immediately at place, should not we better let it be conserved in any environmentally friendly form as a stock of sequestered CO_2 for the next generations as a future resource of fossil fuel or fertile soil?**

References

1. Slavyansky, A.K., Sharkov, V.I., Liverovsky, A.A., Buevskoy, A.V., Mednikov, F.A., Lyamin, V.A., Solodky, F.T., Tsatska, E.M., Dmitrieva, O.A., Nikandrov, B.F. 1962. Wood chemistry technology. Moscow, Goslesbumizdat. 576 p. (In Russian.)

2. Wood chemistry: Lignin and its utilization. 1968. Proc. All-Union Conference, October 1966, Riga. Zinatne. 400 p. (In Russian.)

3. Khol’kin, Y.T. 1989. Technology of the hydrolysis industry. Moscow, Lesnaya Promyshlennost’. 496 p. (In Russian.)

4. Chudakov, M.I. 1983. Industrial lignin utilization. Moscow, Lesnaya Promyshlennost’. 200 p. (In Russian.)

5. Simonova, V.V., Shendrik, T.G., Kuznetsov, B.N. 2010. Methods of industrial lignins utilization. J. Siberian Fed. Univ. Chem. Ser. 4(3), pp. 340–354.

6. Pat. RU2109216. 1998. Process of burning of hydrolyzed lignin in boiler furnace.

7. Pat. RU2183658. 2002. Liquid fuel composition and method of preparation thereof.

8. Pat. RU2132361. 1999. Method of briquetting of hydrolysis lignin.

9. Pat. Appl. RU2004131076. 2006. Sorbent for collecting oil and oil products, method for producing sorbent and method for collecting oil and oil products.

10. Pat. RU2209196. 2003. Hydrolysis lignin-based organomineral fertilizer.

11. Romanchuk, N.I. 2008. Effect of organic-mineral fertilizer based on hydrolysis lignin on the fertility of turf-podsolic soil and productivity of the main agrocenoses in the middle taiga. Ph.D. Diss. Syktyvkar.

12. Pat. RU2409539. 2011. Method of converting lignin to liquid and gaseous hydrocarbons and derivatives thereof.

13. Sharypov, V.I., Beregovtsova, N.G., Kuznetsov, B.N., Baryshnikov, S.V., Cebolla, V.L., Weber, J.V., Collura, S., Finqueneisel, G., Zimny, T.J. 2006. Co-pyrolysis of wood biomass and synthetic polymers mixtures: Part IV: Catalytic pyrolysis of pine wood and polyolefinic polymers mixtures in hydrogen atmosphere. J. Anal. Appl. Pyrol. 76, pp. 265–270.

14. Sharypov, V.I., Beregovtsova, N.G., Kuznetsov, B.N. 2010. Investigation of the composition of liquid products of thermal lignin conversion. J. Siberian Fed. Univ. Chem. ser. 4(1), pp. 36–44.

15. Pat. RU2342339. 2008. Complex additive for concrete mixes and water mortars.

16. Pat. RU2272009. 2005. Raw mix for manufacturing heat-insulation articles.

17. Pat. SU981323. 1982. Process for producing molding composition from hydrolysis lignin.

18. Pat. RU2280057. 2006. Composition for the light concretes gluing and the method for the composition production.

19. Pat. RU2132769. 1999. Method of preparing molding material for manufacturing facing layer of chipboards.

20. Pat. RU2229454. 2004. Raw meal for fabricating ceramic brick.

21. Kapustina, I.B., Yakimtsov, V.P., Kazazyan, V.I. 2003. Application of hydrolysis lignin in the production of composite materials. Chemistry for sustainable development 11(3), pp. 489–492.

22. Pat. SU610854. 1978. Method of reprocessing hydrolysis lignin.

23. Pat. SU706120. 1979. Apparatus for flushing collactivite.

24. Pat. SU1010066. 1983. Process for producing nitrogen-containing derivative of hydrolysis lignin.

25. Pat. SU907003. 1982. Method for preparing nitrogen- and sulphur-containing lignin derivatives.

26. Pat. SU994548. 1983. Process for producing coal from hydrolysis lignin.

27. Pat. SU1578147. 1990. Method of processing hydrolysis lignin.

28. Pat. SU1663009. 1991. Method of producing carbon from hydrolysis lignin.

29. Pat. RU2130895. 1999. Method for producing granulated activated carbon.

30. Pat. RU2205166. 2003. Drilling solution.

31. Pat. RU2291173. 2007. Corrosion modifying agent.

32. Pat. RU2302866. 2007. Enterosorbent and method for its preparing.

33. Pat. RU2350369. 2009. Technique for disposal site and peatland fire suppression and prevention.

34. Pat. RU2141334. 1999. Method of preparing agent “Olipifat” for treatment of patients with nononcological pathology in body.

35. Pat. RU2217463. 2003. Method for preparing huminic acid salts.

The Lignoworks Strategic Network – a Canadian approach to value-added lignin products

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Abstract

The Lignoworks Strategic Network is a five-year project whose mandate is to develop technology platforms for conversion of forest-derived lignin to value-added chemicals and materials. Funding is primarily from Canada's Natural Sciences and Engineering Research Council with additional cash and in-kind resources provided by the four industrial partners: FPInnovations, Alberta-Pacific, Lignol and Weyerhaeuser. A Lignin Users' Forum provides an additional opportunity for potential downstream users to interact with Network Investigators and Industrial Partners.

As befits a university-based network, the focus is on high value, second- and subsequent generation products. Projects in thermal and catalytic processing seek to disassemble lignin into platform chemicals that are suitably functionalized for reassembly into novel and useful polymers and lignin-based materials. Interesting developments in the first half of the Network's life include electromagnetic carbon nanofibres, potential incorporation of lignin-based aldehydes into organic semiconductors, pyrolysis of kraft lignin in bubbling fluidized beds, purification of pyrolysis oils using green, switchable solvents and the discovery of lignin-degrading bacteria.

Introduction

In the coming months and years significant new volumes of lignin will become available in North America, either as a by-product from production of cellulose-based fuels or by precipitation from the black liquor of kraft pulp mills. Many biorefinery schemes propose that this lignin should displace fossil fuels to provide heat and power for the rest of the biorefinery operation or kraft mill. In the current North American context of historically low natural gas prices and low or non-existent carbon taxes, such schemes do not generally have a compelling business case. To create a robust and diverse lignin industry, a suite of value-added, lignin-derived products must be developed.

While the use of lignin in phenol-formaldehyde resins is expected to be an important market, commercial development of this technology has been underway for some time. Thus, as a university-based network, Lignoworks is concentrating on the high-value second and subsequent generations of lignin-based products.

After a brief description of the structure of forest industry research in Canada, this paper will describe the mandate of the Lignoworks Network and present a few highlights that have emerged at the halfway point of its existence.

National Forest Sector Innovation System

Since 2005, the major stakeholders in Canadian forest research – individual companies, industry associations, federal and provincial governments, FPInnovations and university researchers – have worked to develop what has become known as the National Forest Sector Innovation System. The objective of the system is to improve communication and comprehension of the industry's most critical needs, to ensure that limited research resources are aligned with these needs, to avoid unnecessary duplication of effort and to ensure that the most effective solutions are moved rapidly from the lab bench through pilot plant and demonstration scale testing and finally to commercialization.

Strategic Research Networks

The primary funder of university science and engineering research in Canada is the Natural Sciences and Engineering Research Council of Canada (NSERC). NSERC's Research Partnerships Program provides a variety of initiatives for industrial research, ranging from short projects of a few months duration to complex Research Networks.

The Strategic Networks Program is targeted at industrial problems whose scope and complexity requires collaboration across a number of science and engineering disciplines. It is thus an ideal tool to implement an important component of the National Forest Sector Innovation System – the creation of university networks to fill strategic gaps, address unique opportunities and complement existing research programs.

Strategic Networks are funded by NSERC at a level of $1M/year for five years. A critical requirement for a successful Strategic Network is the engagement of industrial partners, who provide additional cash and in-kind resources. Equally important, their participation validates that the proposed problem is in fact an important one. The industrial partners participate actively through Network meetings and, where appropriate, direct collaboration in individual projects. They also provide important feedback on the viability of proposed solutions and the industrial potential of results that may not be immediately obvious to academic researchers.

Information communicated at Network meetings is confidential to the partners until such time as it appears in peer-reviewed journals. Ownership of arising intellectual property is handled according the policies of each individual university; the industrial partners have a right of first refusal to negotiate a license to any intellectual property that arises from Network-funded research.

FIBRE – Forest Innovation by Research and Education

There are currently seven NSERC Strategic Networks that serve the complete forest sector value chain – from silviculture and harvesting through lumber, engineered wood products and building systems, biomaterials and biomass-derived chemicals and fuels. These Networks include over 100 principal investigators, 400 graduate students and post-doctoral fellows and most of Canada's major research universities.

FIBRE – Forest Innovation by Research and Education – is an association of the Scientific Directors of these seven Networks, who meet regularly to search for opportunities to leverage resources across the Networks and to speak with a single voice to other stakeholders in the National Forest Sector Innovation System. FIBRE also includes ArboraNano, who is playing an important role in developing nanotechnology in the forest sector, with a particular focus on nanocrystalline cellulose. ArboraNano's structure and mandate differs from the Strategic Networks, but it shares the broad goal of developing new products form forest resources.

Lignoworks

The Lignoworks Strategic Network was established in January, 2010, with a mandate to create technology platforms for novel materials and chemicals from forest-based lignin to replace fossil-fuel based chemicals and products.

Currently, Lignoworks includes fifteen principal investigators, sixteen graduate students and twelve post-doctoral fellows located in nine Canadian Universities. We are particularly proud of having attracted many distinguished researchers in diverse fields – catalysis, microbiology, polymer chemistry, materials science, pyrolysis and green chemistry – to bring a fresh perspective to the problem of converting lignin to value-added materials. Three of our Network Investigators, Professor Franco Berruti, Professor Philip Jessop and Professor Tom Baker are recent recipients of the Chemical Institute of Canada's Green Chemistry Awards.

Lignoworks industrial partners are Alberta-Pacific, FPInnovations, Lignol and Weyerhaeuser. Additional industrial partners are still welcome, particularly those interested in manufacturing lignin products. An additional way to interact is through a Lignin User's Forum, whereby companies interested in using lignin as a feedstock can receive regular updates of Lignoworks publicly-available research and interact with Network Investigators and Industrial Partners to communicate the performance requirements of products of interest.

Structure and Organization

The sixteen projects within the Lignoworks Network are organized into three discipline-based themes, Polymeric Products, Thermochemical Processing and Catalytic Processing, each lead by a theme leader. A list of the projects, themes and theme leaders is shown in Table 1.

Each project is also classed according to its contribution to the Network's two technology platforms: Functionalized Aromatics and Lignin-based Materials. Most projects in the Thermochemical and Catalytic Themes will produce Functionalized Aromatics, i.e., low molecular mass platform chemicals, which can then be assembled into Polymeric Products. In some cases, of course, catalytic or thermal processes may retain lignin's polymeric nature and may produce a polymeric product or lignin-based material directly.

Major Infrastructure

Several Lignoworks investigators belong to specialized research units in their respective universities and bring to the Network access to these facilities.

Three participants in the Thermochemical theme are members of the Institute for Chemicals and Fuels from Alternative Resources (ICFAR, www.icfar.ca) at Western University in London, Ontario. ICFAR focuses on pyrolysis and hydrothermal processing of biomass and the best use of the resulting bio-oil, biochar and biogas. This 1 900 m^2 facility consolidates lab and office space for faculty, staff and students, an array of analytical equipment and high-bay pilot plant space. All this will allow promising pyrolysis and hydrothermal technologies to move quickly from the lab to pilot and large-scale commercial testing.

Professor Tom Baker leads the Lignoworks Catalytic Processing theme and is also the Director of the University of Ottawa's Centre for Catalysis Research and Innovation (www.catalysis.uottawa.ca). The Centre has state-of-the-art facilities for automated high-throughput catalyst screening, including analysis of reaction products. For problems that are less amenable to direct experiment, the Centre also has the latest tools for computational chemistry. Finally, heterogeneous catalysts can be characterized with a complete array of analytical equipment: transmission and scanning field-effect electron microscopes, X-ray photoelectron spectroscopy, single-crystal X-ray diffraction, thermal analysis, surface area and porosity and electrochemical analysis.

Table 1. Lignoworks Themes and Projects.

Polymeric Products, John Kadla (University of British Columbia), lead	
Mesophase materials from lignin for high performance carbon fibres	John Kadla, UBC
Lignin-based carbon nanofibres produced by electrospinning	Frank Ko /John Kadla, UBC
Lignin-based carbon aerogels and nanostructures	John Kadla/Frank Ko, UBC
Renewable green composites	Amar Mohanty, Guelph
Novel peptidic and conducting polymers	Bruce Arndtsen, McGill
Thermochemical Processing, Cedric Briens (Western University), lead	
Fluidized bed pyrolysis of lignin for the production of aromatics	Franco Berruti/Cedric Briens, Western
Conversion of lignins to aromatics	Charles Xu, Western
Microwave pyrolysis of lignin for the production of aromatics	Jamal Chauouki, Ecole Polytechnique
Extraction of aromatics from lignin pyrolysis oils	Franco Berruti/Cedric Briens, Western
Using switchable solvents to extract aromatics	Philip Jessop, Queen's
Catalytic Processing, Tom Baker (University of Ottawa), lead	
Lignin oxidation using air and base metal catalysts	Tom Baker, Ottawa
Ruthenium complex-catalyzed lignin conversion	Brian James, UBC
Catalytic upgrading of lignins to value-added chemicals	Gregory Patience, Ecole Polytechnique
Bacterial transformation of lignin	Lindsay Eltis, UBC
Catalytic lignin depolymerization in ionic liquids	Robert Singer, Saint Marys
Catalysts for the functionalization of monolignols	Doug Stephan, Toronto

Research Highlights

The remainder of this paper will give a brief overview of the objectives of each of the three research themes and a few highlighted results.

Theme 1: Polymeric Products

Theme 1 is lead by John Kadla, Professor of Wood Science at the University of British Columbia and the Network's Scientific Director. Projects in this theme are attempting to convert lignins via electrospinning into carbon fibres and nanofibrous porous structures, to create thermoplastic/kraft lignin blends and to use functionalized aromatics to create novel polymers.

Professor Kadla and Professor Frank Ko (also of UBC) have used electrospinning to create electromagnetic carbon nanofibre mats. Unlike strength reinforcement applications, where lignin-based carbon fibre has significantly inferior properties compared to polyacrylonitrile (PAN)-based fibres, electrospun, lignin-based carbon fibres had comparable electromagnetic properties (conductivity, saturation magnetization, remanence, coercivity) to PAN-based fibre. Potential applications for such lignin-based materials are for electromagnetic shielding for the microprocessor-based devices that are ubiquitous in modern life.

Professor Bruce Arndtsen and post-doctoral fellow David Leitch have developed a one-pot synthesis for poly-Münchnone conducting organic polymers [1]. These are constructed from carbon monoxide, acyl chlorides and imines; the latter two can be derived from lignin-based aldehydes, carboxylic acids or alcohols. The band gap of such organic semiconductors can be tuned over a wide range, by varying the substituents on each monomer. However, synthetic procedures used to date involved laborious multi-step syntheses. The one-pot procedure provides a rapid way to screen a large variety of candidates and may also provide an avenue for the use of lignin derivatives in organic electronics, a market estimated to be worth almost $33 billion by 2017 [2].

Theme 2: Thermochemical Processing

Theme 2 is lead by Cedric Briens, Professor of Chemical Engineering at Western University. The two main thrusts in this theme are: 1) thermal breakdown of lignin to platform chemicals by fluidized bed pyrolysis, microwave assisted pyrolysis and hydrothermal deoxygenation, 2) extraction and separation of value-added chemicals from the resulting bio-oil. A notable achievement in the theme has been the first successful pyrolysis of unmodified kraft lignin in a bubbling fluidized bed.

To purify bio-oils, Professor Jessop is adapting switchable-solvent technology originally developed to extract soy oil [3, 4]. The essence of the technique is that a hydrophobic amine solvent such as dimethylcyclohexyl amine can be made hydrophilic by passing CO_2 through it to generate the corresponding amine bicarbonate salt. The crude soybean oil is extracted into the hydrophobic form of the solvent. Water and CO_2 are added, causing the amine to "switch" to its hydrophilic form and separation of the phases. After separation of the purified oil, CO_2 is removed from the aqueous layer to regenerate the hydrophobic solvent and water, which can be recycled.

Theme 3: Catalytic Processing

Theme 3 is lead by Tom Baker, Professor of Chemistry at the University of Ottawa. Projects in this theme cover the gamut of catalysis science: enzymatic lignin degradation, homogeneous oxidation and reduction catalysts, heterogeneous catalytic cracking, catalytic reactions in ionic liquids and catalytic conversion of monolignols to value-added chemicals.

Professor Lindsay Eltis is working on development of *Rhodococcus jostii* RHA1*,* a lignin-degrading bacteria [5, 6]. While there has been much research on fungal degradation of lignin over the past three decades, few commercial applications have appeared, partly because fungi are often difficult to work with on an industrial scale. Bacteria such as *Rhodococcus*, on the other hand, are easily scaled to industrial fermentation. The significance of Professor Eltis' findings to the development of bio-based chemicals and fuels has been recognized by the journal *Science* [7]. The project within Lignoworks is complemented by additional funding for the metagenomic aspects of the work from a Genome Canada Large-Scale Applied Research Project.

Summary

Lignoworks, a NSERC Strategic Network comprised of fifteen professors in nine Canadian universities and four industrial partners, was established in 2010 to develop a platform of technologies to turn convert lignin into value-added materials. The long-term objective is to diversify the traditional revenue streams of the forest industry by providing biobased feedstocks for industrial materials for the plastics, automobile and construction sectors.

Lignoworks is concentrating on the second and subsequent generations of lignin-based products. Unique resources available to Network Partners include pilot-scale pyrolysis apparatus at Western University's Institute for Chemicals and Fuels from Alternative Resources (ICFAR) and state-of-the-art facilities for catalyst development and characterization at the University of Ottawa's Centre for Catalysis Research and Innovation.

Early technical successes include electromagnetic lignin-based carbon nanofibres with properties comparable to PAN-based fibre, potential incorporation of lignin-based monomers in organic semiconductors, the first successful pyrolysis of unmodified kraft lignin in a bubbling fluidized bed, purification of pyrolysis oils using green, switchable solvents and the discovery of lignin-degrading bacteria.

We look forward to many more scientifically and commercially interesting developments during the Network's latter phase. Readers interested in becoming Industrial Partners or participating in the Lignin Users' Forum can contact either of the authors through the Network's web site: www.lignoworks.ca.

References

1. Siamaki, A.R., Sakalauskas, M., Arndtsen, B.A. 2011. A Palladium-Catalyzed Multicomponent Coupling Approach to π-Conjugated Oligomers: Assembling Imidazole-Based Materials from Imines and Acyl Chlorides. Angew. Chem. Int. Ed. 50, p. 6552.

2. Global Electronics Market to Reach US$32.8 Billion by 2017 30-8-2012 http://www.prweb.com/releases/organic_electronics/OLED_displays/prweb8953929.htm.

3. Jessop, P., Phan, L., Carrier, A., Robinson, S., Dürr, C., Harjani, J.R. 2010. A solvent having switchable hydrophilicity. Green Chem. 12, p. 809.

4. Jessop, P., Kozyca, L., Rahami, Z.G., Schoenmakers, D., Boyd, A.R., Wechsler, D., Holland, A.M. 2011. Tertiary amine solvents having switchable hydrophilicity. Green Chem. 13, p. 619.

5. Ahmad, M., Roberts, J.N., Hardiman, E.M., Singh, R., Eltis, L.D., Bugg, T.D.H. 2011. Identification of DypB from *Rhodococcus jostii* RHA1 as a lignin peroxidase. Biochem. 50, p. 5096.

6. Roberts, J.N., Singh, R., Grigg, J.C., Murphy, M.E.P., Bugg, T.D.H., Eltis, L.D. 2011. Characterization of DyP peroxidases from *Rhodococcus jostii* RHA1. Biochem. 50, p. 5108.

7. Chong, L.D. 2011. Editor's Choice. Science, 332, p. 1483.

Lignin-based sustainable packaging solutions

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Abstract

Oil-based barrier coatings were replaced by lignin-based coatings, and packaging materials made of recycled fibers were reinforced by lignin addition.

A solvent fractionation method was developed to produce pure and homogeneous lignin fractions with increased thermoplasticity compared to the starting material.

Another way to successfully increase lignin's thermoplasticity was chemical modifications by esterification reactions. Lignins esterified with fatty acids formed films without any external plasticizers. Lignin fatty acid esters coatings on paper board reduced significantly water vapour and oxygen transmission rates. Barrier properties against water vapour were as good as, or even better, than those of commercial PLA (poly lactic acid).

Unmodified softwood and hardwood kraft lignins precipitated on recycled fibers increased strength, bonding and water resistance of packaging materials, e.g. corrugated boards. Accordingly, at least 20% of fibers can be replaced by lignins.

The carbon footprint results for two new lignin-based products indicated reductions in greenhouse gas emissions by including lignin either in the furnish to compensate fibres and gain lighter weight or as barrier material to replace oil-based barrier coatings.

Introduction

Lignin is one of the most abundant natural polymers, together with cellulose and hemicellulose. During the annual production of 130 million tonnes of chemical pulp, ca. 60 million tons of kraft lignin is annually produced. However, only 1–2% of that is isolated for chemicals and material applications. The rest of lignin serves as fuel. The only important producer of kraft lignin (and its derivatives) is the US Company MeadWestvaco, with an estimated annual production of ca. 50 000 tons. Metso has, however, started sales of commercial LignoBoost isolation plants.

Most industrially used kraft lignin is first converted to water soluble products, e.g. to sulfonated lignins, before various uses [1]. The LignoBond technology for reinforcement of packaging materials used high molar mass kraft lignin on fibres from various sources [2]. A new application is to use lignin as a barrier material in fiber-based packages. The main products used in functional and barrier coatings on paper and board at the moment are extrusion polymers and aluminium. The aim of the present work was to replace oil-based barrier materials by lignin-based coatings, and to reinforce packaging materials made of recycled fibers by different lignin additions.

Experimental

The lignins used were softwood (SW) kraft lignin (Indulin AT, MeadWestvaco) and hardwood (HW) kraft lignin (PC13-60, MeadWestvaco) both obtained as gift. Lignin esters were achieved by the standard acid chloride esterification. Commercial paperboards (200g/m^2) were coated with lignin esters in solutions using an Erichsen coater. The samples were applied as a single or double coating layer.

The Oxygen Transmission Rates (OTR) were determined according to the standard ASTM F2622-08. The tests were carried out at 23°C and 50% relative humidity. *The Water Vapour Transmission Rates (*WVTR) were determined gravimetrically according to a modified ASTM E-96 procedure (wet cup method) at 23°C and 50% relative humidity.

Results and discussion

Solvent fractionation

In efforts to improve lignin's thermoplastic properties a sequential extraction method was developed for softwood and hardwood kraft lignins (Figure 1). The main soluble fractions were the acetone fraction; 23% and 39% for softwood and hardwood lignins, respectively. The main part of lignins – 76% of softwood and 60% of hardwood lignins – remained as insoluble residue [3].

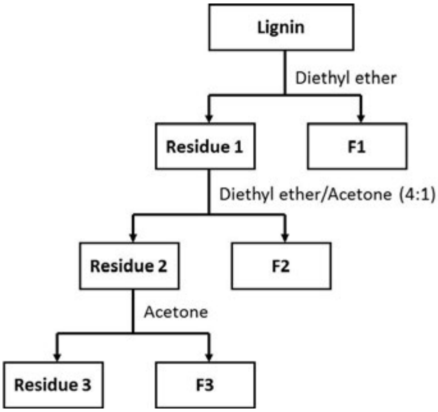

Figure 1. Fractionation of lignin by sequential solvent extraction [3].

The properties of the acetone fractions were different from those of the other fractions. The acetone soluble fractions had smaller weight average molar mass compared to the starting lignin or residual fractions, whereas the residues had slightly higher molar mass than the starting lignins. The isolated acetone fractions were rather homogenous with narrow molecular weight distributions (Figure 2). They were also chemically different and more hydrophilic; i.e. the phenolic hydroxyl groups and carboxyl group contents were higher. The glass transition temperature (Tg), determined by Differential Scanning Calorimetry (DSC), of the acetone soluble softwood fraction was significantly lower (83°C) than that of the starting material (148°C), which makes it potential for material applications that require thermoplastic properties.

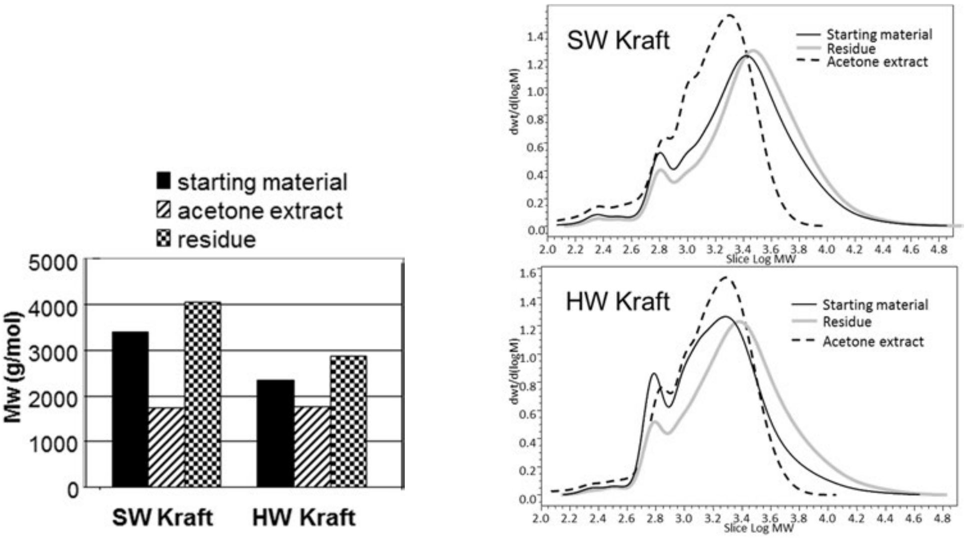

Figure 2. Weight average molar masses of the lignin fractions and molar mass distributions.

Esterification by fatty acids

Both hardwood and softwood lignins were esterified with fatty acids having different carbon chain lengths. The fatty acids used were palmitic acid (C16), lauric acid (C12) and tall oil fatty acid fraction (TOFA). The TOFA used in the project was a gift from Forchem (Rauma, Finland). It contained 3.5% saturated fatty acids (C16 palmitic acid 1.2%, C18 stearic acid 1.5%, C20 arachidic acid 0.8%) and 86.3% unsaturated fatty acids (C18:1 oleic acid 24.9%, C18:2 linoleic acid 52.4%, C18:3 linolenic acid 9.0%). Depending on the dosage of fatty acid (chloride) used the degree of lignin esterification can be adjusted. Esterifications decreased significantly lignin's glass transition temperature. The higher the degree of esterification, the lower was the Tg observed for the ester. Lignin TOFA ester in which all hydroxyls groups were esterified had a Tg below 0°C.

Lignin fatty acid esters as coating and barrier materials

All the lignin ester coatings improved the water vapour and oxygen barrier properties of the paper board, i.e. WVTR and OTR values decreased (Table 1). As expected, in most cases the double coatings gave better results than the single coatings.

Lignin palmitate coatings provided better water vapour and oxygen barrier than the lignin laurate coatings [4]. HW lignin palmitate coatings gave the lowest OTR values. This can be explained by lignin's increased thermoplasticity and film forming ability with decreasing Tg due to the different chain length of the fatty acids. Palmitic acid with a longer carbon chain (C16) gave better results than lauric acid with the shorter chain (C12). It has been shown earlier that the Tg of organosolv lignin esters decreased linearly as the number of carbon atoms in the ester substituent increased [5].

Lignin TOFA-ester (all hydroxyl groups esterified) coating [6] gave as low WVTR value as SW lignin palmitate coatings and significantly lower OTR values. The results thus show that the degree of esterification had a significant effect on barrier properties. The water vapour barrier properties of the lignin ester coated paper boards were even better than those of the PLA (polylactic acid) extrusion coated reference.

Table 1. WVTR and OTR of lignin palmitate (C16), laurate (C12) and TOFA-ester coated paperboard normalized to coat weight of 10 g/m^2. (TOFA-L-100: all hydroxyl groups esterified; TOFA-L-50: 50% of the total hydroxyl groups esterified).

Sample	WVTR (g/m^{2}x24h)	OTR (cm^3/m^{2}x24h)
Paperboard	740	>400 000
SW palmitate	122	24 200
SW laurate	238	62 900
SW palmitate, double coated	156	31 400
SW laurate, double coated	216	55 000
HW palmitate	118	1 500
HW laurate	243	59 100
HW palmitate, double coated	42	1 800
HW laurate, double coated	234	55 200
SW TOFA L-50	529	42 300
SW TOFA L-100	110	8 300
SW TOFA L-100, double coated	101	9 200
PLA (extrusion coated paperboard)	300	-

LignoBond – Strength and water-resistance

The LignoBond technology was successfully widened for new lignin material sources. Unmodified kraft lignins and VTT organosolv lignin [7] (20% calculated as dry/dry fibres) were added to recycled fibers (i.e. 50% magazine and 50% newsprint). After the addition of lignin pH was adjusted to pH 4 with sulphuric acid in order to precipitate the lignin on the fibres. The retention was further improved by adding alum and a retention agent. All the lignins increased paper sheet's strength by 20–50% and water resistance by 90%. The remarkable increase of air resistance indicates that the addition of lignin has created barrier properties to the sheet. A prerequisite is that the lignin is converted into a soluble form before adding it to the pulp slurry. With lignin addition the brightness was, however, decreased (Table 2).

Table 2. Change of sheet properties as percentage compared to the reference pulp.

Change as percentage	SW lignin	HW lignin	Organosolv lignin.
Brightness	- 64	- 64	- 51
Air resistance Gurley	+ 165	+ 266	+ 318
Tensile strength index	+ 25	+ 21	+ 20
Tensile stiffness index	+ 40	+ 40	+ 30
Compression strength SCT	+ 52	+ 52	+ 48
Water abs. Cobb60	- 92	- 90	- 91

Sustainability evaluation – Two new lignin-based cases

Our aim was to direct the research of new products to a sustainable direction by environmental evaluation using life cycle assessment (LCA), as well as economic and social feasibility study and SWOT analysis. Sustainability evaluation was carried out for two reference products: 1) corrugated cardboard box and 2) FBB (folding board box) cereal package with plastic bag inside and for the corresponding new lignin containing products.

In the carbon footprint, fossil greenhouse gases (CO_2, CH_4 and N_2O) are included and expressed as carbon dioxide equivalents (CO_2 eq.). The carbon footprint was calculated from cradle to gate (corrugated board manufacturing) so the end of life was not included. In this calculation, it was assumed that lignin was extracted from black liquor with carbon dioxide. The lignin was then assumed to be added to the whole corrugated board compensating fresh fiber 1:1. The added amount of lignin DS / fiber DS was here 20%. However, the amount could also be higher. The increased strength and thereby lower weight of the corrugated board was in this case assumed to be 20%. So the reference board was 442 g/m^2 while the board with added lignin was 353 g/m^2. Carbon footprint for the new lignin-based product is 20% lower than that for the reference. In case 2 the lignin was added to test liner only reducing test liner weight by 20% and total weight reduction of corrugated board was thus 10% (Figure 3).

The LCA calculations in the cereal package case were done with TOFA-lignin and with lignin palmitate (PA). The carbon footprint of cereal package is 20% lower when TOFA-lignin is used as barrier material instead of a plastic bag (HDPE). The carbon footprint is, however, slightly higher with lignin palmitate compared to the reference case (Figure 3).

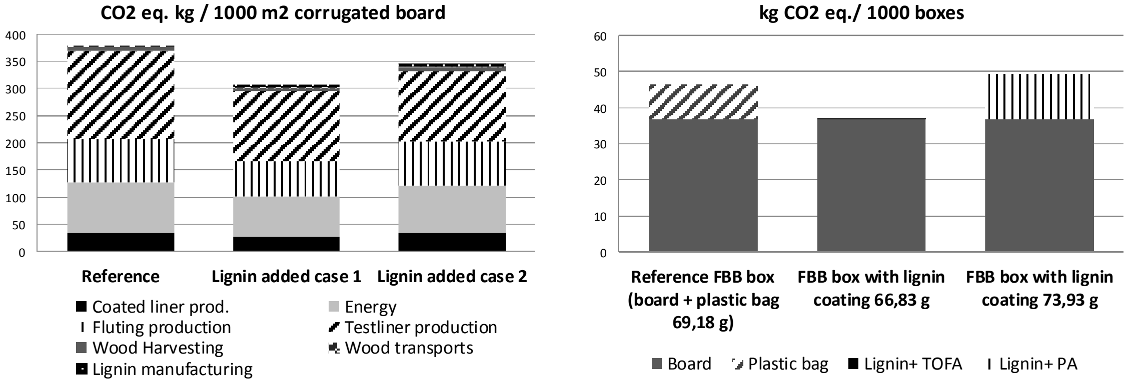

Figure 3. Carbon footprint for the new lignin-based product compared to reference: 1) Corrugated card box 2) folding board box, e.g. cereal package with plastic bag inside and for the corresponding new lignin containing products.

The SWOT analysis included the prices, costs, acceptance, markets, carbon and water footprint and end of life analysis of the products.

As conclusion, the lignin-based products look promising from the carbon footprint point of view. If the whole value chain of the cereal packaging is considered, the advantages of the new lignin based products are the lightness in the transportation chain. Also, lignin can compensate virgin fibre and oil based products and can have lower environmental impacts. Packaging also meets the greener demands of consumers in many ways. Opportunities to achieve competitive marketing advantage through water footprint can also be seen. In addition, the products have light weight and are thus ecological.

Conclusions

- Lignin esterification by fatty acids and lignin fractionation by solvents are potential technologies to prepare thermoplastic lignin materials for various applications.
- Lignin fatty acid esters are potential materials for coatings of fiber based packaging materials, reducing significantly water vapour and oxygen transmission rates. Barrier properties against water vapour are comparable to those of commercial PLA (poly lactic acid).
- LignoBond technology is a smart and simple process to improve the compression strength and reduce the water absorption for corrugated and fiber board by lignin precipitation.
- The new lignin-based products look promising from the carbon footprint point of view, and the products have light weight and are thus ecological.

Acknowledgements

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References

1. Ek, M. 2005. The status of applied lignin research. Processum, Report No. 2.

2. Forss, K.G., Fuhrmann, A., Toroi, M. 1988. Procedure for manufacturing lignocellulosic material product. EP 0 355 041 B1, WO 8807 104.

3. Ropponen, J., Räsänen, L., Rovio, S., Ohra-aho, T., Liitiä, T., van de Pas, D., Tamminen, T. 2011. Solvent extraction as a means of preparing homogeneous lignin fractions. Holzforschung 65(4), pp. 543–549.

4. Hult, E.-L., Koivu, K., Wrigstedt, P., Ropponen, J., Asikkala, J., Sipilä, J., Tamminen, T., Poppius-Levlin, P. 2011. Novel lignin based barrier material for packaging. 16th International Symposium on Wood, Fiber and Pulping Chemistry, Tianjin, P.R. China, 1. P. 253.

5. Glasser, W.G., Jain, R.K. 1993. Lignin derivatives, I Alkanoates. Holzforschung 47(3), p. 225.

6. Tamminen, T., Ropponen, J., Hult, E.-L., Poppius-Levlin, K. 2011. Functionalized lignin, US Patent Filing date, 07.10.2011. Application No 61/544303.

7. Mikkonen, H. 2008. Process for defibering a fibrous raw material, PCT/FI/2008/050671, WO2009/066007.

Lignin based carbon fibres – recent progress

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Abstract

Kraft lignin can be easily isolated from black liquor giving a fairly pure product suitable as a biofuel, but it can also be further valorized to provide new lignin products. Lignin-based carbon fibres (CFs) have been identified as the potentially most value-added product from a wood pulp biorefinery. This new application area has attracted great attention, driven also by the need to find alternative raw materials for CF to cover the demand on light-weight composites for structural applications. The processing conditions for traditional raw materials, mainly of petrochemical origin, are tailor-made depending on raw material and target properties. Thus, the optimal processing conditions for lignin-based CF are by far not given and have also proven to depend on the type of lignin including the processing conditions.

At Innventia research has been conducted to evaluate the potential for kraft lignin-based CF by studying the raw material, the effect of different treatments as well as the thermal behavior of lignin on the melt-spinning and the further transformation into a CF. The presentation will give an overview of these results with emphasis on the stabilization step.

Introduction

Due to the increased competition among the producers of kraft pulp it is important to evaluate future profitable products from the wood raw material including valorization of the side streams to transform the kraft mill into a biorefinery. Besides of the main fibre product, large amounts of lignin is dissolved the black liquor during kraft pulping. The development of the LignoBoost (1) process has made it possible to isolate large quantities of lignin of high purity without disturbing the chief mill operation. The technology is now owned and commercialized by Metso. Currently a LignoBoost installation has been purchased (in the US) and two other installations have been decided in two European kraft mills. This lignin is conventionally used to generate heat but can also partly be used as an external energy product and/or for new value-added applications.

The potentially most value-added lignin product is carbon fibre (CF), which constitutes the load-bearing component in polymer composites. The raw materials used today are mainly derived from petrochemical sources; polyacrylonitrile (PAN, about 90%) or pitch (about 9%), but to a minor extent also regenerated cellulose. The fibres (or better; filaments) are made by conventional techniques such as wet spinning and melt spinning, the latter applied to petroleum or tar derived pitches. The carbon rich filaments are then converted to CFs in consecutive steps to achieve a carbon content of above 90%, but commonly 96–98%, see Figure 1. The processing of the so-called green fibres starts with a low temperature oxidative stabilization step which is followed by a high temperature carbonisation step and sometimes also a graphitization step at even higher temperatures, before it is surface treated through activation and sizing. The condition of each of the production steps is tailor-made depending on the raw material and the target application.

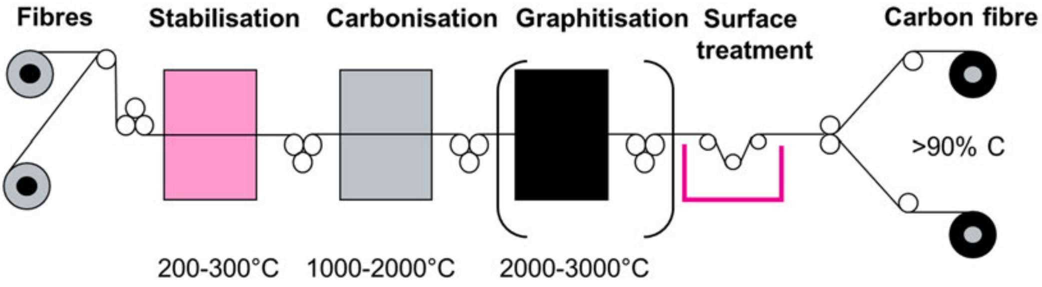

Figure 1. Unit operation steps of the carbon fibre process of PAN-, pitch- or rayon-based yarns. Specific conditions depend on raw material and the graphitisation step is applied for certain target qualities.

Although originally developed for the aerospace industry, the final use of CF today includes markets such as automotive, energy conversion (e.g. wind turbine rotor blades) and sports equipment. The total global demand, as estimated from the use of PAN-based CFs, is estimated to grow from about 40 000 metric tonnes in 2010 to 150 000 metric tonnes in 2020, the driving force being the industrial applications. The expected increase in demand has also put focus on development of alternative starting materials due to the high costs of the conventional raw materials. In this context lignin, having a carbon content of 61–66%, has been recognized as an interesting raw material.

The suitability of several types of lignins for CF production has been investigated throughout the years, and the main emphasis has been put on how to form a precursor fibre of good quality. The only commercial CF derived from lignin, the Kayocarbon fibre made from lignosulphonate using polyvinylalcohol (PVA) as plasticizer, was marketed between 1967 and 1973 [2]. Besides of the Kayocarbon fibre, melt-spinning has been used to obtain lignin precursor fibre and almost all studies have been laboratory scale studies of single filaments. It has been demonstrated that CF can be made from hardwood lignin originating from the steam explosion process after lignin modification [3, 4], organosolv lignin such as acetosolv lignin from hardwood or softwood [5, 6] and Alcell lignin with addition of polyethylene oxide (PEO) as softening agent [7]. After pretreatment, melt-spinning of hardwood kraft lignin (HKL) has been reported using either PEO or polyethylene terephthalate (PET) as softening agent and the obtained fibres could be further processed into CFs. The so far best mechanical properties of lignin-based CFs has been reported for blends of HKL/PET (75/25) [8]. Recently, encouraging results regarding multifilament spinning and CF production of a HKL purified with organic solvents has been reported [9]. Although the mechanical properties achieved were lower than those reported for a HKL/PET combination it demonstrates promising prospects for continuous production of kraft lignin-based CF. In contrast, softwood kraft lignin (SKL) has for long been considered unsuitable for melt spinning into fibres [e.g. 6, 8].

Research to evaluate the potential of making kraft lignin-based CF has been going on at Innventia for about five years. It has comprised fundamental characterization of kraft lignin as isolated by the LignoBoost technology, studies on the thermal behavior of kraft lignin, the melt-spinning of kraft lignins, as well as the following conversion into lignin-based CF including surface treatment. Results from successful melt-spinning of SKL into fibres were reported last year. These results have constituted a foundation on deeper studies of the stabilisation of kraft lignin precursor fibres. The presentation will give an overview of these results, with special attention on recent findings regarding stabilization.

Experimental

Detailed description of the kraft lignins and conditions is given in the corresponding literature references.

Result and discussions

Making precursor fibres from kraft lignin

Kraft lignin isolated from black liquor by the LignoBoost process has a fairly high purity with respect to carbohydrate and ash content, making it suitable to commercialize as a biofuel. In order to make it suitable for processing into CFs, the lignin fraction needs to be more homogeneous. This can be accomplished through extended acid washing and/or fractionation of the black liquor prior to isolation and/or modification of the lignin. Other ways to improve the processability of kraft lignin is to add a softening agent.

In a comprehensive study [10] it was shown that filtration with ceramic membranes gives permeate lignin fractions with considerably lower molecular mass distributions and dispersities. The concomitant decrease in glass transition temperature (T_g) also indicated a possible positive influence on the melt-spinnability of the studied fractionated lignins, i.e. originating from paper-grade pulping of birch (HKL), eucalypt (*E. globulus*, EKL), spruce/pine (SKL) or high-yield pulping (liner) of spruce/pine blends (LL). Using PEO as softening agent for HKL, continuous fibres were obtained by melt spinning of unfractionated and permeate kraft lignins [11]. Later it was also demonstrated that, by using a lignin-derived softening agent (POL2), melt spinning of unfractionated SKL also can be performed rendering in precursor fibres of apparently good quality as revealed by scanning electron microscopy (SEM) [12]. In Figure 2, a lignin-based CF made from a blend of SKL/10% POL2 precursor fibre is shown. The possibility to make SKL-based fibres, encouraged studies at our laboratory on how to further process the precursor fibre into CFs. In this context studies on the response to thermal treatment under different conditions have been studied on lignin powders and precursor fibres.

Response to thermal treatment

The thermal behavior of fractionated lignin powders (HKLP, EKLP, SKLP, LLP) was conducted in the temperature range from 200 to 900°C to determine the stability of kraft lignins as well as the composition of thermally induced emission [13]. The major material loss with respect to phenol products as detected by step-wise pyrolysis GC/MS, was found in the temperature range 500–600°C where the dominant emitted products consisted of mono phenols with alkane and alkene side-chains, and nucleus typical of guaiacyl- and syringyl lignins respectively.

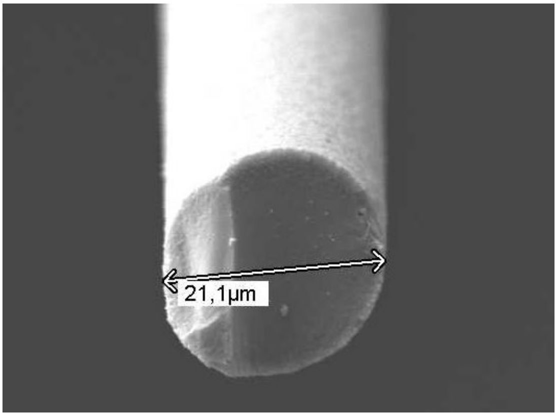

Figure 2. Lignin-based carbon fibre based on softwood kraft lignin (SKL) and 10%POL2. The precursor fibre was oxidatively stabilised at a heating rate of 0.2°/min to 250°C for one hour and carbonised by heating at 1°/min to 600°C and thereafter 3°/min to 1 000°C.

Previously [10] it was found that the main loss of material, as observed by thermal gravimetric analysis (TGA), is at around 400°C for all lignin samples and a total yield of about 40% when treating the samples to 1 000°C under inert conditions. The major weight loss observed in the temperature range 200–300°C with the pyrolysis-GC/MS analysis was attributed to guaiacol and elimination of water from the side-chain of the lignin molecule. Above 700°C no pyrolysis phenol products could be observed due to transformation of the lignin to stable structures. After oxidative (air) treatment at 250°C, i.e. conditions typically used for oxidative stabilization of lignin fibres, the major amount of oxidized and non-oxidized phenol products released was shifted towards higher temperatures (600°C), indicating an increase in stability. This conclusion was also supported by the decrease in the overall material loss in the temperature range up to 800°C. The greatest influence of oxidative treatment was observed for the softwood kraft lignins; the two hardwood kraft lignins appear to be less stabilized under the applied conditions. This reflects that the CF process must be tailor-made depending on kraft lignin origin to achieve optimal stabilisation and carbonization conditions.

Stabilisation of precursor fibre

The stabilisation step is important for the processing of CFs. The purpose is to transform the precursor fibre into a thermoset which will prevent the fibre from fusing in the following carbonization. It is also a time consuming step, and thus needs to be carefully optimized. It has been reported that a slow heating rate is necessary to allow the shift in T_g be higher than the actual treatment temperature [14]. The type, presence and amount of a synthetic softening agent influence the possible heating rate (final temperature 250°C for one hour). Studies on powdered extrudates of HKL, indicate that the heating rate should be below 0.06°/min [14], for stabilization of HKL/PEO fibres containing less than 5%PEO a heating rate of 2°/C is possible [7], whereas for the oxidative stabilisation of HKL/PET (75/25) precursor fibres a heating rate of 0.2°/min can be used [8]. A heating rate below 0.1°/min was recently reported necessary for oxidative stabilization of precursor fibres made from HKL purified by organic solvent extraction [9].

The influence of heating rate (0.2–1.0°/C), final temperature (230–280°C) and treatment time 0.5–2h) on the yield of fractionated lignin powders (HKLP, EKLP, SKLP) was evaluated using a factorial design [15]. The most important factor for increasing the yield after stabilization was to lower the holding time. On the other hand, the highest yield (47–58%) for the hardwood kraft lignins after carbonization at 1 000°C was obtained using a heating rate of 0.2°/min to 280°C and two hours treatment time, but for the softwood kraft lignin this was observed for the mildest conditions, i.e. at slowest heating rate, lowest temperature and shortest final time, giving a yield of about 50%. A considerable increase, or even absence, of T_g was observed for all stabilization conditions, and could therefore not be evaluated with the factorial design. Again, a difference in response towards oxidative stabilization could be observed between softwood kraft lignin and hardwood kraft lignin, the former being more easily stabilized and completely stabilized (no detectable T_g) when applying the slowest heating rate. Furthermore it was found that oxidatively stabilized precursor fibres made from (unfractionated) HKL and 5% PEO became un-evenly oxidized over the cross section of the fibre, as revealed from small spot analysis mode of X-ray photoelectron spectroscopy (XPS). This can be explained by the competition between the diffusion of oxygen into the fibre and the oxidative reactions, the latter resulting in a skin-core structure which aggravates the diffusion of oxygen into the fibre.

Recent results on stabilization of precursor fibres made from unfractionated SKL and lignin-derived softening agent show that a fast stabilization can be obtained at non-oxidative stabilization conditions as well, reflecting the inherent structural difference between guaiacyl and syringyl lignins and the potential to use SKL for making lignin-based CFs of commercial cost per performance solutions.

Conclusions

Despite the short period of time research activities related to lignin-based CF has been going on by a limited number of research groups, promising results have been achieved towards the understanding and optimization of the processing of lignins into CFs.

Findings at Innventia show that precursor fibres can also be made from softwood kraft lignin, besides of the previous reports about its hardwood kraft counterpart, provided that an appropriate softening agent is used. The observed difference in response to thermal treatment is manifested as a faster stabilization of softwood kraft lignin as compared to hardwood kraft lignin.

Acknowledgements

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References

1. Öhman, F., Theliander, H., Tomani, P., Axegård, P. 2006. Method for separating lignin from black liquor. Patent WO2006031175.
2. Otani, S. 1981. Carbonaceous mesophase and carbon fibers. Mol. Cryst. Liq Cryst. 63, pp. 249–264.
3. Sudo, K., Shimizu, K. 1992. A new carbon fiber from lignin, J. Appl. Polym. Sci. 44(1), 127–134.
4. Sudo, K., Shimizu, K., Nakashima, N., Yokoyama, A. 1993. A new modification method of exploded lignin for the preparation of a carbon fiber precursor, J. Appl. Polym. Sci. 48, pp. 1485–1491.
5. Uraki, Y., Kubo, S., Nigo, N., Sano, Y. Sasaya, T. 1995. Preparation of carbon fibers from organosolv lignin obtained by aqueous acetic acid pulping. Holzforschung 49(4), pp. 343–350.
6. Kubo, S., Uraki, Y. Sano, Y. 1998. Preparation of carbon fibers from softwood lignin by atmospheric acetic acid pulping. Carbon 36(7–8), pp. 1119–1124.
7. Kadla, J.F., Kubo, S., Venditti, R.A., Gilbert, R.D., Compere, A.L., Griffith, W. 2002. Lignin-based carbon fibers for composite fiber applications, Carbon, 40, pp. 2913–2920.
8. Kubo, S., Kadla, J.F. 2005. Lignin-based carbon fibers: effect of synthetic polymer blending on fiber properties. J. Polym. Environ. 13(2), pp. 97–105.
9. Baker, D.A., Gallego, N.C., Baker, F.S. 2011. On the characterization and spinning of an organic-purified lignin toward the manufacture of low-cost carbon fiber. J. Appl. Polym. Sci. 124, pp. 227–234.
10. Brodin, I., Sjöholm, E., Gellerstedt, G. 2009. Kraft Lignin as Feedstock for Chemical Products. The Effects of Membrane Filtration. Holzforschung 63, pp. 290–297.
11. Sjöholm, E., Brodin, I., Drougge, R., Gellerstedt, G. Carbon fibre – a new application for lignin. 11th European Workshop on Lignocellulosics and Pulp (EWLP). Hamburg, August 16–19, 2010. Pp. 1–4.
12. Nordström, Y., Sjöholm E., Brodin, I., Drougge, R., Gellerstedt G. 2011. Lignin for carbon fibres. 3rd Nordic Wood Biorefinery Conference (NWBC). Stockholm, March 22–24, 2011. Pp. 156–160.

13. Brodin, I., Sjöholm, E., Gellerstedt, G. 2010. The Behaviour of Kraft Lignin during Thermal Treatment. J. Anal. Appl. Pyrolysis 87, pp. 70–77.

14. Braun, J.L., Holtman, K.M., Kadla, J.F. 2005. Lignin-based carbon fibers: Oxidative thermostabilization of kraft lignin, Carbon 43, pp. 385–394.

15. Brodin, I., Ernstsson, M., Gellerstedt, G., Sjöholm, E. 2012. Oxidative stabilisation of kraft lignin for carbon fibre production. Holzforschung 66, pp. 141–147.

Rapid refining of lignocellulosics to carbohydrates and lignin-based new materials (lignophenols) and design of sustainable industrial network connecting forests and chemical industries

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Abstract

In order to achieve the cascade-type flow of lignocellulosic components as functional materials in human life, a novel conversion system (phase-separation system) has been developed and a new type of structure-controllable lignin-based polymers (lignophenols) has originally been designed. A key point of the process is to set up two different solvents which are immiscible each other for selective modification and separation of lignin and carbohydrates: hydrophobic solvent for hydrophobic lignin and hydrophilic solvent for hydrophilic carbohydrates. This conversion process works within 60min without any heating and pressing to give lignophenols and soluble sugars almost quantitatively. The resulting lignophenols have unique functions, which conventional lignins do not have: highly phenolic property, no conjugated system, light color comparable to native lignin, structure-variable function and solid-liquid transformation. The separated carbohydrates include water-soluble monomers, oligomers, and polymers. These are easily converted to valuable chemicals such as alcohols, lactic acid, furfural, xylitol, etc. In order to create sustainable human society without petroleum, aliphatic and aromatic types of industrial raw materials must be derived sustainably from biomaterials (lignocellulosics). A new sustainable industrial network initiated from forests is designed.

Carbon flow in the ecosystem

The keywords, “Energy”, “Materials”, and “Environment”, are of importance for sustainable human society. Lignocellulosics are typical materials including these three keywords. Lignocellulosics are fundamental materials, forming long-term sustainable carbon flow in the ecosystem through three phases (Figure 1): carbon dioxides are assembled by photosynthesis to form big composites “trees” [Molecular assembling (potential up) stage, Phase I]. The trees (concentrated carbons state) are kept through the life system for a long time (Potential equivalent stage, Phase II) These assembled molecules are gradually released finally to give carbon dioxides [Molecular releasing (potential down) stage, Phase III]. In order to create sustainable human society without disturbing the ecosystem, lignocellulosics have to be utilized through cascade-type and long term functionality control system, following the eco-carbon flowing system including Phase I, II and III. But in the present human society, after forest resources are utilized as wood and papers, the most of those are immediately reconverted to carbon dioxides by burning. This means that the molecular level potential of forest resources (Phase III activity) is cut, disturbing the ecosystem. The phase III activities in molecular level after conventional forest and wood industries must be created in order to keep sound eco-carbon flowing system. Lignocellulosics are composed of three polymers, cellulose, hemicellulose and lignin. Two breakthrough technologies are required for achieving phase III activities: perfect refining of lignocellulosic composites and sequential functionality control of the resulting lignin and carbohydrate moieties.

Lignin–*Sustainable aromatic resource*

Recently biomaterials have attracted the attention because of their sustainability. There have been lots of trials for lignocellulose utilization in molecular level. However, the carbohydrate utilization only, for example bioethanol production, has been done all over the world. Lignin has very important functions: (a) Increase the mechanical strength for standing upright on the earth, (b) Protect the body against the attack of insects and microorganisms, (c) Protect the body against strong UV irradiation, (d) Seal fiber cell walls for water transportation, (e) Combine fiber cells to form the body, etc. Nevertheless, lignins have been always wastes in the previous and present industrial systems. There have been lots of patents and research papers on lignin utilization in the world. This situation means that the conventional technologies lack some important factors for lignin. A new sight is now required for lignin.

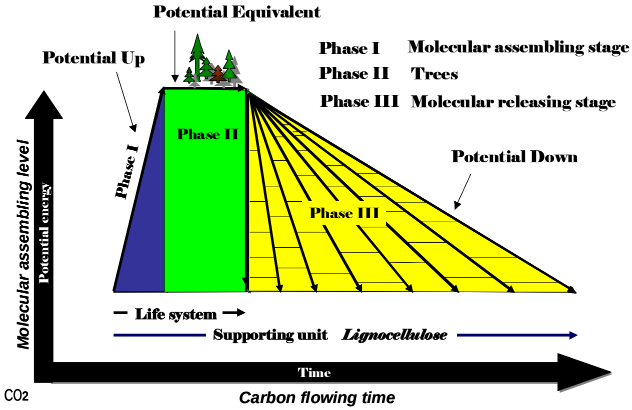

Figure 1. Schematic illustration of eco-carbon flowing system.

Though carbohydrates and lignin both are biopolymers, the fundamental molecular designs are totally different: carbohydrates have universal design, same structures on the earth, while lignin has environmental design. Every lignin has different structure, optimized for the environment. Environmental factors are incorporated in lignin structures. The combination of environmental and universal designs (2:8) is a key for sustainable material designs in next generation because the most durable biomaterials are woods in the ecosystem. It is required for us to understand the environmental design and incorporate it into material productions for the new generation without disturbing the ecosystem.

Lignins are classified as phenolic polymers (polyphenols) because lignin precursors (coniferyl alcohol, sinapyl alcohol, p-coumaryl alcohol) are phenolic monomers. However, lignin should be classified as polyethers or polyalcohols because of low phenolic activity (0.1–0.2/C9) and the presence of lots of aliphatic OH and ether linkages. Furthermore, all lignin units have reactive sites at C1 (benzyl) positions. Lignins are latent phenolic polymers including reactive points. The major environmental designs incorporated within lignin are as follows (Figure 2): Various functionality at C1 of side chain, High frequency of aryl ether at C2 of side chain, Blocked phenolic activity, C-C linked branched units.

These features are optimized for the environment around lignin, minimizing the internal stress in lignin. The flexible reactivity quickly responding to environmental change leads to long term circulation of lignin in the ecosystem. On the other hand, these features of lignin incorporating environmental factors prevent its universal use under every environment such as petro-based materials.

How to sequentially release the environmental factors incorporated within lignin becomes a key for effective cascade-type lignin utilization leading to Phase III activities. Conventional industrial processes including high energy input such as hydrolysis, pulping or steam explosion destroy important structural units nonselectively, preventing the following functionality control (sequential utilization).

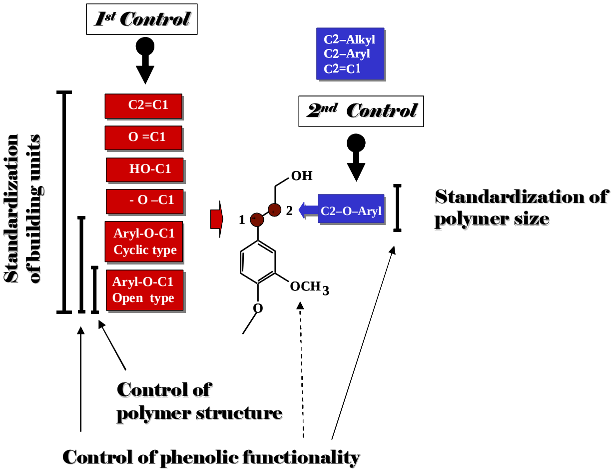

Figure 2. Distribution of functional groups in lignin.

Selective transformation of native lignin and perfect refining of lignocellulosics

Sequential releasing system of environmental factors within lignin has been designed [2–8] (Figure 3).

[Design I] Standardization of building units (C1 control)
[Design II] Standardization of polymer structures (C1 control)
[Design III] Standardization of polymer size (C2 control).

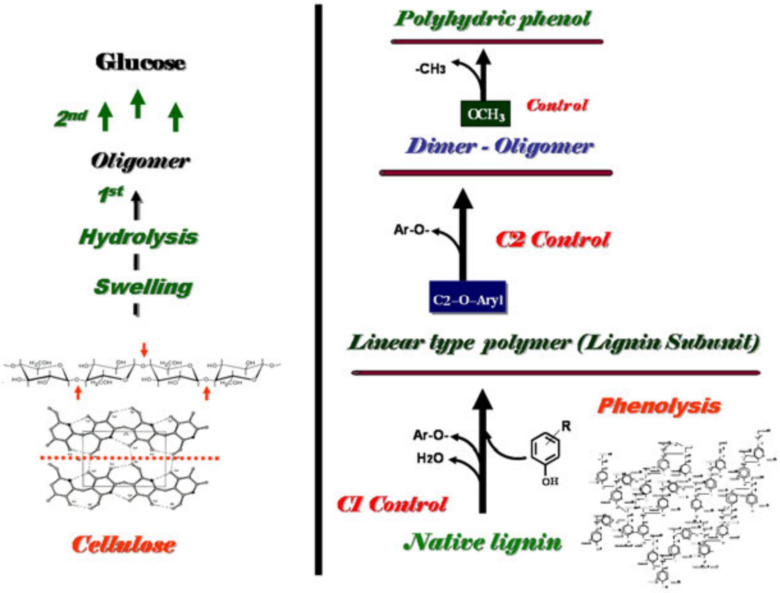

Figure 3. Selective structural conversion of lignin and carbohydrates.

Lignin forms semi-interpenetrating polymer network (IPN) structures with carbohydrates within the cell wall. The functionalities of lignin and carbohydrates have to be controlled selectively and simultaneously through single treatment for direct synthesis of lignin-based polymer from lignocellulose composites. Furthermore, both of lignin and carbohydrates must be converted to structure-controllable functional materials for achieving sustainable Phase III activities without disturbing the ecosystem. The precious reactivity control, selective functionality control and matching of reaction system are required. This is the most important and difficult breakthrough point for cascade-type, total utilization of lignocellulosics.

The originally designed process [2–8] includes the phase-separative reaction system composed of the organic phase (hydrophobic phenol derivatives) and the aqueous phase (concentrated acid), which are immiscible each other under normal condition. The concentrated acid is a solvent for carbohydrates, leading to swelling carbohydrates, followed by depolymerization by hydrolysis, and furthermore, works as a catalyst for the fragmentation and phenolation of lignin. The phenol derivatives act as phenolation agents for C1 standardization, a barrier to minimize the attack of acid on the lignin through solvation, and a solvent for the lignin fractions.

Lignocellulosic particles are solvated with hydrophobic solvents (for example, alkylphenols) first, and then, are contacted with the acid at the interface between both solvents. The carbohydrates are swollen, partially hydrolyzed, while lignins are phenolated at reactive C1 positions selectively to give 1,1-bis(aryl)propane type structures. The cleavage of reactive C1 (benzyl) aryl ethers, followed by phenolation results in the release of network lignin to subunits. The hydrophilic carbohydrates released from IPN pass through the interface to the aqueous phase, while lignins always stay in the hydrophobic organic layer, leading to the perfect separation of carbohydrates and lignin. This separation process is achieved quickly (within 60min for softwoods, 30min for hardwoods, 10min for grasses) under normal condition without any heating and pressing.

The resulting lignin-based materials (lignophenols) are of high brightness comparable to milled wood lignin, and quickly dissolved in solvents such as methanol, ethanol, acetone, dioxane and pyridine. The amount of grafted phenols is about 25% (about 0.7 mol/C9) in softwood lignophenols and about 30% (about 0.9 mol/C9) in hardwood lignophenols. The difference between the species is due to both the flexibility of the molecule and the frequency of reactive functional groups in the side chains which are caused by the balance of guaiacyl and syringyl units within the molecules. The TMA curves of lignophenols indicate an apparent change of the phase at ca.130°C in hardwood and at ca.170°C in softwood, at which those are transformed to clear liquid state. That is, native lignins, three dimensional network polymers, are converted to branched linear-type polymers with high frequency of 1,1-bis(aryl)propane-2-O-aryl ethers during the process. The branched structures are formed mainly by coupling at guaiacyl C5. The molecular weights of softwood and hardwood lignophenols are 5 000–10 000 (Mw) and 3 000–5 000 (Mw), respectively, reflecting the size of subunits constructed by radical coupling.

It usually takes a long time to perfectly swell and dissolve cellulose within lignocellulosics by the acid treatment. This is due to the belt effect of lignin with highly rigid structures which are formed through the self-condensation in the early stage of acid treatment. However, this effect of lignin to cellulose disappears by the effective phenolysis of lignin during the phase-separation treatment, leading to the rapid separation of both constituents. Furthermore, the rapid and selective phenol grafting of native lignin is due to the lignin distribution within the organic phase: native lignins, which are rich in hydrophilic functional groups, are distributed near the interface with the aqueous phase, resulting in frequent contact with acid to give rapid structural modifications. The resulting lignin derivatives, which are much more hydrophobic than native lignins, are moved far from the interface area to escape from the frequent attack by the acid.

By the combination of plant species (softwood, hardwood, grass) and process chemicals, the functionality of lignophenols are controlled: thermoplasticity, hydrophobicity, hydrophilicity, molecular weight, recyclability, stability, network formation, linear formation, structure control, functionality control, composites formation, etc.

This process has been termed “Phase-separation process”. The system plants designed specially for total utilization of lignocellulosics have been constructed in Japan: 1st (2001 in Mie Univ. campus) and 2nd (2003 in Kitakyushu) plants with batch system, and 3rd (2008 in Wakayama) with continuous system. The latest system plant (continuous system) was constructed in Tokushima in 2012 (Figure 4), including the production of lignophenols and soluble sugars, followed by alcohol fermentation, and the recovery of process chemicals.

1,1-Bis(aryl)propane-2-O-aryl ether units formed frequently in the lignin molecules through Design I can be used as switching devices for the structure control (phenolic functionality and molecular weight) [9–16]. The phenoxide ions of grafted phenols readily attack the electron deficient C2 nucleophilically, resulting in the cleavage of C2-aryl ether linkages with the exchange of phenolic functionality from C1-grafted nuclei to lignin nuclei. Through this switching treatment, molecular weights of lignophenols are dramatically decreased, while total phenolic activity remains unchanged. Since this type of neighboring group participation is very quantitative, the functionality of lignophenols can strictly be adjusted by the frequency control of C2-attackable phenolic nuclei (switching devices) within the molecules. The switching devices are divided into two types: one is the reactive device with a reactive point on the nucleus, and the other is the stable device without any reactive point. The phenols linked to lignin side chains through p-position to phenolic hydroxyl group do not work as switching devices, due to the steric factor and can be used as control devices for controlling the frequency of switching devices within the molecule. There is a good correlation between the controlled molecular weights of lignophenols and the frequency of switching devices within the molecule. The switching function is controlled by the structure of switching unit at C1. The compact phenols with high basicity work rapidly as switching devices. The rate of switching function gets slower with the extension of side chains attached to switching unit. Using reactive- and stable devices, network type- and linear type polymers can be prepared, respectively. By hybridizing reactive- and stable devices in the lignin molecules, the polymer network structures from lignophenols can be controlled. By the combination of original lignophenol units, spacer units and terminal units, the structures of lignophenol-based polymers can be designed so as to meet the properties required. The resulting lignophenol polymers can be readily released to subunits using intramolecular switching units and monomers-oligomers by the nucleus exchange technique [3], producing new raw materials for the next industrial system.

Effective utilization of lignins

Lignin is a natural polymer with very complicated network structures. The complexity is due to the combination patterns between building units, which are controlled by environmental factors. The C1 of side chain has a reactive substituent (hydroxyl group, carbonyl group or ether linkage). The selective phenol grafting at C1-positions leads to the formation of new phenylpropane units between grafted phenolic units and lignin propane units. This results in a dramatic change of the original lignin functions, forming a new type of lignin-based polymers composed mainly of 1,1-bis(aryl)propane type units.

The applications of lignophenols are shown below [17–48].

(a) Recyclable composites with cellulose, biopolyesters, and inorganic materials (glasses, metals)
(b) Raw materials for recyclable polymers
(c) Detachable adhesives, Switching devices for material recycling
(d) Electromagnetic shielding materials
(e) Carbon molecular sieving membranes
(f) Enzyme supports for bioreactors and affinity chromatography
(g) Adsorbents for proteins and metals
(h) Performance control agents for lead-acid battery and enzymes
(i) Photoresists
(j) Antioxidants,
(k) UV barriers
(l) Hydrogel
(m) Medical agents, etc.

Figure 4. Fourth system plant in Japan for refining lignocellulosics into lignophenols and carbohydrates.

Concluding remarks

The carbon flow in the ecosystem is working as the material network from upstream (high potential stage) to downstream (low potential stage). The direct production of post-petroleum (downstream materials) from biomaterials in the upstream disturbs the eco-carbon flowing system with “Energy”, “Function” and “Time” factors, leading to the environmental destruction. That all biosystems are balanced through sustainable flow of energy and materials should be recognized deeply. In order to create sustainable human society without disturbing the ecosystem, a novel design of human society is required, following the ecosystem and linking the agricultural- and industrial fields through functional materials.

References

1. H. Sandermann, D. Scheel, T. Van der Trenck, J. Appl. Polym. Sci. 37 (1983) 407.

2. M. Funaoka I. Abe, Mokuzai Gakkaishi 24 (1978) 256.

3. M. Funaoka, 6.6 *Nucleus Exchange Reaction, in S.Y. Lin and C.W. Dence Eds.), Methods in Lignin Chemistry, Springer-Verlag, Berlin Heidelberg, 1992, pp. 369–386.

4. M. Funaoka, Tappi J. 72 (1989) 145.

5. M. Funaoka, M. Matsubara, N. Seki, S. Fukatsu, Biotechnol. Bioeng. 46 (1995) 545.

6. M. Funaoka, Holzforschung 50 (1996) 245.

7. M. Funaoka, Polymer International 47 (1998) 277.

8. M. Funaoka, Macromol. Symp. 201 (2003) 213.

9. M. Funaoka, H. Ioka, T. Hosho, Y. Tanaka, J. Network Polymer J. 17 (1996) 121.

10. M. Funaoka, Polymer Processing 48(1999) 66.

11. Y. Nagamatsu, M. Funaoka, Trans. Materials Res. Soc. J. 26 (2001) 821.

12. Y. Nagamatsu, M. Funaoka, Sen'I Gakkaishi 57 (2001) 54.

13. Y. Nagamatsu, M. Funaoka, Sen'I Gakkaishi, 57 (2001) 75.

14. Y. Nagamatsu, M. Funaoka, Sen'I Gakkaishi, 57 (2001) 82.

15. Y. Nagamatsu, M. Funaoka, J. Adhesion Soc. J. 37 (2001) 479.

16. Y. Nagamatsu, M. Funaoka, J. Advan. Sci. 13 (2002) 402.

17. M. Funaoka, H. Ioka, N. Seki, Trans. Material Res. Soc. J. 20 (1996) 163.

18. M. Funaoka, M. Maeda, M. Matsubara, Trans. Material. Res. Soc. J. 20 (1996) 167.

19. M. Uehara, Y. Nagamats, M. Funaoka, Trans. Mater. Res. Soc. J. 26 (2001) 825.

20. E. Ohmae, M. Funaoka, S. Fujita, Trans. Mater. Res. Soc. 26 (2001) 829.

21. J. Kadota, K. Hasegawa, M. Funaoka, T. Uchida, K. Kitajima, J. Network Polymer, Japan 23 (2002) 142.

22. H. Kita, M. Hamano, M. Yoshino, K. Okamoto, M. Funaoka, Trans. Materials Res. Soc. J. 27(2002) 423.

23. Y. Nagamatsu, M. Funaoka, Material Sci. Res. International 9 (2002) 108.

24. Xiao-S. Wang, T. Suzuki, M. Funaoka, Y. Mitsuoka, T. Yamada, S. Hosoya, Material Sci. Res. International 8 (2002) 249.

25. H. Kita, K. Nanbu, T. Hamano, M. Yoshino, K. Okamoto, M. Funaoka, J. Polymers. Environment 10 (2002) 69.

26. Xiao-S. Wang, N. Okazaki, T. Suzuki, M. Funaoka, Chemistry Letters 32 (2003) 42.

27. N. Seki, K. Ito, T. Hara, M. Funaoka, Trans. Mater. Res. Sci. J. 29 (2004) 2471.

28. Y. Akao, N. Seki, N. Yoshihiro, Y. Hong, K. Matsumoto, Y. Ito, K. Ito, M. Funaoka, W. Maruyama, M. Naoi, Y. Nozawa, Bioorganic & Medicinal Chemistry 12 (2004) 4791.

29. D. Parajuli, H. Kawakita, K. Inoue, M. Funaoka, Ind. Eng. Chem. Res. 45 (2006) 8.

30. J. Kadota, K. Hasegawa, M. Funaoka, J. Network Polymer, Japan 27 (2006) 118.

31. S. Sato, S. Fujita, M. Funaoka, M. Komori, M. Kurasaki, Basic & Clinical Pharmacology 99 (2006) 353.

32. M. Aoyagi, M. Funaoka, J. Photochem. Photobiol. A Chem. 181 (2006) 114.

33. T. Kimura, M. Terada, H. Tamura, M. Funaoka, Trans. Mater. Res. Soc. J. 32 (2007) 1091.

34. M. Aoyagi, N. Umetani, M. Funaoka, Trans. Mater. Res. Soc. J. 32 (2007) 1107.

35. M. Aoyagi, M. Funaoka, Trans. Mater. Res. Soc. J. 32 (2007) 1115.

36. T. Shinano, M. Funaoka, Y. Shirai, M.A. Hassan, Trans. Mater. Soc. J. 33 (2008) 1185.

37. H. Ren, M. Funaoka, Trans. Mater. Soc. J. 33 (2008) 1141.

38. K. Tsujimoto, N. Imai, H. Kageyama, H. Uyama, M. Funaoka, J. Network Polymer, Japan 29 (2008) 192.

39. K. Mikame, M. Funaoka, Trans. Mater. Res. Soc. J. 33 (2008) 1149.

40. K. Suzuki, T. Suzuki, N. Takazawa, M. Funaoka, Holzforschung, 62 (2008) 157.

41. T. Yoshida, R. Ru, S. Han, K. Hattori, T. Katsuta, K. Ikeda, K. Sugimoto, M. Funaoka, J. Polym. Sci. A Polym. Chem. 47 (2009) 824.

42. S. Horii, M. Funaoka, Trans. Mater. Res. Soc. J. 34 (2009) 735.

43. K. Mikame, M. Funaoka, Trans. Mater. Res. Soc. J. 35 (2010) 975.

44. T. Shinano, M. Funaoka, Y. Shirai, M.A. Hassan, Trans. Mater. Res. Soc. J. 35 (2010) 937.

45. M. Jung, M. Funaoka, Trans. Mater. Res. Soc. J. 35 (2010) 955.

46. T. Norikura, Y. Mukai, S. Fujita, K. Mikame, M. Funaoka, S. Sato, Basic & Clinical Pharmacology & Toxicology 107 (2010) 813.

47. S. Horii, M. Aoyagi, M. Funaoka, Trans. Mater. Res. Soc. J. 36 (2011) 3.

48. Y. Mukai, T. Norikura, S. Fujita, K. Mikame, M. Funaoka, S. Sato, Molecular and Cellular Biochemistry 348 (2011) 117.

Sugars and lignin from cellulosic source – high quality, high value products – the “wet wood milling” approach

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High purity monosaccharides and lignin are obtained from wood through a “wet wood milling” approach, that similarly to corn milling optimizes a multi step process to extract maximal value of all useful components in the wood.

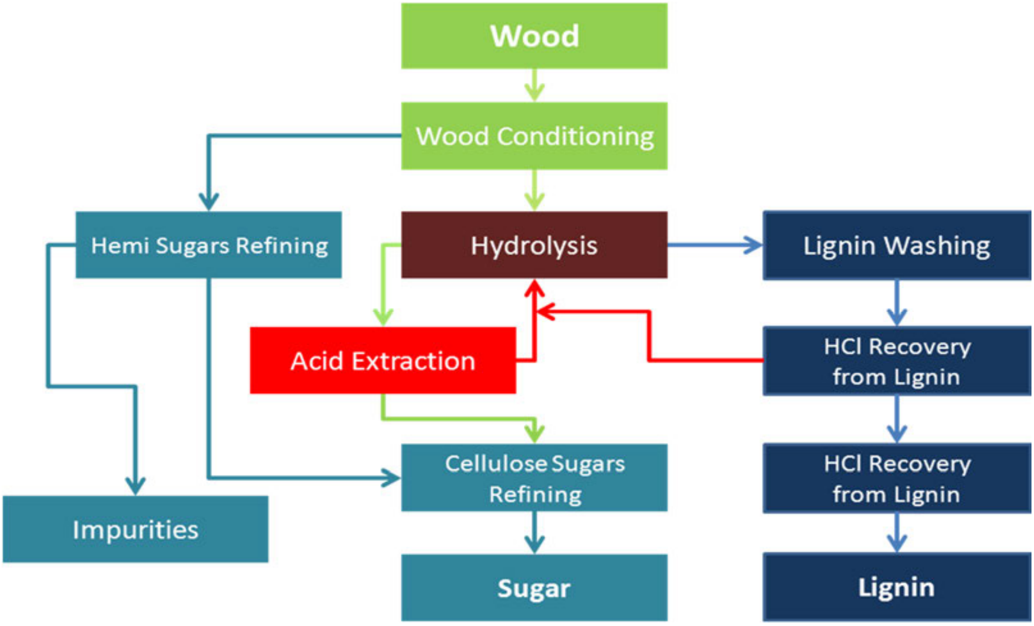

Figure 1. Scheme of the “wet wood milling” approach.

Cost effective operation of the wet wood milling is achieved by chemical and physical means. Major steps consist of sizing the wood and extracting the organic extractives and ash as well as most of the moisture, and at the same time hydrolyzing the hemi sugars to monomeric C_5 and C_6 (composition depends on feedstock); the hemi sugars are recovered and refined, while the impurities are separated; the clean wood chips follow to cellulose hydrolysis, conducted simultaneously with the separation of the resulting hydrolyzed sugars from the solid lignin; finally, the products are recovered and purified: a sugar syrup (80% DS containing C_5 & C_6) having ~90% monomers of 99% purity, and >99% purity lignin. The acid and solvents used in these processes are fully recovered.

The sugar syrup has been successfully fermented or chemically converted without further purification by over 20 companies from Fortune 50 to technology startups, to obtain amino acids, baker’s yeast, carboxylic acids, p-xylene, diesel, and ethanol. In the framework of a BIRD GREEN project the C_5 & C_6 mixture was used by Virent Energy Systems to catalytically produce high quality jet fuel, which was successfully tested by the US Airforce to be compatible with petroleum fuel.

The lignin product (Figure 2). is isolated as an odorless solid, containing residual cellulose (2%), low ash (<0.4%) and minimal sulfur and chloride (<300 and <4 000 ppm respectively). It can be solubilized in water by a proprietary process and refined further to the 99+% need for carbon fiber making and other applications that require high purity lignin.

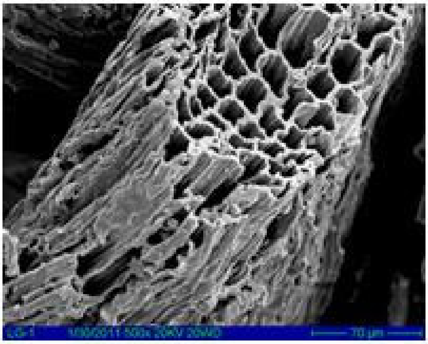

Figure 2. SEM image of lignin particle, x500.

Virdia is operating its Process Development Unit at Denville, VA since April 2012. Capacity of the PDU is 300 pounds ds sugar and 160 lbs dry lignin per day.

Ionic liquids in wood and biomass dissolution and fractionation

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Abstract

The efficient dissolution of cellulose, lignin and even wood in ionic liquids (ILs) has opened new possibilities to fractionate, refine, derivatize, and generally process and utilize lignocellulosic materials more selectively and efficiently. We have screened families of different types of ILs for their efficiency in the processing and fractionation of wood to its components. A new mild method of fibrillating wood in neat ionic liquid media has been identified and characterized. These studies have also improved our understanding of structure-property relationships concerning wood processing in general with ILs. This study has also provided new insights into the connectivity of wood components and wood architecture. This presentation summarizes recent developments, utilizing ILs for wood biorefining.

Introduction

The insolubility of wood in common molecular solvents has severely hampered the development of new methods towards the efficient utilization of wood and its components. Today, the most common pathway for the utilization of lignocellulosic materials is through chemical pulping, where the lignin polymer is broken down by alkaline or acidic cooking to produce cellulose fibers. The released lignin is typically burned to produce energy to fuel the process.

The first report to use molten salts for lignocellulose processing came from Graenacher [1] who used alkylpyridinium chlorides to dissolve cellulose, allowing for efficient chemical modification. The melting points of most alkylpyridinium chloride salts are above 100°C and as such, don't fall under the tentative definition of ionic liquids. Quite some time later, Lu and Ralph demonstrated that after extensive ball-milling, wood becomes soluble in dimethylsulfoxide-tertrabutyl ammonium fluoride (DMSO-TBAF) and dimethylsulfoxide-imidazole (DMSO-Imidazole) binary solvent mixtures, [2] which may already be considered as ionic reaction media, for wood processing. Finally, in 2002 the work of Swatlowski demonstrated that some imidazolium-based ionic liquids, as pure molten salts melting below 100°C, were highly efficient solvents and reaction media for cellulose. [3] Along these lines, we demonstrated that these same solvents are capable of fully dissolving fine sawdust giving homogenous solutions. [4]

Fractionation of wood using ILs

The gentle and simple dissolution process, provided by ionic liquids (ILs), as well as their relatively inert nature provides efficient means for the fractionation of wood. As the whole wood material can be essentially completely dissolved in ILs, a straightforward approach for fractionation is complete dissolution followed by selective precipitation of the dissolved components. It has been demonstrated that cellulose-rich and lignin-rich fractions can be recovered, and that the IL can be recycled multiple times. [5, 6] However, it seems on basis of literature and on our own experiments that this kind of fractionation only leads to partial enrichment of some of the components.

An alternative approach for wood fractionation is to seek for ILs that are able to selectively dissolve some of the components. It has already been demonstrated by MacFarlene *et al*. that *N,N*-

dimethylammonium-*N',N'*-dimethylcarbamate (DIMCARB), formed from the addition of dimethylamine to carbon dioxide, is able to efficiently extract tannins, from certain plant species. [7] We have also recently demonstrated that some imidazolium-based ILs can fibrillate wood chips efficiently, from the extraction of minor components. [8]

Recycling and reactivity of ILs

So far, most of the published literature concerning lignocellulose processing has been concentrated on the application of imidazolium-based ILs. However, the true sustainability of prospective processes will depend on the chemical stability of solutes and ionic liquids under process and recycling conditions. There are already some indications that ionic liquids such as [emim][OAc] react chemically with lignocellulosic solutes. [9] This may lower the recovery of the media upon recycling although, in the case of the reaction of C2 imidazolium positions with C1 reducing end groups of cellulose, [9] labile functionalities may be cleaved by subsequent water treatments. A bigger concern is the method of recycling to yield a pure ionic liquid. High purity ionic liquid, for most processes, will be required to maintain efficiency of dissolution and overall sustainability of the process.

There already exists some examples of truly recyclable ILs that have potential for lignocellulose processing. The DIMCARB approach is an example of a reversible IL, which can be purified by distillation of the components. [8] We have also recently demonstrated that short-chain [TMGH]+ carboxylates are both capable of rapidly dissolving cellulose and are technically ‘distillable’ to high purity (> 99% purity, > 99% yield), by temperature assisted dissociation, vaporization and recombination of the component neutral species. [10]

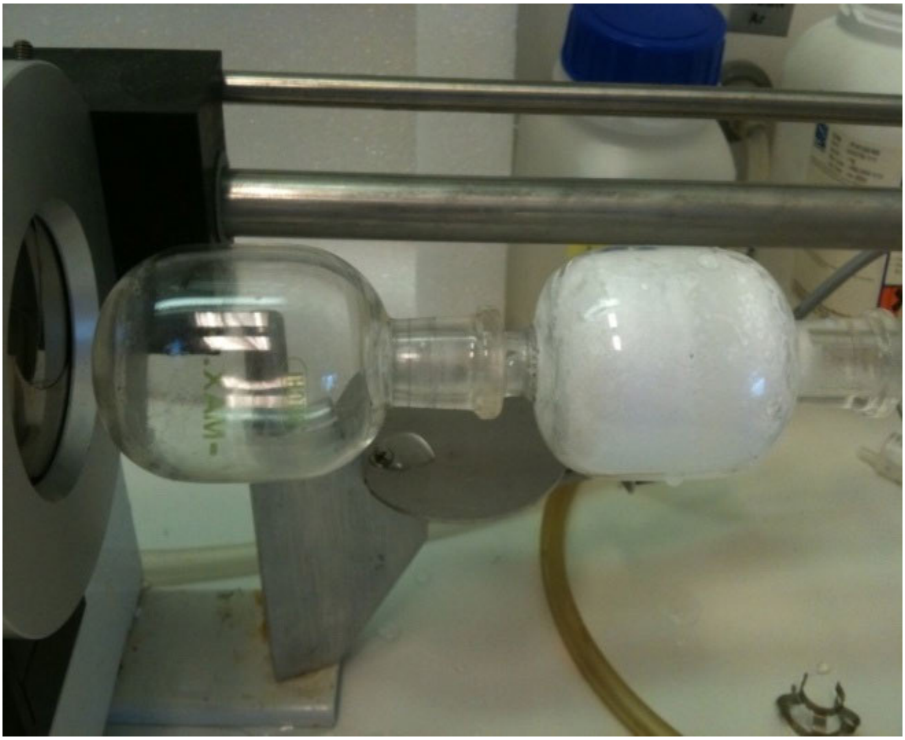

Figure 1. Distillation of $[TMGH]^+$Propionate in a short path distillation apparatus (Kugelrohr).

References

1. C. Graenacher, US 1943176, 1934.

2. Lu, F., Ralph, J. 2003. Plant Journal 35(4), pp. 535–544.

3. Swatloski, R.P., Spear, S.K.H., Rogers, R.D.J. 2002. Am. Chem. Soc. 124(18), pp. 4974–4975.

4. Kilpeläinen, I., Xie, H., King, A., Granström, M., Heikkinen, S., Argyropoulos, D.S. 2007. J. Agric. Food Chem. 55(22), pp. 9142–9148.

6. Sun, N., Rahman, M., Qin, Y., Maxim, M.L., Rodriguez, H., Rogers, R.D. 2009. Green Chem. 11(5), pp. 646–655.

7. Lee, S.H., Doherty, T.V., Linhardt, R.J., Dordick, J.S. 2009. Biotechnology and Bioengineering 102(5), pp. 1368–1376.

8. Tan, S.S.Y., MacFarlane, D.R., Upfal, J., Edye, L.A., Doherty, W.O.S., Patti, A.F., Pringle, J.M., Scott, J.L. 2009. Green Chem. 3, pp. 339–345.

9. Chowdhury, S., Vijayaraghavan, R., MacFarlane, D.R. 2010. Green Chem. 12, pp. 1023–1028.

10. **a)** Liebert, T., Heinze, T. 2008. BioResources 3, pp. 576–601; **b)** Ebner, G., Schiehser, S., Potthast, A., Rosenau, T. 2008. Tetrahedron Lett. 49, pp. 7322–7324; **c)** Çetinkol, Ö.P., Dibble, D.C., Cheng, G., Kent, M.S., Knierim, M., Auer, D.E., Wemmer, J.G., Pelton, Y.B., Melnichenko, J.R., Simmons, B.A., Holmes, B.M. 2010. Biofuels 1, pp. 33–46.

11. King, A.W.T., Asikkala, J., Mutikainen, I., Järvi, P., Kilpeläinen, I. 2011. Angewandte Chemie 50, pp. 6301–6305.

Ethanol-based organosolv biorefineries: feedstock-flexibility & economic evaluation

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Abstract

An economic analysis was made to investigate the economic potential of different feedstocks in an organosolv biorefinery, producing cellulose, lignin and furfural. Calculations were based on an experimental optimization study to find the best reactor conditions for the process.

Results show that birch is economically the most attractive feedstock with an expected payback time of about 6 years. It might also be economically interesting to have a feedstock-flexible process, allowing the choice of the cheapest feedstock. Despite a higher investment, reduced feedstock costs make this option economically interesting too.

Introduction

Biorefining is the sustainable processing of biomass into a spectrum of marketable products (food, feed, materials, chemicals) and energy (fuels, power, heat). ECN is developing an organosolv-based biorefinery technology suitable for conversion of hardwoods and herbaceous crops into 2nd generation biofuels and chemicals [2]. Although the motivation for the development of biorefineries finds its origin in targets for the reduction of greenhouse gases and a decreased dependence on foreign energy sources, the primary driver for the successful implementation of such a biorefinery is its profitability.

The organosolv biorefinery is able to fractionate lignocellulosic biomass into its main components by extracting lignin into an ethanol/water mixture at elevated temperature and pressure. Simultaneously, the hemicellulose is hydrolysed and its monomeric components and degradation products dissolve into the same solvent. This enables the removal of the cellulose fraction from the mixture by filtration. The lignin is subsequently removed from the hemicellulose hydrolysate by removal of the ethanol from the mixture. This lowers the lignin solubility, so that the lignin precipitates. A second filtration step is then used to recover the lignin.

The process produces three main products: a solid hydrolysable cellulose fraction which can be used for e.g. cellulose ethanol production, a high purity lignin product for use in performance materials and chemicals, and furfural, which is a suitable platform chemical for biobased chemicals and fuels production.

ECN has performed laboratory experiments on four different types of feedstock: wheat straw [1], rice straw, birch and poplar. The goal of these experiments was to find those organosolv process conditions that give the best fractionation. The ‘best’ fractionation is defined by the combined value of the main products, i.e. cellulose and lignin. The process temperature, residence time, the ethanol:water ratio and amount of catalyst (H_2SO_4) were varied in a parametric study to find the optimal conditions for the four biomass feedstocks.

A conceptual process design, based on earlier work [3], was constructed using Aspen Plus simulation software. The goal of this conceptual process design was to investigate the economic differences between the different types of feedstock, which is caused by the different product yields as well as the different feedstock prices. In addition, it was investigated whether it is economically interesting to have a feedstock-flexible process, which can use multiple types of feedstock.

Process description

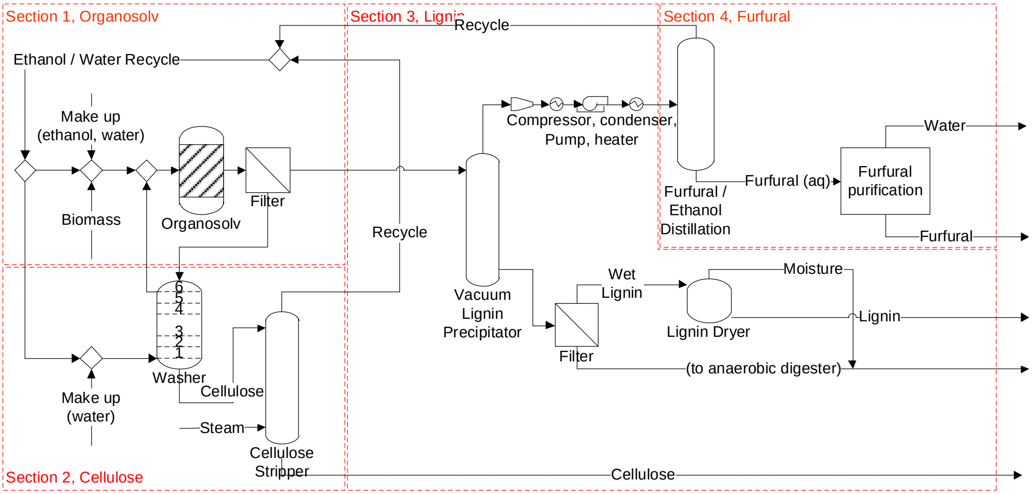

Figure 1. Process flow sheet of the organosolv biorefinery.[3]

The organosolv biorefinery is divided into four sections: the organosolv section, and three sections for the three products: the cellulose, lignin and furfural sections. The organosolv section includes a size-reduction (not included in the figure), the organosolv reactor where the biomass is fractionated, and a filter where the solid cellulose pulp is separated from the liquid phase.

In the cellulose section, first the cellulose is washed to remove undesirable components from the adhering liquid, such as dissolved lignin. The ethanol is then removed from the cellulose by steam stripping so it can be recycled.

The lignin section contains the lignin precipitator, where lignin precipitates because the ethanol is removed from the solution to be recycled. The ethanol vapour is compressed and recycled. The remaining liquid is removed from the solid lignin in a filter and a subsequent dryer. The liquid thus obtained contains some sugars and other organic components, and this can be used in an anaerobic digester to produce bio-gas. However, this is outside the scope of the current study.

In the furfural section, furfural and a few other small components such as acetic acid are removed from the recycle. Of those components, furfural is the only one that is considered a product, and it is therefore purified. Other components leave the process in the waste water stream.

Results

The optimal process conditions, as found in the screening for the four lignocellulosic feedstocks are presented in Table 1. These optimal process conditions are used as input for the conceptual process design.

Table 1. The optimal process conditions for the four lignocellulosic feedstocks.

Feedstock	**Birch**	**Wheat straw**	**Rice Straw**	**Poplar**
Temperature (°C)	190	200	210	190
H_2SO_4 (mM)	30	50	15	5
EtOH:H_2O (w/w)	60:40	60:40	60:40	50:50
CGCE (% wt) (*)	98%	89%	~100%	99%
Lignin recovery (% wt) (*)	79%	86%	95%	80%

(*) *CGCE (cellulose to glucose conversion efficiency) and lignin recovery are based on the raw dry weight biomass material*

Conceptual process design

Table 2 presents the mass balances of the four conceptual process designs. The products from the four types of feedstock are identical: cellulose, furfural and lignin. The product yields of cellulose, lignin and furfural as shown in Table 2 are the actual experimental results. The other results (moisture contents, as well as the waste water streams) originate from of the process modelling. In all cases, cellulose is the main product. Lignin is the second product, and furfural is the smallest product stream.

Table 2. Weight ratios of raw materials and products required for the organosolv process (biomass input = 1).

IN	**Birch**	**Wheat straw**	**Rice Straw**	**Poplar**
Biomass (dw)	1	1	1	1
Biomass (moist.)	0.116	0.116	0.116	0.116
Ethanol	0.004	0.004	0.004	0.004
Water (total)	1.54	1.56	1.55	1.56
OUT				
Cellulose (dw)	0.545	0.457	0.531	0.465
Cellulose moist.	0.774	0.649	0.754	0.660
Lignin (dw)	0.156	0.177	0.113	0.172
Lignin moisture	0.038	0.043	0.027	0.042
Furfural (pure)	0.012	0.040	0.067	0.039
waste water	0.333	0.320	0.320	0.320
CO_2	0.018	0.018	0.018	0.018
To digester	0.788	0.973	0.840	0.960

Economic analysis

In this analysis, five scenarios are included: four biorefineries using only a single type of feedstock, and a fifth concept where a biorefinery has the flexibility to change its feedstock, allowing the choice of the cheapest feedstock. The assumed costs of the feedstock are shown in Table 3. It is assumed that the four biorefineries using a single feedstock will pay the year average feedstock price, while the feedstock-flexible biorefinery will pay the lower values.

It is also assumed that the process is located in Western Europe. Wheat straw, birch and poplar are grown locally, and rice straw is imported. Transportation costs are included. The scale of the factory is 150 kton/yr. The process runs for 8 000 hrs/yr.

Table 3. Feedstock prices.

Biomass	Year average (€/ton dw)	Low value (€/ton dw)
Birch	60	45
Wheat Straw	70	55
Rice Straw (imported)	70	55
Poplar	60	45

Below, the economic analysis of the feedstock-flexible biorefinery is shown as an example. In this analysis, it is assumed that the feedstock-flexible biorefinery uses equal amounts of all four types of biomass. The amounts and costs of the raw materials are shown in Table 4.

Table 4. Raw materials costs of the feedstock-flexible biorefinery.

In	Scale (kton/yr)	price (€/ton dw)	M€/yr
Birch (dw)	37.5	45	1.69
Wheat straw (dw)	37.5	55	2.06
Rice Straw (dw)	37.5	55	2.06
Poplar (dw)	37.5	45	1.69
Ethanol	0.525	750	0.39
Water	234	1.75	0.41
Sub Total			8.30

The process is fully heat integrated. It is assumed that steam production is outsourced, and a price of 27 €/ton is assumed for steam. The waste water stream is assumed to cost 5 €/ton, even though it contains valuable organic components which can be used to produce bio-gas in an anaerobic digester. The utilities are listed in Table 5.

Table 5. Utilities of the feedstock-flexible biorefinery.

Item	Amount (kton/yr)	Price (€/ton)	Costs (M€/yr)
Steam (heating only)	183.6	27	4.96
Cooling water	10 903.3	0.05	0.55
Waste water treatment	174.6	5	0.87
	kWh/yr	Price (€/kWh)	M€/yr
Electricity	9 440 000	0.1	0.94
Total			7.32

The operating costs are estimated using a standard literature method [4]. The main items are the raw materials (8.30 M€/yr, Table 4), utilities (7.32 M€/yr, Table 5) and maintenance (6.55 M€/yr, or 7.5% of the capital investment costs). Other items such as labour, plant overhead and taxes bring the total operating costs to 32.8 M€/yr.

The plant income is the sum of the revenues from the three main products. Cellulose is the primary product, both in quantity as well as economically. It should be noted that cellulose quality was optimized for enzymatic hydrolysis, not for paper production.

Table 6. Income of the feedstock flexible biorefinery concept.

Product	Production (kton/yr)	Price (€/ton)	Income (M€)
Pulp (Cellulose)	74.9	350	26.2
Lignin	23.2	750	17.4
Furfural	5.9	625	3.7
Total			47.3

The capital investment was estimated using a standard literature method [4], and was based on the modelling results. The total fixed capital investment of all five biorefinery cases are shown in Table 7. The variation in the costs of the sections in the different scenarios depends on the different flow rates, which result from different product yields in the organosolv reactor. It was assumed that the size reduction (e.g. milling) is 50% more costly in the case of a flexible feedstock.

In all cases, the organosolv section is the most expensive, accounting for about a third of the total CAPEX. The organosolv section is also the process section where the uncertainty about the investment costs is highest.

The payback time is calculated using the income, operating costs (OPEX) and capital costs (CAPEX) as input. Table 7 shows that the organosolv biorefinery using birch as feedstock is the most profitable, which is largely due to the expected lower costs of the feedstock. The flexible-feedstock biorefinery is also economically interesting, despite being the concept with the highest investment costs.

Table 7. Overview economics of the organosolv biorefinery concepts.

	Birch	Wheat straw	Rice Straw	Poplar	Mixed feed
Income (M€/yr)	47.3	47.7	46.9	47.4	47.3
OPEX (M€/yr)	33.2	35.9	35.7	34.2	32.8
CAPEX (M€/yr)	81.7	82.0	80.0	81.8	87.3
Payback time (yr)	5.78	7.00	7.15	6.19	6.04

Conclusion

The process conditions of the organosolv process were optimized for four types of lignocellulosic feedstock. These optimized process conditions, and the resulting product yields were used as input for a conceptual process design and an economic evaluation. The economic evaluation shows that birch is the most economically interesting feedstock, because it is expected to be cheaper than for example straw, while almost the same amount of income can be generated.

It might also be economically interesting to have a feedstock-flexible process, allowing the choice of the cheapest feedstock. Despite a higher investment, reduced feedstock costs make this option economically interesting too.

The study has shown that a significant additional investment can be made without any penalties regarding the economic payback time of the process. Payback times of around 5–7 years seem feasible.

Acknowledgement

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References

1. Wildschut, J., Smit, A.T., Reith, J.H., Huijgen, W.J.J. 2012. Optimisation of ethanol-based organosolv fractionation of wheat straw for the production of lignin and enzymatically digestible cellulose. (Submitted.)

2. Huijgen, W.J.J., Smit, A.T., Reith, J.H., den Uil, H. 2011. Catalytic organosolv fractionation of willow wood and wheat straw as pretreatment for enzymatic cellulose hydrolysis. Journal of Chemical Technology & Biotechnology 86(11), pp. 1428–1438.

3. van der Linden, R. 2011. Conceptual Process Design and Sensitivity Analysis of an Organosolv Based Wheat Straw Biorefinery, XIX ISAF conference, Verona, Italy.

4. Sinnott, R.K. 1983. Coulson & Richardson’s Chemical Engineering, Volume 6, Butterworth Heinemann, Oxford.

Biobutanol from forest residues – a process utilizing SO_2-ethanol-water fractionation and ABE fermentation

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Abstract

A process for the production of biobutanol from forest residues, such as branches, tree tops and stump wood, is presented. Target of the process is to utilize cellulose and hemicellulose derived wood sugars as a feedstock for biofuel production by ABE (acetone-butanol-ethanol) fermentation technology. The presentation concentrates on the biomass fractionation technology and enzymatic hydrolysis to obtain sugars from biomass. Additionally, a summary is provided of the results obtained from spent liquor conditioning and subsequent fermentation of sugars to butanol.

It is demonstrated that the SO_2-ethanol-water (SEW) fractionation technology (which is used by API in a patented Biorefinery process called AVAP^{TM} [1]) efficiently fractionates both softwood and hardwood biomass in only 30 min at 150°C temperature. Hemicellulose sugars are dissolved in high yield (80%) in the spent fractionation liquor and of these up to 50% are in monomeric form. Sugar degradation products are not formed in notable quantities due to the short treatment time. Delignification is efficient, being 89% for HW biomass and 64% for SW biomass after only 20 min treatment. The spent liquor is conditioned for the recovery of cooking chemicals and to improve its properties for fermentation.

Cellulose remains as solid residue which therefore is enzymatically hydrolysed to obtain glucose. Glucose yields up to 95% are achieved for HW cellulosic residues utilizing a commercial enzyme mixture at 3% enzyme dosage on substrate whereas the SW residues are shown to require higher enzyme dosages. The differences in enzymatic digestibility are partially explained by the chemical characteristics of these feedstocks.

Fermentation of conditioned spent fractionation liquor has been successfully carried out using a patent pending fermentation column technology where wood pulp is used as cell immobilization material. ABE solvent mixtures were produced by a *Clostridium acetobutylicum* strain with productivity of 4.86 g/L/h and total yield of 0.27 g/g sugars with conditioned liquor from spruce chips fractionation. We are also developing a metabolically engineered Clostridium strain which is producing isopropanol instead of acetone in the ABE mixture.

Introduction

Global demand for biofuel is increasing fast. It is clear that in the future biofuels will be produced from lignocellulosic biomass such as agricultural and forest residues, energy crops and waste paper. Nevertheless, there are several obstacles to overcome in developing an economically viable process for the conversion of these feedstocks into biofuel. Cost effective fractionation and conversion technologies have to be developed. Ideally those should be able to treat various different types of biomass locally available.

This study presents a promising process where forest residues (tree tops, branches, stumps) are converted into a biofuel consisting of a mixture of isopropanol, butanol and ethanol. The flow diagram of the process is presented in Figure 1. In the first stage of the process forest biomass is fractionated using the SO_2-ethanol-water (SEW) fractionation technology to dissolve hemicelluloses and lignin in the spent liquor [2, 3]. The method is highly suitable for biorefineries since contrary to acid sulphite treatment it is omnivorous, does not require an impregnation stage or cause oxidation of sugars. Additionally, it allows more economical scale due to the simple recovery of ethanol and SO_2 by evaporation and condensation/absorption.

After evaporation to recover cooking chemicals, the spent liquor is conditioned through steam stripping, liming and catalytic oxidation to improve its properties for fermentation [4, 5]. SO_2 has to be fully removed and recovered due to its toxicity to the ABE bacteria, as well as due to the economical viability of the process. Other inhibitors including lignin, furanic compounds and formic acid must also be removed.

Cellulose is preserved in the solid residue and undergoes enzymatic hydrolysis for the recovery of glucose from cellulose and mannose and xylose from residual hemicelluloses in the pulp [6]. The target of our studies was to determine the rate of hydrolysis, glucose yields and the effect of pulp properties on enzymatic digestibility.

In the final stage of the process, sugar streams are subjected to acetone-butanol-ethanol (ABE) fermentation by Clostridia to produce biochemicals suitable as drop-in fuel [7, 8]. A metabolically engineered *C. acetobutylicum* strain which is producing isopropanol instead of acetone is also under development [9]. In this presentation, we review the most important outcomes of this research project.

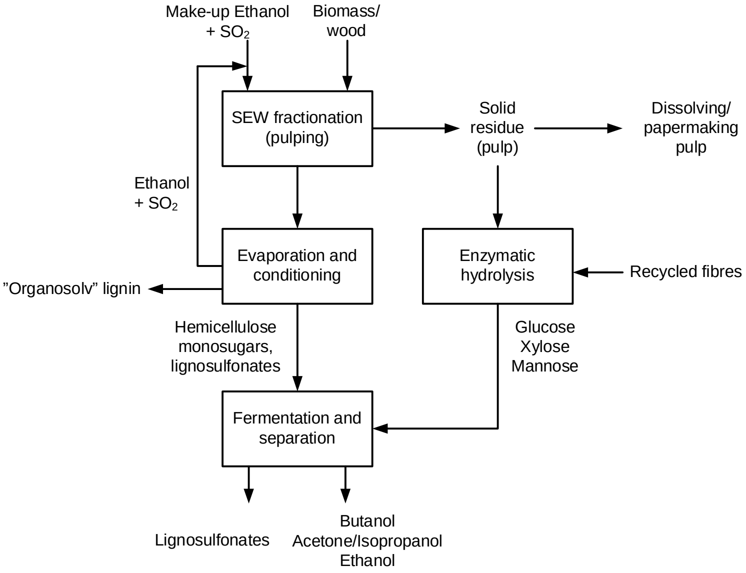

Figure 1. Flow diagram of the process.

Experimental

The raw materials used in the fractionation experiments were air dried screened hardwood (HW) and softwood (SW) biomass residues consisting of logging residues such as branches. The biomass was fractionated using the SEW fractionation method at the following conditions: temperature 150°C, SO_2 concentration 12%, ethanol concentration 55% (v/v), liquor-to-wood ratio (L:W) 6:1 L/kg and fractionation time 20/30/60 min. Experiments have also been demonstrated at a lower L:W ratio (3:1) more suitable for commercial practise [5]. Mass balances of fractionation were determined by analysing the chemical composition of raw materials, solid residues of fractionation (pulps) and spent liquors. More details about the fractionation method and the analysis methods used have been published earlier [2, 3].

Enzymatic hydrolysis experiments were carried out according to NREL technical report [10]. The commercial enzyme mixture Cellic CTec2 from Novozymes was used.

The spent liquor was conditioned by first evaporating it under vacuum until about 70% weight reduction to remove SO_2 and ethanol. Subsequently, steam stripping was done where residual SO_2 was almost totally removed. Overliming with $Ca(OH)_2$ was done to remove some inhibitors and to make liquor suitable for fermentation [11]. Finally, the liquor was catalytically oxidized to convert residual sulfite ions to sulfate and fully eliminate the remaining SO_2. The iron catalyst also functioned as a micronutrient source to Clostridia bacteria. [5]

At lab scale, batch as well as column fermentation experiment were performed using spent liquor as a substrate for *Clostridia acetobutylicum* DSM 792. The batch experiments were carried out in 125 ml screw cap bottles with 50 ml production medium. It was purged with nitrogen and autoclaved at 105 Pa (121°C) for 20 min and cooled. It was inoculated (5% v/v) with 20 h actively growing seed culture and incubated for 96 h at 37°C. The effect of dilution of SEW liquor was studied on production of solvents. The SEW spent liquor was diluted as 2-fold, 4-fold and 8-fold with water to make it suitable for growth and fermentation of clostridia. The effect of supplementing extra glucose (15, 25 and 35 g/l) to the 4-fold diluted SEW liquor was also studied to simulate the addition of glucose derived from the pulp. The medium composition obtained was tested for continuous operation. The effect of dilution rate on solvent production, productivity and yield was studied in column reactor consisting of immobilized *Clostridium acetobutylicum* on wood pulp.

Results and discussion

The results obtained and published [2–8, 12] in this project have revealed the high potential of this process as a future biorefinery platform during the past four years. Here, we shortly discuss the main findings obtained within each stage of the process.

Fractionation of biomass

SEW method has been shown to fractionate different types of biomass very rapidly and the kinetics of fractionation are similar for different species [2, 3]. Also HW and SW biomass derived from forest residues are efficiently fractionated by this method. For example, 30 min treatment (including the heat-up time) at 150°C temperature dissolves 80% of hemicellulose sugar in the spent liquor without notable degradation of the dissolved sugars. About half of the dissolved hemicelluloses are present in monomeric form and the share increases during subsequent conditioning. Cellulose remains in the solid residue. Acetyl groups and uronic acids from the hemicellulose side chains are almost fully dissolved within the first 30 minutes. However, if fractionation time is extended, uronic acids and hemicellulose sugars start to gradually degrade forming products such as CO_2 and furfural, respectively.

Delignification is rapid especially for HW biomass since 90% of lignin is removed within 20 min treatment. SW biomass delignification is notably slower; only 64% lignin is removed within 20 minutes. Reasons related to the slow delignification are suspected to be the higher ash and extractives content in SW biomass.

Figure 2 presents the mass balances of HW and SW fractionation based on the components distribution in the raw material, solid residue and spent liquor.

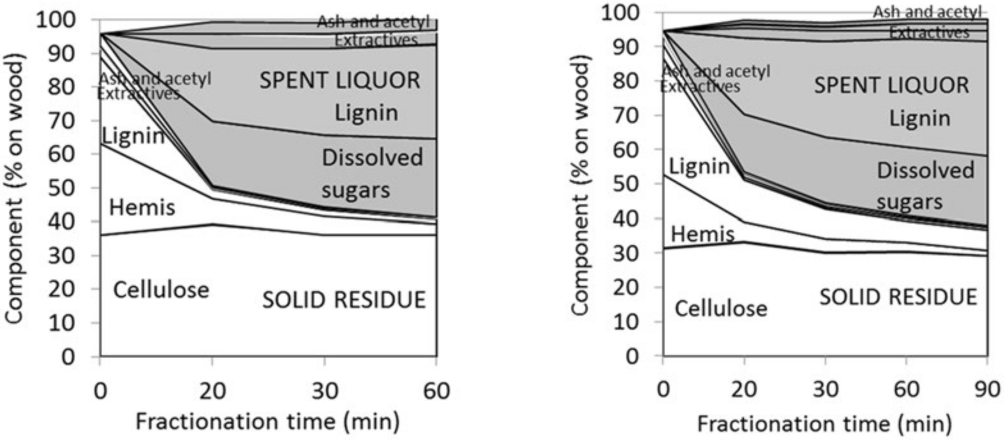

Figure 2. The distribution of wood components in solid residue and spent liquor during HW (left) and SW (right) biomass SEW fractionation at 150° and 12% SO_2 concentration.

Enzymatic hydrolysis of the solid residues of fractionation

The results obtained on enzymatic hydrolysis have revealed that SEW residues can be efficiently hydrolysed as long as their lignin content is low [6]. In our studies, the main inhibitor for efficient hydrolysis was found to be the residual lignin in the solid residues. Thereby, HW pulps with low lignin content (4–6%) gave 95% glucose yields with 3% enzyme dosage on pulp (4.8 FPU/g cellulose), whereas SW pulps (lignin content 17–21%) required 10% dosage on pulp (19.2 FPU/g cellulose) to reach 85% glucose yields. Nevertheless, the enzymatic digestibility of SEW SW pulps is comparable to that reported in the literature for a variety of different pretreated SW biomass feedstocks. We also found that hydrolysis yields of SW pulps can be improved and enzyme dosage reduced by optimizing the enzyme mixtures. We are also working on improving the delignification of SW biomass since this was found to be critical for successful enzymatic hydrolysis.

Spent liquor conditioning

The conditioning results of the SW spent liquors [5] show that the final treated liquor is suitable for fermentation. The amount of fermentation inhibitors in the liquor is very low and about 70% of the sugars are present in monomeric form. Sugar concentrations of 62.0 g/L or 13.0 g/ 100 g OD SW biomass have been obtained for the final conditioned liquor. However, there is still room for improvement since about 30% of the sugars are lost during the entire conditioning process. Additionally, a more complete removal of lignin from the spent liquor may be necessary to increase the liquor fermentability.

ABE fermentation

The ABE fermentation technology has been optimized for the production of commodity chemicals from SEW conditioned spent liquors. Within this project a patent pending fermentation column, which facilitates efficient fermentation with high solvent productivity, has been demonstrated [12]. ABE fermentation tests show that the conditioned and resin treated spruce chips liquors are fermentable by *C. acetobutylicum* DSM 792 upon 4-fold dilution and supplementation with glucose. In batch experiments, the maximum concentration of total ABE was found to be 8.79 g/l using 4-fold diluted SEW liquor supplemented with 35 g/l of glucose. In continuous column experiments, ABE solvents are produced at a total yield of about 0.27 g/g sugars and with productivity of 4.86 g/L/h [8].

Further improvements in productivity and yields of solvents are expected as part of present work to scale-up the column technology.

We are also working on the metabolically engineered Clostridium strain which produces isopropanol instead of acetone. Additionally, a continuous solvent recovery system will be developed.

Conclusions

The SO_2-ethanol-water method is an attractive option for the fractionation of lignocellulosic biomass. Lignin and hemicelluloses rapidly dissolve in the spent fractionation liquor whereas cellulose fraction fully remains in the fibers as a source of glucose obtained in high yield by enzymatic hydrolysis.

Ethanol and SO_2 are recovered from the spent fractionation liquor, and then the liquor is conditioned to form an aqueous solution containing a high concentration of hemicellulose monosugars. The final conditioned liquor is fermentable by Clostridia bacteria to isopropanol, butanol and ethanol with or without supplementation by glucose obtained from the enzymatic hydrolysis. Further optimization and improvement of all process steps of this Biorefinery platform are ongoing.

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References

1. Retsina, T. et al. Method for the production of fermentable sugars and cellulose from lignocellulosic material, U.S Patent No. 8,030,039, October 4, 2011.

2. Iakovlev, M. 2011. SO_2-Ethanol-Water (SEW) Fractionation of Lignocellulosics. Doctoral dissertation, Aalto University, Finland.

3. Yamamoto, M., Iakovlev, M., Van Heiningen, A. 2011. Total mass balances of SO_2-ethanol-water (SEW) fractionation of forest biomass. Holzforschung 65(4), pp. 559–565.

4. Sklavounos, E., Iakovlev, M., Yamamoto, M., Teräsvuori, L., Jurgens, G., Granström, T., Van Heiningen, A. 2011. Conditioning of SO_2-ethanol-water spent liquor from spruce for the production of chemicals by ABE fermentation. Holzforschung 65(4), pp. 551–558.

5. Sklavounos, E., Iakovlev, M., Van Heiningen, A. 2012. Study on conditioning of SO_2-ethanol-water spent liquor from spruce chips/softwood biomass for ABE fermentation. European Workshop on Lignocellulosics and Pulp (EWLP), Espoo, Finland, August 27–30.

6. Yamamoto, M., Iakovlev, M., Van Heiningen, A. 2012. Enzymatic hydrolysis of hardwood and softwood biomass fibers released by SO_2-ethanol-water fractionation. European Workshop on Lignocellulosics and Pulp (EWLP), Espoo, Finland, August 27–30.

7. Jurgens, G., Survase, S., Berezina, O., Sklavounos, E., Linnekoski, J., Kurkijärvi, A., Väkevä, M., van Heiningen, A., Granström, T. 2012. Butanol production from lignocellulosics. Biotechnology Letters 34(8), pp. 1415–1434.

8. Survase, S.A., Sklavounos, E., Jurgens, G., van Heiningen, A., Granström, T. 2011. Continuous acetone-butanol-ethanol fermentation using SO_2-ethanol-water spent liquor from spruce. Bioresource technology 102(23), pp. 10996–11002.

9. Lee, J., Jang, Y.-S, Choi, S.J., Im, J.A., Song, H., Cho, J.H., Seung, D.Y., Terry Papoutsakis, E., Bennett, G.N., Lee, S.Y. 2012. Metabolic Engineering of Clostridium Acetobutylicum ATCC 824 for Isopropanol-Butanol-Ethanol Fermentation. Applied and Environmental Microbiology 78(5), pp. 1416–1423.

10. Selig, M., Weiss, N., Ji, Y. 2008. Enzymatic Saccharification of Lignocellulosic Biomass. NREL Laboratory Analytical Procedure (LAP).

11. Qureshi, N., Saha, B.C., Dien, B., Hector, R.E., Cotta, M.A. 2010. Production of butanol (a biofuel) from agricultural residues: Part I – Use of barley straw hydrolysates. Biomass Bioenergy 34, pp. 559–565.

12. Survase, S.A., van Heiningen, A., Granström, T. 2012. Continuous bio-catalytic conversion of sugar mixture to acetone-butanol-ethanol by immobilized Clostridium acetobutylicum DSM 792. Applied Microbiology and Biotechnology 93(6), pp. 2309–2316.

Upgrading pulp mill waste streams for integration with fish farming

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The Processum pre-study

Background

Processum Biorefinery Initiative has, financed by Vinnova, made a pre-study of the technical and economical potential to integrate a pulp mill with land based fish farming in recirculated systems. The investigation was performed by ÅF in collaboration with Eurocon. A reference group with experts from the Domsjö mill and connected industries, fish handling and distribution companies, experienced fish farmers, regional organisations with interests in fish farming and researchers from SLU, were consulted during the project. The main purpose of the pre-study was to assess the potential synergies in utilizing waste heat from the industry for warming, cross utilization of waste water nutrients and fermentation of sugars into fish feed proteins.

The concept has a potential to decrease the environmental impact from fish farming and promote more sustainable fish production by minimizing water effluents both from pulp mills and fish breeding and simultaneously avoiding large scale “vacuum cleaning” of oceans for scrap fish converted into fish feed.

With the Domsjö sulphite mill as the case studied, the investment and operating costs have been assessed for a plant producing 300 t/y of Tilapia. The technical concept evaluated in this study is based on experience from Dr. Ragnar Johannsson and the pilot plant for production of tilapia which has already been in successful operation on Iceland for several years. Eurocon has modified the concept to be applicable for the northern Swedish conditions and integration with the Domsjö Mill.

Results and conclusions

The Processum pre-study results in a design of a possible fish breeding plant integrated with the Domsjö mill placed in an available building. The pre-study also shows a first investment- and profitability calculation and important connections have been made with possible partners regarding fish-handling and distribution.

The pre-study concludes that 300 t/y is a too small production but that a 10 times larger scale may have the potential to be economically viable, provided that “sustainable grown fresh fish filets” can be marketed at price levels comparable to high quality salmon or perch filets.

The values of the synergies are tentatively estimated and the conclusion is that the largest potential is in integrated protein production from dissolved and hydrolyzed sugars in the spent black liquor and waste streams. The fermentation of these into suitable high quality proteins are presently under study by Processum Biorefinery Initiative in a couple of projects.

Issues that need to be further investigated, besides finding a location which makes a ten times larger plant possible, are to evaluate the identified synergies for this larger scale plant, for example:

- Possibilities to use nitrogen and phosphorus from the fish plant waste water to reduce chemical costs in the mill external cleaning plant.

- Possibilities to replace the most expensive proteins in the commercial fish feed with proteins produced from the mill waste streams.
- Evaluation of the advantages with locally produced fish feed.

Production of tropical fish and fish feed – experience from Iceland

Background

Constant innovation has made it possible to farm tropical and subtropical fish in cold climates. Faming close to the target markets has a benefit for producers and profitable units can be built to bend the course of nature and produce fresh products that otherwise would have to be imported from elsewhere to meet market demands.

The performed Processum pre-study is based on several years of experience regarding production of the tropical fish tilapia in a pilot plant on Iceland.

Tilapia grows very fast at 28°C and is not prone to sicknesses and easy to farm. Tilapia has been farmed all over the world for centuries – as far back as ancient Egypt. In fact, many believe tilapia is the fish Jesus used to feed the 5 000. Tilapia is one of the top five most popular fish in the USA. Tilapia filets are white and firm with mild flavour. The production per unit is much higher than in trout or char per unit area which makes tilapia more productive in a sustainable way than producing trout or arctic char. As an omnivorous species (eat both plant and animal material as their primary food sources) tilapia feed formulation can include more varieties of raw materials than carnivores fish like trout.

Recirculation systems and Benefits of Closed Culture Systems

Recirculation systems are aquaculture systems (RAS) in which the majority of water is reused following the removal of solids and the biological conversion of dissolved ammonia to nitrate. Water quality and chemistry is often modified before the water is returned to the fish. Regulations of water supplies (quality and quantity), waste discharges and health regulations are becoming more and more onerous for the industry. The Major system components are the following:

- Solids Removal: The first step in recirculation of water is the removal of solids. Inadequate solids removal can result in elevated ammonia levels, low oxygen levels, lower system carrying capacity, reduced water clarity, higher aeration/oxygenation costs and a poorer quality fish product. Solids removal is very important because it dramatically reduces the organic content of the water. For solids removal drum filters with 100 µm filter are used.
- The next step is bio-filtration. Bio-filtration is the use of naturally occurring bacteria to convert toxic ammonia to non-toxic nitrate through the toxic intermediate nitrite. This process is often called nitrification or ammonia oxidation. Two genera (or groups) of bacteria accomplish this process. The group of bacteria that convert ammonia to nitrite is named Nitrosomonas and the group of bacteria that convert nitrite to nitrate is named Nitrobacteria.
- Circular tanks are used to ensure good hydraulic properties and proper self-cleaning of the tanks. Aeration and Oxygenation: Following bio-filtration, the water requires further water quality or chemistry modification before returning to the fish. As previously mentioned, nitrifying bacteria remove dissolved oxygen and lower pH. Therefore, water has to be aerated to remove CO_2 from the water and oxygenated before returning to production tanks.

Benefits of fish farming close to pulp production site

Water exchange in a RAS farm projected is in the range of 5–15% although lower exchange can be achieved. The water demand of a 500 ton farm would be in the range of 3–5 liters per second of new cold water. The water needs to be heated to 28°C. Freshwater of sufficient quality for farming of tilapia and low temperature heat is usually available on pulp production sites. The waste water from the farming can be processed in the waste water treatment system of the plant and in some cases depending on characteristics of receiving water bodies, be directly sent away after in-house solids removal in farm.

How to continue?

Although the Processum pre-study concludes that the scale studied here is too small to be profitable, possible future potential is identified for larger scale production. For different reasons the Domsjö Mill today do not have the possibility to prioritize working with these issues. However, there are a couple of contractors interested in building and running a plant, if, the right mill and the right location can be found.

In order to move towards realization of the idea with an industrially integrated fish plant a couple of questions need to be answered before a sharp investment calculation can be made.

Initial key questions are:

- Location, are there suitable buildings or areas available?
- Do you have access to warm waste water, what amounts and temperatures?
- Is it possible to use the existing biological treatment plant? (Are there room for extra load today?)

Welcome to unconditional initial discussions!

References

1. Dey, R. 2012. Coming from the Cold. Fish farming International January 2012, p. 23 http://www.intrafish.com.

2. Mutter, R. 2012. The Tropics come to England. Fish farming International August 2011, p. 34. http://www.intrafish.com.

3. Dey, R. Poles apart. Fish farming International April 2012, p. 28. http://www.intrafish.com.

FPInnovations’ novel fractionation process for lignocellulosic biomass

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Abstract

Despite tremendous research efforts around the world, the recalcitrance of cellulosic biomass remains a critical challenge for the lignocellulosic biomass-based biorefinery. Due to the nature of many pretreatment technologies that generate various inhibitors, many sugar streams produced from lignocellulosic biomass have difficulty to be directly fermented into the target bio-products.

FPInnovations has developed a mechanical fractionation process (MFP) which converts cellulosic biomass into various value-added bio-products. The process includes biomass pretreatment, enzymatic hydrolysis and lignin extraction technologies. The pretreatment of biomass consists of a mild chemical treatment and a mechanical refining stage that can be easily retrofitted into an existing pulp mill infrastructure at a large scale. Based on commercial enzymes, we successfully developed an enzyme formulation which can achieve simultaneous hydrolysis of both glucan and xylan with yields above 90% at high solids loading. Our results also show that the clean and highly-concentrated sugar stream (140 g/L) from this process can be directly fermented to butanol, ethanol, succinic acid, and lactic acid at yields of 33%, 47%, 76%, and 84%, respectively.

Introduction

The polysaccharides (hemicellulose and cellulose) present in native lignocellulosic biomass are highly resistant to enzymatic hydrolysis. This is mainly attributed to: 1) a high degree of polymerization and crystallinity of the cellulose; 2) the close association and complexity of the lignin-carbohydrate complexes (LCC); and 3) lignin and hemicellulose both acting as barriers preventing the access of cellulase enzymes to cellulose. Besides, lignin also appears to reduce enzyme hydrolysis efficiency by acting as an attractant to enzyme proteins resulting in non-productive binding. To overcome the recalcitrance of the cellulosic biomass, partial removal of hemicellulose and lignin are believed to be essential to improve digestibility of biomass. During the last two decades, tremendous efforts have been made in developing the biomass pretreatment technologies and numerous pretreatment methods have been developed. These pretreatment technologies are generally categorized as mechanical, physico-chemical (e.g., autohydrolysis, liquid hot water, steam explosion), chemical (e.g., alkali, acid, organic solvents, oxidizing agents) and biological (e.g., fungi) processes or combinations of these approaches [1, 2].

Despite the tremendous efforts, pretreatment remains a critical step in the process for converting lignocellulosic biomass to bio-fuel and other valuable chemicals. It is still one of the most costly steps and has a major influence on the cost of both prior (e.g., size reduction) and subsequent (e.g., enzymatic hydrolysis and fermentation) operations [3]. Among the existing technologies, steam explosion is the closest to commercialization, and there are several pilot and pre-commercial plants based on steam explosion pretreatment technology (e.g., Iogen, Chemtex, and Mascoma). However, steam explosion is expensive to scale-up to industrial scale; other limitations of this technology also include partial degradation of hemicelluloses, incomplete disruption of the biomass structure, and generation of inhibitors (furfural and 5-hydroxymethyl furfural (HMF) etc.) for subsequent fermentation processes [4, 5].

FPInnovations has developed a patent-pending novel Mechanical Fractionation Process (MFP) for lignocellulosic biomass. The technology produces a highly digestible biomass from which a clean, concentrated sugar stream and a high-quality, sulfur-free lignin can be generated on large scales. The MFP technology opens the door for producing various biofuels and biochemicals from a renewable non-food lignocellulosic biomass. The paper will discuss the results on aspen wood chips.

Novel Fractionation Process for Lignocellulosic Biomass

FPInnovations patent-pending biomass fractionation process mainly includes three technologies: 1) a unique biomass pretreatment technology; 2) a robust enzymatic hydrolysis technology; and 3) a lignin extraction technology. As illustrated in Figure 1, lignocellulosic biomass will first be pretreated to produce a highly digestible biomass. After enzymatic hydrolysis, the biomass will be separated into tow streams: 1) a mixed C5/C6 sugars; and 2) hydrolysis lignin which contains about 55–65% lignin depending on the carbohydrates conversion yield in the enzymatic hydrolysis process. A high purity, sulphur-free lignin (E-lignin) can also be extracted from the hydrolysis lignin. All process streams will be used to generate various bioproducts.

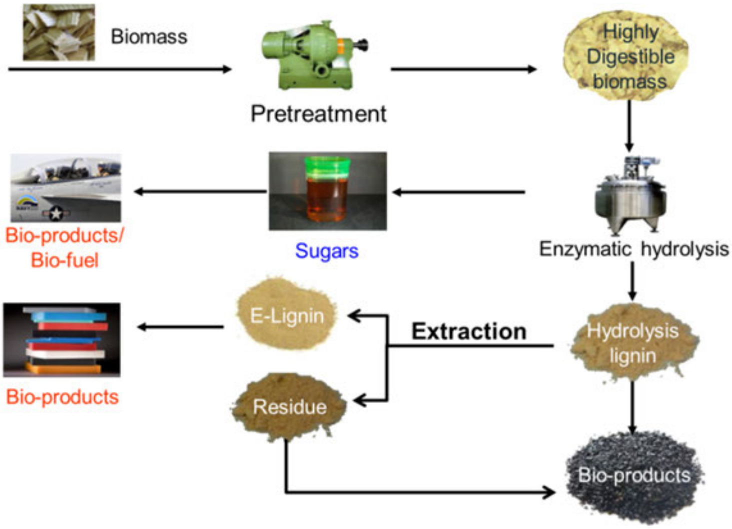

Figure 1. Mechanical Fractionation Process.

Unique biomass pretreatment technology

The pretreatment technology consists of a mild chemical treatment and a mechanical refining. Compared to current pretreatment technologies such as steam explosion, hot water-extraction, ammonia and lime pretreatment, our pretreatment process has many advantages, and can utilize the existing idled/closed pulp & paper facilities in scaling up. The process employs low-pressure mechanical refining using minimum energy input to disintegrate the lignocellulosic feedstock. This facilitates the separation and fractionation of hemicellulose, cellulose and lignin in the subsequent processes. Due to the mild pretreatment conditions, only a small portion of hemicelluloses and lignin are removed in the pretreatment process. The resulting biomass has very similar chemical composition as the original biomass as shown in Table 1. We believe under such designed mild pretreatment conditions, the chemical linkages between xylan and lignin are modified or cleaved, but the degradations of these two components are minimal.

Table 1. Chemical components in percentage of aspen before and after pretreatment.

	Glucan	**Xylan**	**Lignin**	**Others Carbs.**	**Extractives**	**Total**
Origin biomass	47.07	16.68	23.62	5.60	1.61	94.58
Pretreated biomass	54.71	14.37	23.10	2.91	0.35	95.44

As shown in Figure 2, for grounded aspen coarse particles, the glucose yield from subsequent enzymatic hydrolysis can only reach 14% even at a very high enzyme dosage (60 FPU/g glucan). By refining, glucan conversion can be improved to 31%. Furthermore, by combining a chemical treatment with refining, the glucose yield can be significantly improved to 82%, which is about 5 times higher than that of untreated biomass. The high glucan conversion yield clearly indicated that our pretreated biomass is highly accessible to enzymes. Further optimization of enzyme formulation to match the characteristics of the pretreated biomass has been conducted and a robust enzymatic hydrolysis technology has been developed.

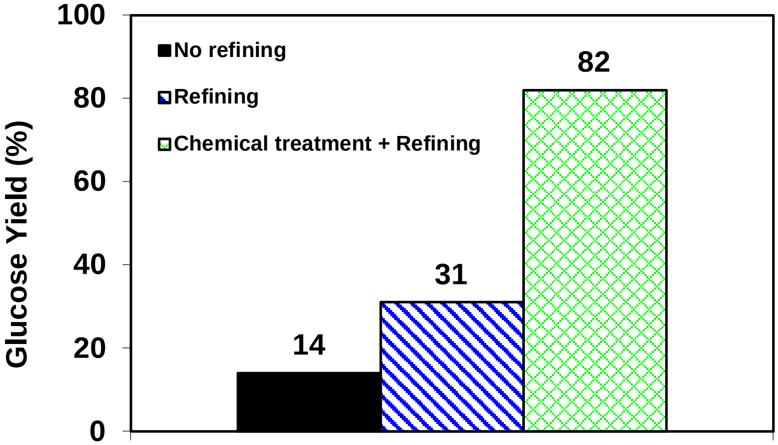

Figure 2. Effect of pretreatment methods on biomass digestibility with Celluclast 1.5L. Enzymatic hydrolysis conditions: 2% solid loading at 60 FPU/g of glucan for 72 hours, 50°C, 150 rpm in shaking incubator, 50 mM sodium acetate buffer at pH4.8, 100g total reaction mass in 250ml flasks.

Robust Enzymatic Hydrolysis Technology

Detailed studies of the enzymatic hydrolysis profiles for both glucan and xylan indicated that the conversion of glucan is the bottleneck of the whole enzymatic hydrolysis process, as shown in Figure 3 (A). With the fact that amount of high lignin and hemicellulose presented in our pretreated biomass, we believe that simultaneously hydrolyzing both glucan and xylan is the key to improve the efficiency of the enzymatic hydrolysis. By supplementing with other enzymes and additives, we developed a set of enzyme formulations based on three key enzymes from Novozymes, namely, Celluclast 1.5L, Novozymes 22C, and Cellic Ctec1. All three formulations worked quite well resulting in carbohydrate conversion yields above 85% in 3 days at an enzyme charge of 20FPU/g of glucan. The most promising formulation (Ctec 1 based *F3*) can simultaneously hydrolyze both glucan and xylan with carbohydrate conversion close to 100% in three days, as shown in Figure 3 (B).

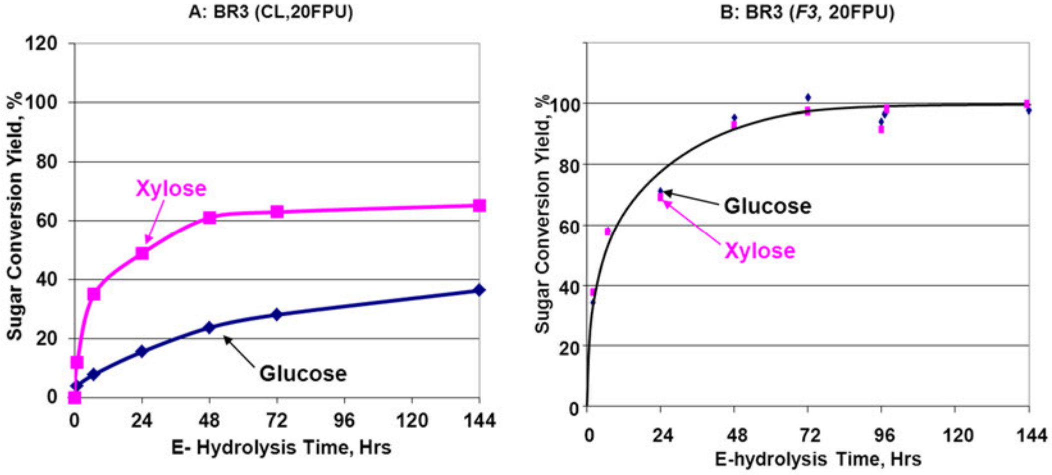

Figure 3. With the enzyme formulation F3 at 20 FPU/g glucan, enzymatic hydrolysis bottleneck is eliminated with glucan and xylan being simultaneously hydrolyzed. A: Celluclast 1.5L alone at 20 FPU/g of glucan; B: the Cellic Ctec1 based formulation at 20 FPU/g of glucan with other supplement enzymes and an additive. Other conditions are the same as in Figure 2.

The statistical model was built to further optimize the enzyme formulation. The additives we identified works extremely well with the pretreated biomass, especially at low enzyme dosage. As shown in Figure 4, an increase of 50% in glucan conversion yield can be achieved at 5 FPU/g of glucan. This is equivalent to an enzyme charge of 2% on the biomass. At this low enzyme dosage, carbohydrate conversion reached 61% and 78% after 3 days and 6 days of hydrolysis, respectively. We believe there is still potential to further improve the hydrolysis efficiency with Novozymes' new Cellic Ctec 3 enzyme formulation.

In the industrial applications, enzymatic hydrolysis at high solids loading is essential for operational and economic reasons. However, much prior research has indicated that increased solids loading will result in a dramatic decrease in the carbohydrate conversion yield. For example, Henning et al. [4] showed that the carbohydrate conversion yield decreased from 90% to below 60% when solids loading increased from 2% to 20%, and stated that cellulose and hemicellulose conversion decreased almost linearly with increasing solids loading. Our research has indicated that biomass liquefaction is the key in high solids loading hydrolysis, and it varied greatly with different hydrolysis reactors. Some reactors required up to 5 days for liquefaction, while other reactors needed only a few hours. We successfully developed a 60-liter reactor able to run enzymatic hydrolysis at up to 20% solids loading. As shown in Figure 5, biomass can be liquefied within 5 hours in general, and carbohydrate conversion can reach greater than 85% in three days at 18 FPU/g of glucan. This indicated that our enzyme formulation and additives also work very well at high solid loading.

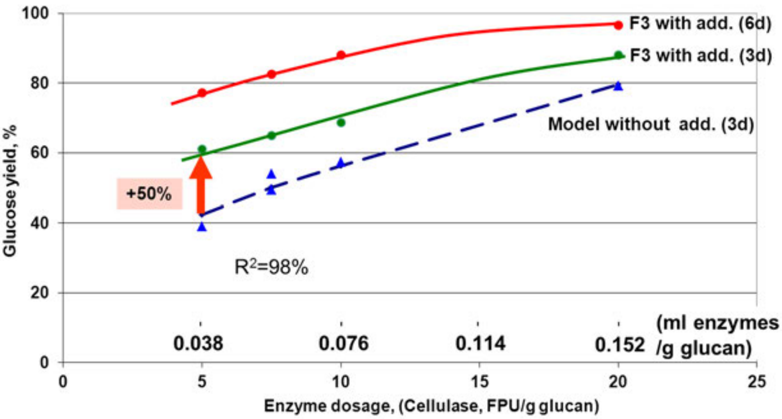

Figure 4. Robust enzyme formulation (*F3*) and additive towards low enzyme dosage. The enzymatic hydrolysis conditions are the same as in Figure 2.

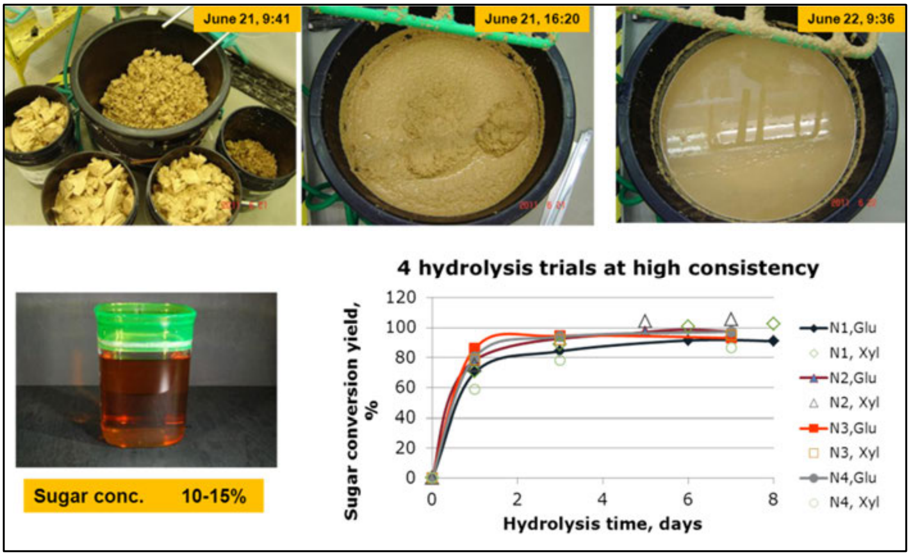

Figure 5. High solid loading enzymatic hydrolysis with *F3* enzyme formulation. Hydrolysis conditions: 15% solid loading (6kg of biomass in 40kg of slurry) at 18 FPU/g of glucan, 50°C, 50 mM sodium acetate buffer at pH4.8, 20 rpm/min (intermittent mixing).

Value-added Products form Lignin and Sugars

Mechanical Fractionation Process generates a clean, concentrated sugar stream due to the mild pretreatment conditions and the high solids enzymatic hydrolysis technology. The sugar stream was free of most inhibitors and only contained a small amount of acetic acid, as showed in Table 2. Without any pre-conditioning of the sugar stream, we further evaluated various fermentation pathways to different sugar products. As summarized in Table 3, the sugar stream from our process can be directly fermented to butanol, succinic acid, lactic acid, and ethanol with yields of 33%, 76%, 84%, and 47%, respectively. These results were obtained with only a few trials under typical fermentation conditions; optimization will most likely further improve the efficiencies of the fermentation for these products.

In addition, we are also working towards developing value-added products from the solid product stream from enzymatic hydrolysis. The mild biomass pretreatment process along with high enzymatic conversion of carbohydrate produces a solid stream enriched in lignin. A pure lignin can be readily extracted from this solid stream with a very mild solvent extraction process. The isolated lignin chemically resembles native lignin, and is of high purity having low carbohydrate, low ash content and sulfur free. This lignin has potential to be used in high value products such as carbon fibre precursor, polyol substitute in polyurethane foams, and phenol substitute in resins etc.

Table 2. Sugar compositions from mechanical fractionation process (20% solid loading in EH).

Component	**Glucose**	**Xylose**	**Oligo-saccharides**	**Furfural, HMF**	**Levulinic acid**	**Lactic, Formic acid**	**Acetic acid**
Conc. (g/L)	90.9	29.0	10.2	0	0	0	3.3

Table 3. Pathways to various value-added sugar products.

Sugar products	**Starting Sugar conc., g/L**	**Consumed sugar**	**Yield, %**	**Product conc., g/L**
Ethanol	74	Glucose	47	34
Butanol	79	Glu/Xyl	33	15
Lactic acid	88	Glu/Xyl	84	69
Succinic acid	77	Glu/Xyl	76	37

Conclusions

FPInnovations has developed a novel mechanical fractionation process (MFP) for lignocellulosic biomass that can produce highly digestible biomass for enzymatic hydrolysis. The process can be easily scaled up for large industrial application. Based on commercial enzymes, we successfully developed an enzyme formulation which can achieve simultaneous hydrolysis of both glucan and xylan with yields above 90% at high solids loading. Our results also showed that the clean and highly concentrated sugar stream from this process can be directly fermented to ethanol, butanol, lactic acid and succinic acid with yields of 47%, 33%, 84% and 76% respectively.

Acknowledgement

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References

1. Hendriks, A.T.W.M., Zeeman, G. 2009. Pretreatments to enhance the digestibility of lignocellulosic biomass. Bioresource Technology 100, pp. 10–18.

2. Wyman, C.E., Dale, B.E., Elander, R.T., Holtzapple, M., Ladisch, M.R., Lee, Y.Y. 2005. Coordinated development of leading biomass pretreatment technologies. Bioresource Technology 96, pp. 1959–1966.

3. Langan, P., Gnanakaran, S., Rector, K.D., Pawley, N., Fox, D.T., Cho, D.W., Hammel, K.E. 2011. Exploring new strategies for cellulosic biofuels production. Energy. Environ. Sci. 4, pp. 3820–3833.

4. Jørgensen, H., Vibe-Pedersen, J., Larsen, J., Felby, C. 2007. Liquefaction of Lignocellulose at high-Solids Concentrations. Biotechnology and Bioengineering 96(5), pp. 862–870.

5. Cantarella, M., Cantarella, L., Gallifuoco, A., Spera, A., Alfani, F. 2004. Effect of inhibitors released Turing steam-explosion treatment of poplar wood on subsequent enzymatic hydrolysis and SSF. Biotechnol Progr 20, pp. 200–206.

6. Garcia-Aparicio, M.P., Ballesteros, I., Gonzalez, A., Oliva, J.M., Ballesteros, M., Negro, M.J. 2006. Effect of inhibitors released during steam-explosion pretreatment of barley straw on enzymatic hydrolysis. Appl Biochem Biotechnol 129, pp. 278–288.

Co-production of renewable polymers and ethanol from eucalyptus-based pulp mills

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Abstract

As biorefinery production plants start to deliver products on a larger scale it is becoming clearer what value chains can be expected to be realized first. One such chain is polyethylene production via ethanol, which is already being commercialized in Brazil on a scale of several hundred thousand tonnes per year. Sugarcane ethanol previously used mainly as a biofuel is thus finding its way into a new market as a chemical intermediate, making it an interesting product both for stakeholders that have the potential to produce clean sugar streams on a large scale and for downstream producers of chemicals that currently rely on fossil raw materials.

Ethanol production from *lignocellulosic* raw materials will generate multiple streams, since only a certain fraction of the material can be converted into sugars and then fermented to ethanol. This requires a 'poly-generation' approach, where by-products also must have high value (e.g. lignin, sugars from hemicellulose). To reach the large scale required for profitability, it is proposed that the best way is to integrate the new processes with existing industries, preferably those that already operate biomass-to-materials or biomass-to-fuels plants. The two largest industry branches in this respect are the pulp and paper and the sugar cane ethanol industries. In a collaborative project, POLYNOL, between Swedish and Brazilian companies, research institutes and universities these opportunities will be explored.

Introduction

The demand for materials, chemicals and fuels produced from renewable raw materials is increasing rapidly, in line with a decreasing supply of fossil resources and increasing costs for these. Industry needs to replace an ever larger share of the non-renewable raw materials, and at the same time ensure that production processes and value chains are as resource efficient as possible. This is a great challenge, since the forest and agricultural products that are possible raw materials demand very large scale handling of large volumes of solid material that needs to be grown, harvested, transported and processed in an efficient way.

The forest industry is today the leading producer of renewable materials, mainly in the form of paper and board, while the agricultural sector is responsible for a major share of the liquid fuels that are produced from renewable raw materials today. Both sectors have a large potential for growth in a shift to a more sustainable society, but to achieve this partly new processes are needed. A challenge in the development of these processes is that the value chain consists of many steps, where each one needs to be developed in relation to the previous one. There is also a need to already at an early stage find buyers for products and intermediate products. From a pure business economics perspective this hinders many initiatives, because the risk for one single actor in the value chain becomes too great. A central idea in the project is therefore to tie actors in the biorefinery value chain together.

The POLYNOL concept

Sweden and Brazil are two of the world's largest producers of paper pulp with considerable knowhow related to wood as a raw material. Brazil is in addition a world leader in the production of first generation ethanol from sugar cane juice. Production of second generation ethanol (or other products) via sugars from lignocellulosic materials includes a relatively costly pretreatment of the raw material in order to separate the lignin from the cellulose. Several technologies have been developed for this purpose, some of which are being demonstrated on pilot scale in e.g. Sweden, Denmark, Italy and the United States. This separation of the wood components already takes place in the chemical pulp mill, and the long proven technology in pulp production known as soda cooking (pretreatment under alkaline conditions) has also shown positive results as a pretreatment method when producing ethanol [1]. The process has been tested in mill-scale trials and has a great advantage in the fact that it can be directly integrated into the recovery of chemicals and energy in the pulp mill. The pulp mills are already very large scale plants to process biomass, and an integrated production of sugars that can be turned into high value products can therefore relatively quickly give a considerable contribution to the supply of e.g. green chemicals or second generation ethanol. The simplified integration of the two processes is a central idea to the project. The concept has been evaluated by Jansson *et al.* [2] for a theoretical pulp mill conversion to ethanol production.

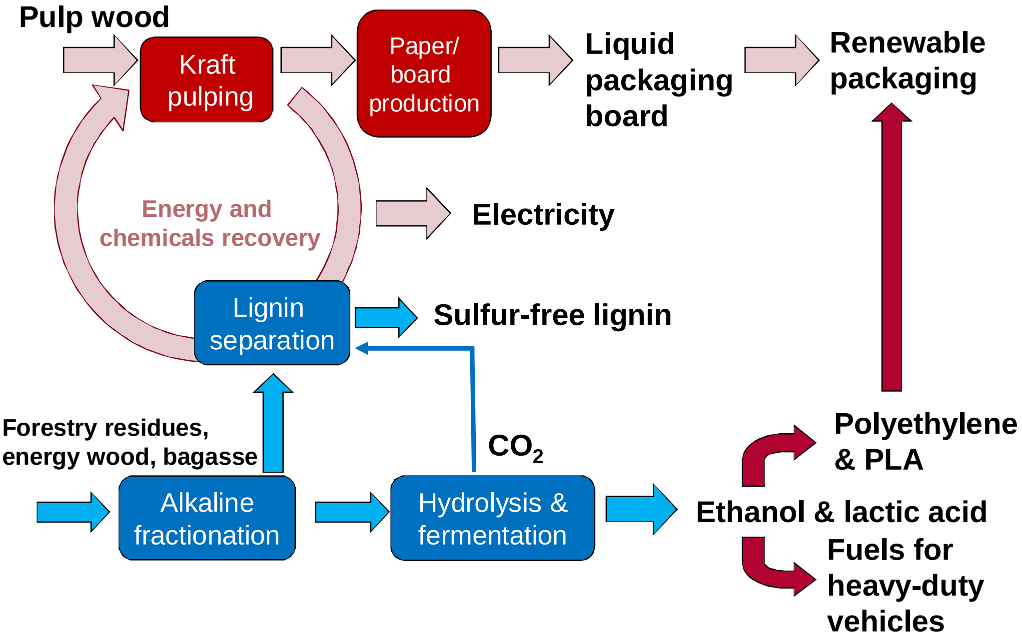

Figure 1. An illustration of how the “Polynol” concept can be integrated with a pulp mill and deliver multiple products in several value chains.

Process integration

Although conversion of an old pulp mill to a biorefinery shows some potential, the major advantage in economy of scale with the POLYNOL concept lies in process integration with large, modern facilities. A greenfield eucalyptus-based kraft pulp mill is able to produce on the order of 1.5 million tonnes of pulp per year and will have an energy surplus corresponding to more than half of the biomass input [3].

Heat integration opportunities in a biorefinery consisting of a modern eucalyptus kraft pulp mill and a lignocellulosic ethanol process have been studied by Innventia and Chalmers and reported by Fornell *et al.* [4, 5]. Results show that this combination gives rise to large opportunities of improving the energy efficiency in the biorefinery if heat integration is considered (Figure 2). The costs and net annual savings have also been calculated for several different alternative designs of the integrated processes, and the results indicate short payback periods (below 3 years) and substantial annual savings (2 M€/year) compared to the base case process.

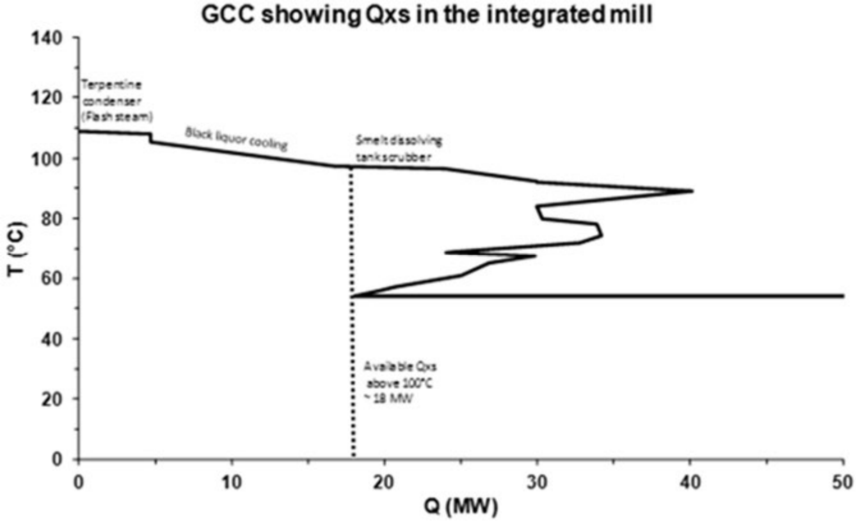

Figure 2. Grand Composite Curve indicating the availability of heat at a high temperature (>100°C) in the integrated pulp mill hot and warm water system of a 4000 ADt/d eucalyptus-based pulp mill.

Raw materials

There are large amounts of lignocellulosic materials available in or near existing pulp or sugar mills, mainly in the form of residues from harvesting (bagasse, forestry residues) and residues from the process (e.g. woodyard rejects). These materials contain significant amounts of cellulose and hemicellulose that can be converted to sugars, but also up to 30% lignin that can be processed separately. One major problem with low-cost residues is that they contain much ash. In a chemical process the ash components will tend to accumulate and cause process disturbances due to precipitation of salts and also lead to increased consumption of chemicals. Annual crops and woody materials can display large differences in ash composition with respect to, e.g., silicon, phosphorus, potassium and chlorine. One way to overcome this problem is to introduce an acidic pre-hydrolysis step prior to the alkaline fractionation. It has been showed that this step can reduce process "disturbing" substances such as metal ions, ash etc. An acidic pre-hydrolysis step can also improve the conditions in the following hydrolysis and fermentation step due to a reduction of metal ions and unreactive C5 sugars, which when present can have a negative effect on the hydrolysis yield. A reduced metal ion content is also an advantage in the further upgrading of the lignin.

Availability of biomass residues in Brazil has been assessed by Ferreira-Leitao *et al.* [6]. Sugarcane residues constitute the largest share, amounting to more than 415 million tonnes per year (195 million tonnes of bagasse and 220 million tonnes of straw and leaves). The contribution from corn and cassava residues is also significant, whereas wheat and rice residues are small in comparison. Forestry residues were estimated to about 39 million tonnes per year, (59% field residues and 41% industrial waste). Total crop land and planted forests constitute about 67 million hectares of Brazilian land use (Figure 3).

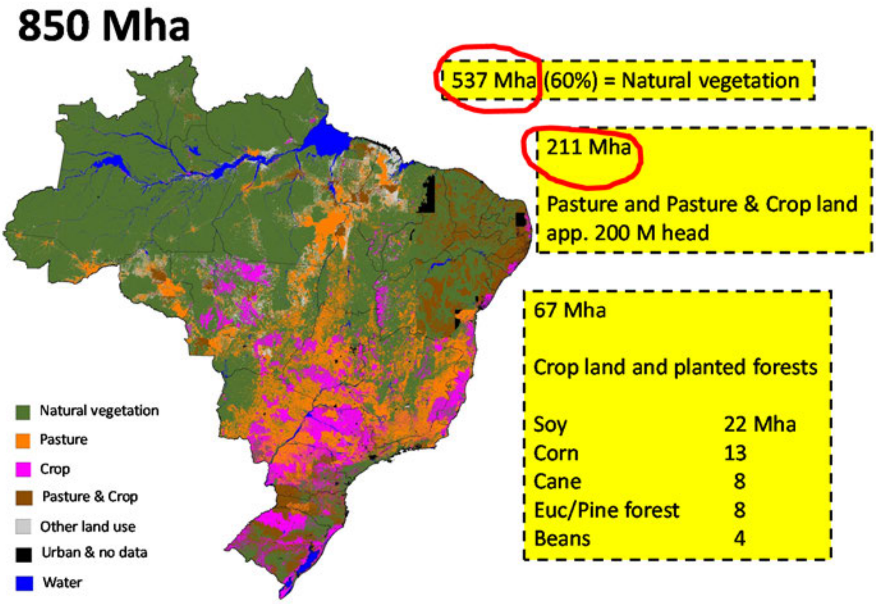

Figure 3. Current land use in Brazil as presented by Sparovek *et al.* [7].

Products

Recently, a technology has been developed aimed at extracting lignin from alkaline liquors and turn it into a purified and well defined product that can be used as a fuel or as an intermediate for chemicals production [8]. This technology can be used also for extraction of lignin in the new integrated concept. The kraft cooking process that is the most currently used separation method in the pulp mills today gives a lignin containing sulphur. However, if the separation of the wood components is performed using the soda cooking process there is also a possibility to obtain a lignin that is sulphur free. This is an advantage in some future possible applications of the lignin as a high-value added product, e.g. carbon fibers.

Other examples of potential products for the lignin are activated carbon, dispersants, binders and phenols.

The studied process will also give the possibility to separate the hemicelluloses of the wood as a third product besides the sugars and lignin. The hemicelluloses can be used as fibre additive, gas barriers and hydrogels.

A part of the sugar cane consists of bagasse, a raw material that is not yet used in commercial ethanol production, since it is similar to wood in composition, e.g. containing lignin. It is of great importance to utilize also this part of the sugar cane in an efficient way. Integration with a pulp mill where the bagasse is processed together with forestry residues to produce sugars (that can be turned into green chemicals or biofuels) at the same time as a pure lignin is produced gives good options for a cost-effective production.

Potential products from sugars include lactic acid, acrylic acid, ethyl acetate, ethyl lactate, propylene glycol, pyruvic acid, and single cell protein.

Market development for fuels, chemicals and materials made from renewable sources is predicted to be rapid in the coming decade, with growth rates many times that of pulp and paper products (cf. table 1). By volume, bioethanol is the product with the highest production rate today [9].

The biomass products can substitute for fossil fuel based products. Chambost *et al.* [10] point out that a distinction can be made between replacement and substitution products. Replacement products are identical in chemical composition to existing products, but are based on renewable resources, e.g. bioethanol. Substitution products have a different chemical composition to existing products, but have a similar functionality, e.g. lactic acid to produce PLA (polylactic acid) which could substitute PET (polyethylene terephthalate) in the production of e.g. plastic bottles.

Table 1. Estimated annual growth rate and global market value of some products from renewable raw materials. Compiled by FPAC [11].

Products	**Annual growth rate 2009–2015 (%)**	**Global value 2015 (billion USD)**
Green chemicals	5.3	62.3
Alcohols	5.3	62.0
Bioplastic and plastic resins	23.7	3.6
Platform chemicals	12.6	4.0
Wood fibre composites	10.0	35.0
Glass fibre market	6.3	8.4
Carbon fibre	9.5	18.6

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References

1. von Schenck, A., Berglin, N., Uusitalo, J. 2011. Ethanol from Nordic wood raw material by simplified alkaline soda cooking pretreatment. International Symposium on Alcohol Fuels XIX, Verona, Italy, October 10–14, 2011.

2. Jansson, M., Berglin, N., Olm, L. 2010. Second generation ethanol through alkaline fractionation of pine and aspen wood. Cellulose Chem. Technol. 44(1–3), pp. 47–52.

3. Berglin, N., Lovell, A., Delin, L., Törmälä, J. 2011. The 2010 Reference Mill for Kraft Market Pulp. TAPPI PEERS Conference, Portland, Oregon, October 2–5, 2011.

4. Fornell, R., Berntsson, T. 2012. Process integration study of a kraft pulp mill converted to an ethanol production plant – Part A: Potential for heat integration of thermal separation units. Applied Thermal Engineering 35, pp. 81–90.

5. Fornell, R., Berntsson, T., Åsblad, A., von Schenck, A. Heat integration opportunities for a combined lignocellulosic ethanol and kraft pulping process. (Submitted for publication.)

6. Ferreira-Leita, V., Gottschalk, L.M.F., Ferrara, M.A., Nepomuceno, A.L., Molinari, H.B.C., Bon, E. 2010. Biomass Residues in Brazil: Availability and Potential Uses. Waste Biomass Valor 1, pp. 65–76.

7. Sparovek, G. 2012. Personal communication, February 2012.

8. Axegård, P., Berglin, N., Lindgren, K., Tomani, P., Öhman, F. 2011. The kraft pulp mill biorefinery platform. 5th International Colloquium on Eucalyptus Pulp, Porto Seguro, Bahia, Brazil May 9–12, 2011.

9. Soccol, C.R., Vandenberghe, L.P., Medeiros, A.B., Karp, S.G., Buckeridge, M., Ramos, L.P., Pitarelo, A.P., Ferreira-Leitão, V., Gottschalk, L.M., Ferrara, M.A., da Silva Bon, E.P., de Moraes, L.M., Araújo Jde, A., Torres, F.A. Bioethanol from lignocelluloses: Status and perspectives in Brazil", Bioresource Technology 101(13), pp. 4820–5025.

10. Chambost, V., McNutt, J., Stuart, P. 2008. Guided tour: Implementing the forest biorefinery (FBR) at existing pulp and paper mills. Pulp and Paper Canada 109(7–8), pp. 19–27.

11. http://www.fpac.ca/publications/BIOPATHWAYS II web.pdf.

Lignin removal from different black liquors

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Abstract

Pulp mill biorefining is still a relatively young area in modern pulping R&D driven by megatrends such as increased costs for fossil oil and wood, but also increased competition on the pulp market. The need for new revenues is obvious if the pulp and paper industry is to maintain its strong position. Biorefining can simplified be defined as the efforts to reach as complete utilization of wood raw material as possible in a pulp mill to reach as high revenues as possible. A pulp mill producing chemical pulp is for several reasons an excellent an industrial platform for biorefining. The chemical pulp mill is able to produce relatively pure cellulose, hemicellulose and lignin. The focus in this paper is on separation of lignin from different types of black liquors, the behavior of these black liquors when they are treated according to the LignoBoost concept and properties of the separated lignin.

Lignin removal from kraft/soda black liquors has been developed (the LignoBoost process) in cooperation between Innventia and Chalmers. The technology was sold to Metso Power 2008 and is now commercially available. Lignin separation, purification, modification and applications have a high priority in R&D work at Innventia.

Introduction

Several black liquors (from different wood species, annul plants) have been studied in the LignoBoost concept by Innventia for about a decade. Information from this database is used to point out similarities and differences in behavior and the final lignin properties. One example of this is the challenge we have had to separate lignin from certain hardwood black liquors. The challenge is in this case a high filtration resistance in the separation of precipitated lignin. We propose a solution in this paper.

In the LignoBoost process a stream of black liquor is taken from the evaporation plant, Figure 1. The lignin in the stream is precipitated by acidification (preferred acid is CO_2) and filtered ("Chamber press filter 1" in Figure 1). Instead of washing the lignin directly after filtration the filter cake is re-dispersed and acidified ("Cake re-slurry" in Figure 1). The resulting slurry is filtered and washed using displacement washing ("Chamber press filter 2" in the Figure 1).

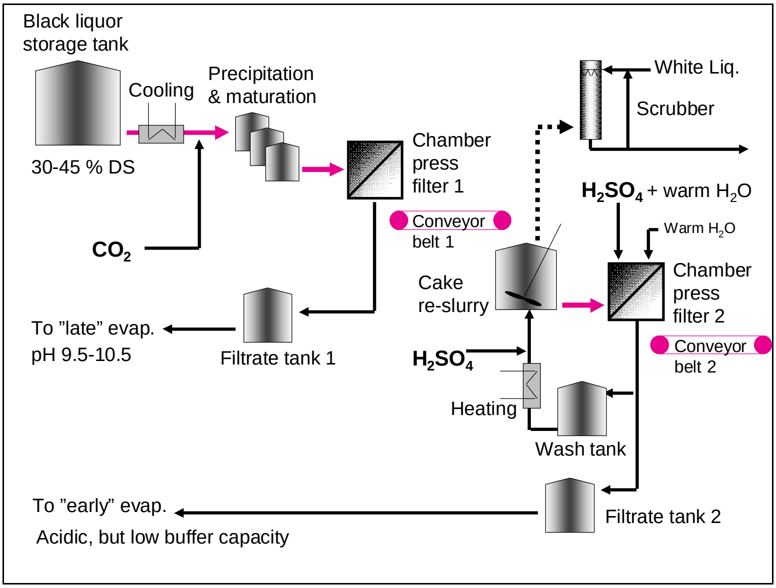


Figure 1. A general layout of the LignoBoost lignin removal process, LignoBoost (post-treatment such as drying & pulverizing is excluded).

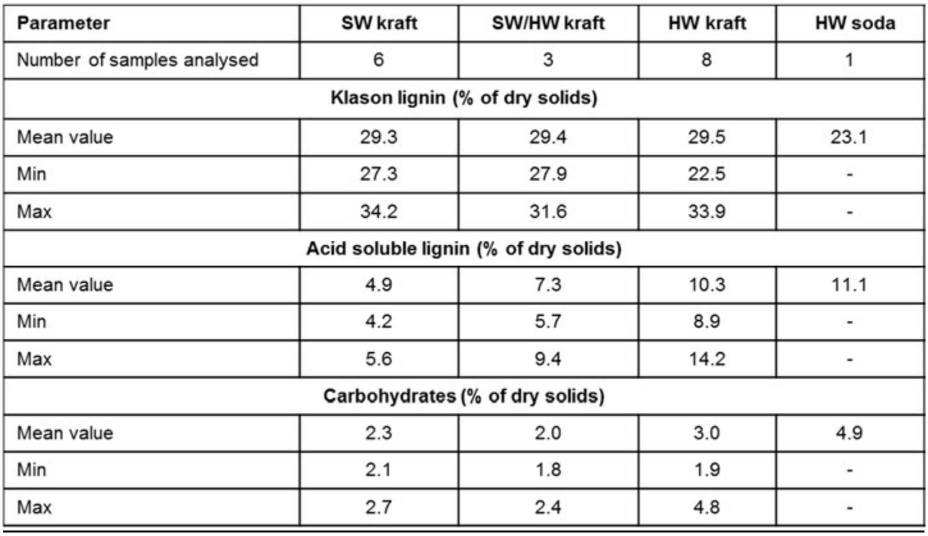
It should be noted that the filtrate from chamber press filter 1 (a filtration and dewatering stage), Figure 1, should be recycled to the mill evaporation plant after the point at which the feed stream to LignoBoost is located. This to avoid a decrease in the lignin concentration in the stream fed to the LignoBoost operation, which would be the result if the filtrate were recycled to the beginning of the evaporation plant. The filtrate from chamber press filter 2 (a filtration, washing and dewatering stage) should be recycled to the weak black liquor.

Results

Different black liquors

Many black liquors have been tested over the years using the LignoBoost concept. We have tested liquors from pulp mills as well as from laboratory trials. The importance of mill liquor tests is that they give a glimpse of the industrial reality, which not always is easy to interpret since you not always have the complete background – wood species, steady-state production or not etc. Some mills also run campaigns where they switch between SW and HW, and this will affect the composition of black liquor and the behavior in lignin separation. The chemical composition of the hardwood black liquors we have studied seem to be more heterogeneous than the softwood black liquors we have studied, Table 1. This can be shown as larger variations in acid soluble lignin and carbohydrates.

Table 1. Chemical composition of industrial laboratory produced black liquors.



Parameter	SW kraft	SW/HW kraft	HW kraft	HW soda
Number of samples analysed	6	3	8	1
Klason lignin (% of dry solids)				
Mean value	29.3	29.4	29.5	23.1
Min	27.3	27.9	22.5	-
Max	34.2	31.6	33.9	-
Acid soluble lignin (% of dry solids)				
Mean value	4.9	7.3	10.3	11.1
Min	4.2	5.7	8.9	-
Max	5.6	9.4	14.2	-
Carbohydrates (% of dry solids)				
Mean value	2.3	2.0	3.0	4.9
Min	2.1	1.8	1.9	-
Max	2.7	2.4	4.8	-

These black liquors, together with some additional liquors, have been studied in the LignoBoost process and the results are summarized below.

Yield and chemical consumption in the LignoBoost process

A summary of lignin yields for precipitation to approximately pH 10 for a number of black liquors from different mills is shown in Figure 2. The yield was measured gravimetrically over the first filtration stage. This assumption is reasonable since the yield is normally very high in the LignoBoost process (and sometimes even above 100% since additional lignin can precipitate from the carry-over filtrate in the re-slurrying stage). The precipitation temperature (final temperature) is normally 65–70°C for softwood and 55–60°C for hardwood black liquors.

The precipitation step in our demonstration plant is normally conducted at a pH slightly higher than 10 and the variation is between approximately pH 10,1 to 10,4. This can explain the lower lignin production rates in the left part of Figure 2.

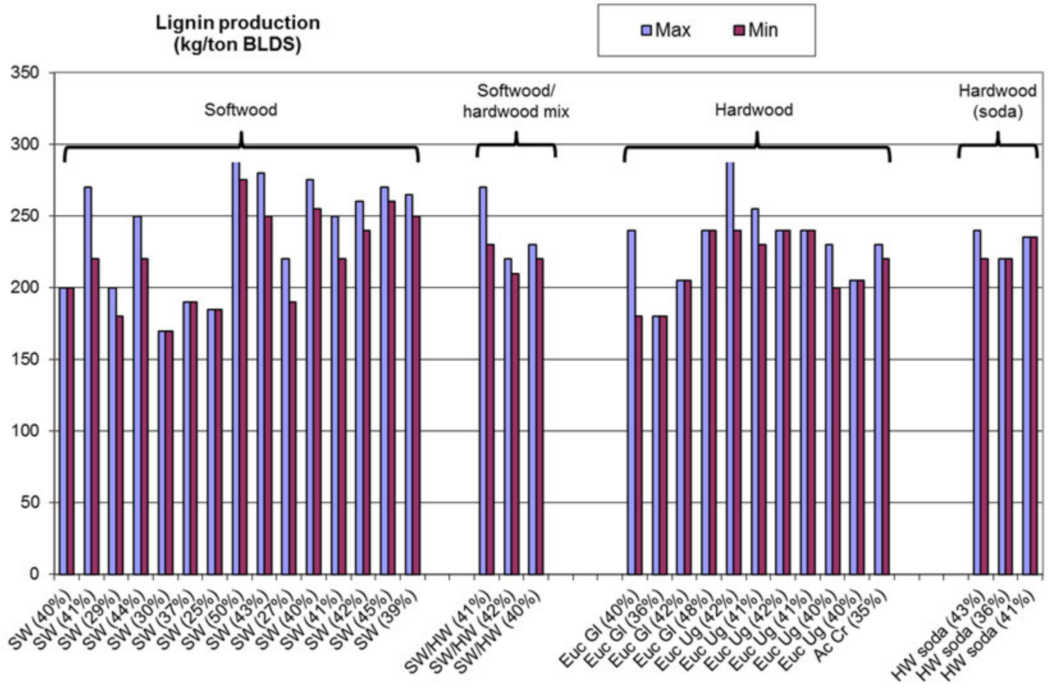


Figure 2. Lignin yield for different black liquors when pH is adjusted to about 10.

The behaviour of lignin in aqueous solution is controlled mainly by the pH, ionic strength and temperature. The main chemical reactions that participate in lowering the pH during CO_2 absorption in alkaline solutions are described in reactions (1) and (2):

$$CO_2(g) \rightleftharpoons CO_2(aq) \tag{1}$$

$$CO_2(aq) + 2OH^- \rightleftharpoons CO_3^{2-} + H_2O \tag{2}$$

The CO_2 consumption has been estimated from titrations on black liquor with 1M HCl to determine the acid consumption, and the consumption of CO_2 was estimated from equilibrium calculations. These experimental and calculated CO_2 consumptions per tonne lignin for precipitation at pH 10 are given in Figure 3.

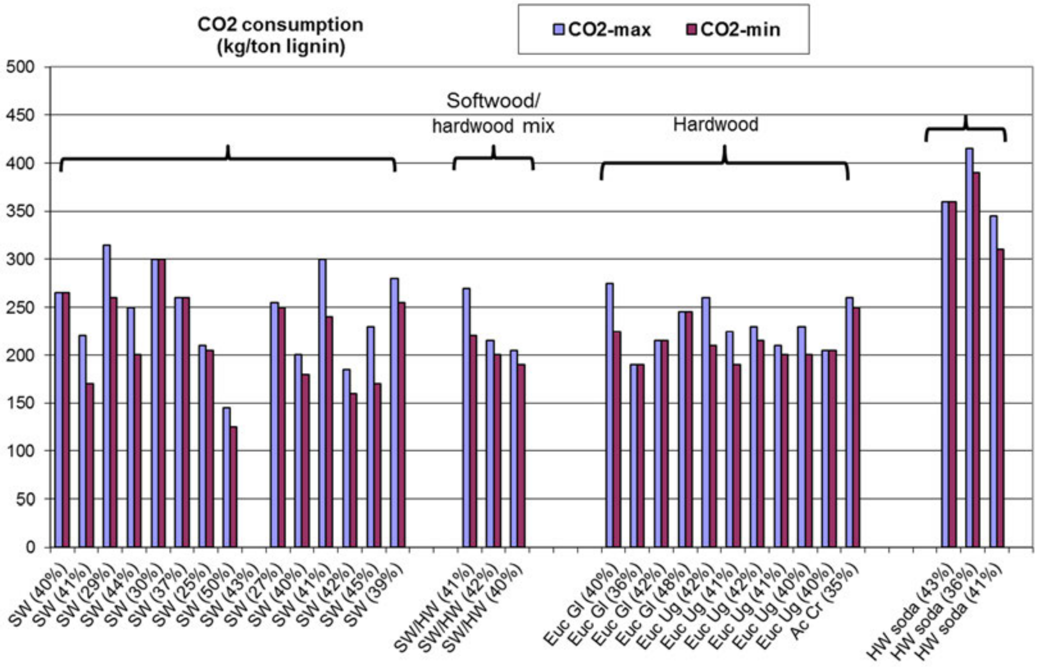


Figure 3. Carbon dioxide (CO_2) consumption for different black liquors when pH is adjusted to about 10 and lignin precipitates.

The dominant component that determines the consumption of CO_2 is the residual alkali in black liquor, Figure 4, but neutralisation of e.g. phenolic groups in lignin and sugar acids also consume CO_2. The chemical consumption for the soda black liquor process was significantly higher than for black liquor from the Kraft process. The residual alkalinity in this specific case is regarded as being very high. Typical values for lowering pH of black liquor to values used in the LignoBoost process is about 50 kg CO_2/BLDS.

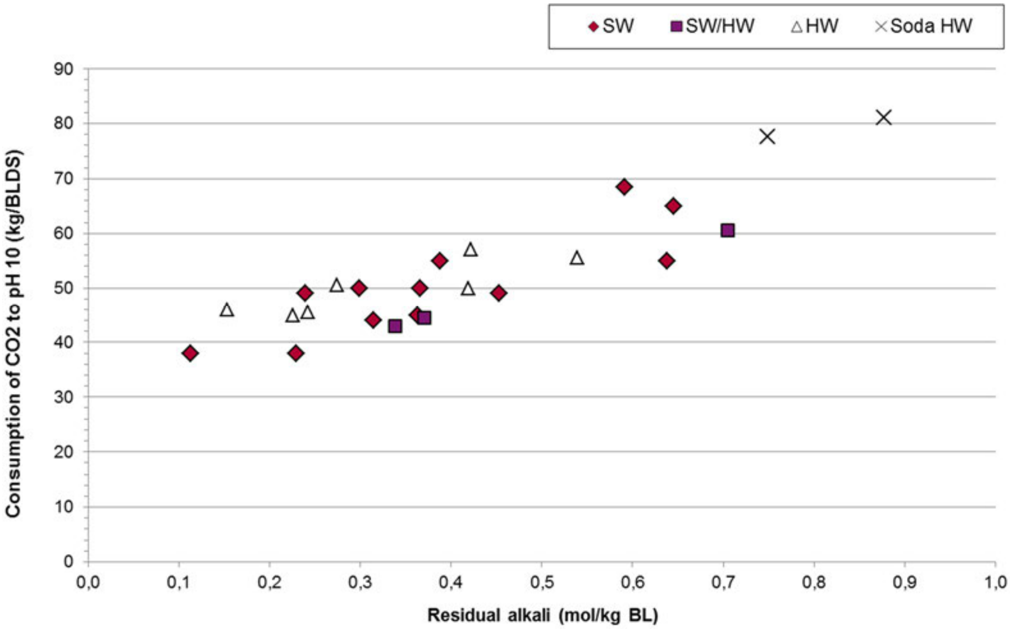


Figure 4. Consumption of CO_2 as a function of residual alkalinity in the black liquor.

The H_2SO_4 consumption has been estimated from titrations on filter cakes and filtrates from either mill trials in bench-scale or laboratory trials with a small chamber press filter, Figure 5. A general assumption is that the lignin concentration in the filter cakes from the first filtration stage can be increased to 50–55 %-w, when the filter operation is scaled up to larger filters where higher pressures are used and “edging effects” are minimised. This concentration has been reached in a number of studies even with a pilot filter press with a filter area of 0.1 m^2. If lower concentrations were obtained (e.g. in the laboratory filter), the H_2SO_4 consumption was re-calculated to a lignin concentration of 50–55%. The black liquors are generally extracted at either 40% DS (variation between 37–44% DS) or 30% DS (27–30 % DS). This means different amounts of carry over which needs to be neutralised.

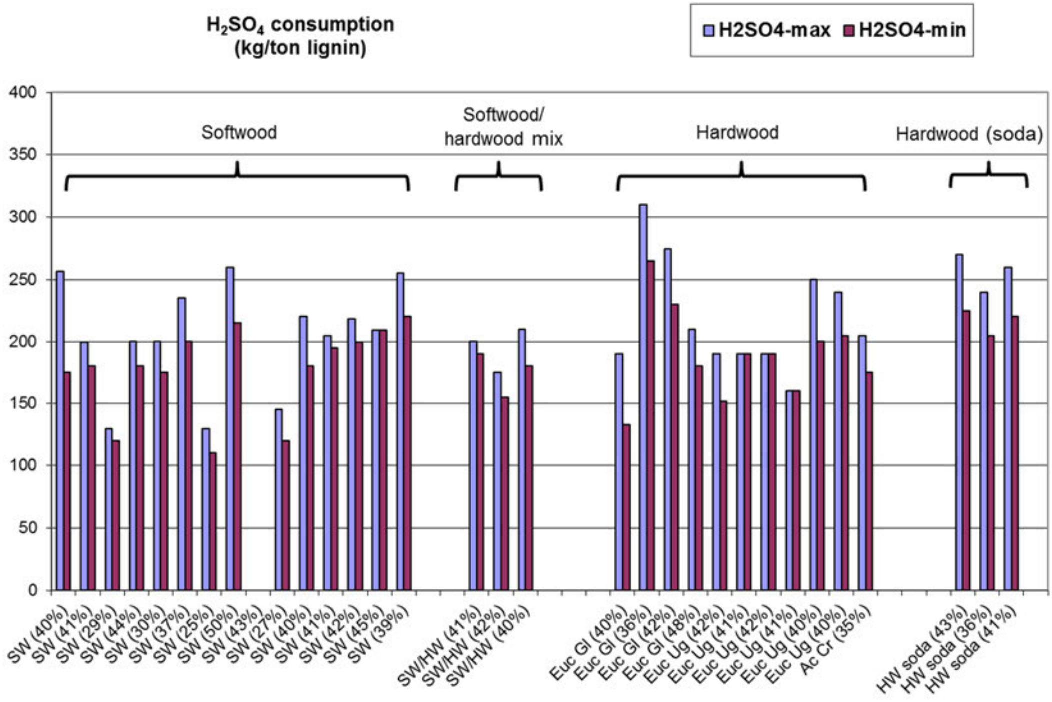


Figure 5. Sulphuric acid (H_2SO_4) consumption for different black liquors when pH is adjusted in the re-slurry stage from about 10 to pH about 2–2,5.

Filterability in the LignoBoost process

The specific filtration resistance is a scientifically not a very clear way to express how easy or difficult it is to separate the lignin by filtration. One way to explain this could be to show the relation between specific filtration resistance and the weight produced lignin expressed as kg lignin/m^2 filter area. This is shown in Figure 6 for the first filtration step (after addition of CO_2 to black liquor). Precipitated black liquor from five different mills using softwood or a mixture of softwood and hardwood has here been used to visualise this correlation. Correlation for hardwood black liquors is generally similar in the beginning of filtration phase, but in some cases there are more than one specific filtration resistance during filtration of some hardwood lignins. The specific filtration resistance for lignin precipitated from hardwood black liquor often increases when thicker cakes are made rapidly (from a magnitude of 1E10 to 1E11 or even 1E12). This indicates that the later parts of the filtration demands larger filtration area.

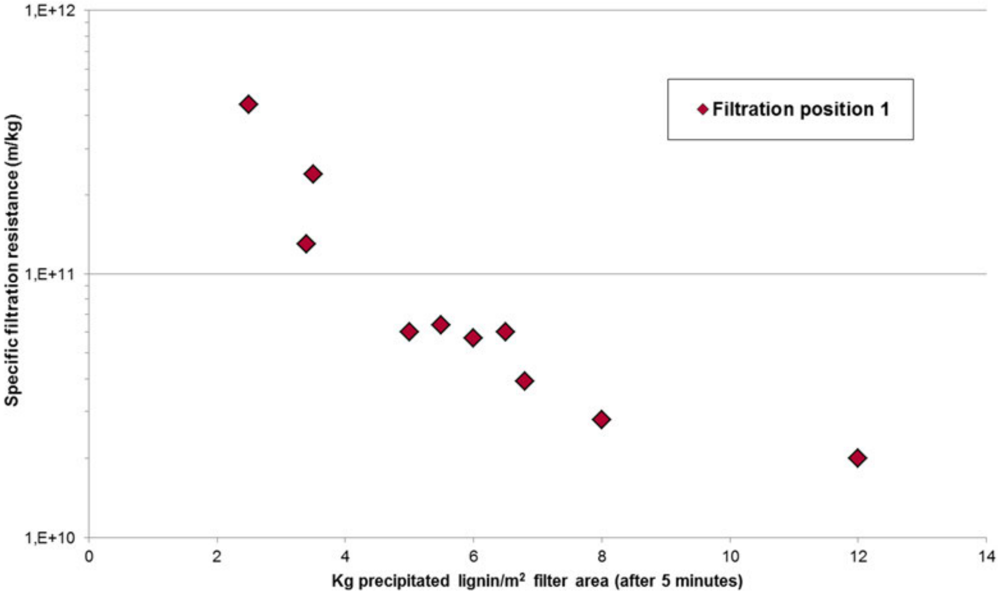


Figure 6. The relationship between specific filtration resistance and build-up of kg precipitated lignin/m^2 filter area.

Several trials were made where dilute carbon dioxide was used as the acid for lignin precipitation. Flue gases from for example the lime kiln was simulated by feeding the bottom of a small adsorption tower with a diluted carbon dioxide at room temperature. The gas mixture then reacted with black liquor, circulating through the tower from the top. Percentage of carbon dioxide in gas inlet, dry solid of black liquor and contact material inside the tower was varied, also different mass flows through the tower was tested. The results showed significant increase in filtration rate (lower specific filtration resistance) when lignin was precipitated slowly in the carbonisation (absorption) tower compared to reference black liquor precipitated in the demo plant at the same temperature and to the same pH, Figure 7. The improvement of filtration rate in the absorption tower was about 150%.

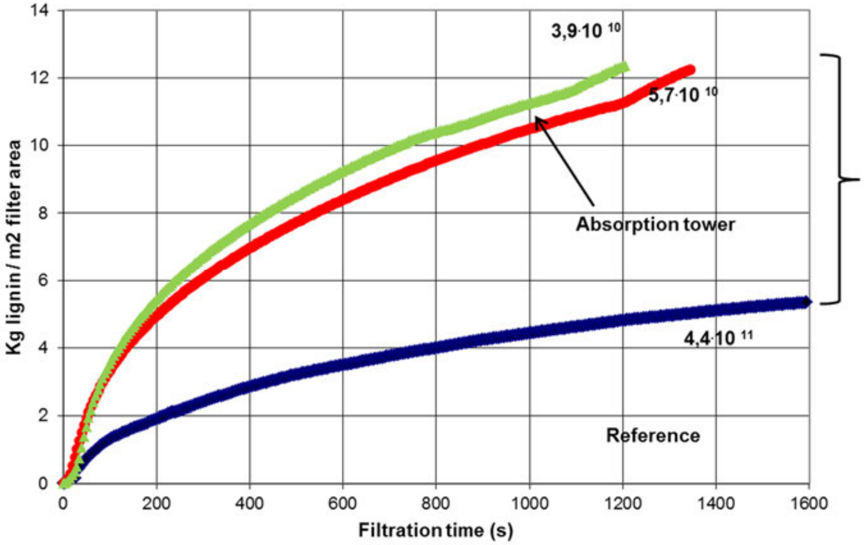


Figure 7. Improvements in filterability when diluted CO_2 is used in the acidification of black liquor.

There are different ways to handle poor filterability of some hardwood lignins. One way is to increase the dry solid content of the incoming black liquor. The lignin concentration will by that be increased which facilitates an effective filtration. However a too high dry solid content in the black liquor increase the risk to form Na_2CO_3 when CO_2 is added to precipitate lignin. This can be positive and lower the filtration resistance but this will cause increased carry-over of carbonate to the re-slurry stage and the acidification which result in increased consumption of H_2SO_4. However, there are ways to avoid solve this, Figure 8, by such as addition of salt and/or recirculated precipitated lignin instead of increasing dry solid content.

Figure 8 shows that dilution of original hardwood black liquor (Aspen 43% DS) will increase the filtration resistance. Addition of lignin and salt to the diluted slurry before precipitation resulted in a lower filtration resistance. The largest effect was obtained when both salt and lignin cake were added. Addition of lignin and/or salt (Na_2SO_4) was made to increase the dry solid content and/or maintain the ionic strength. Experiments made with diluted black liquor (34% DS) and addition of lignin and/or salt (Na2SO4) to 47% DS had positive influence on the filterability. This indicates that it is possible to improve filterability when the lignin content to the precipitation is slightly low.

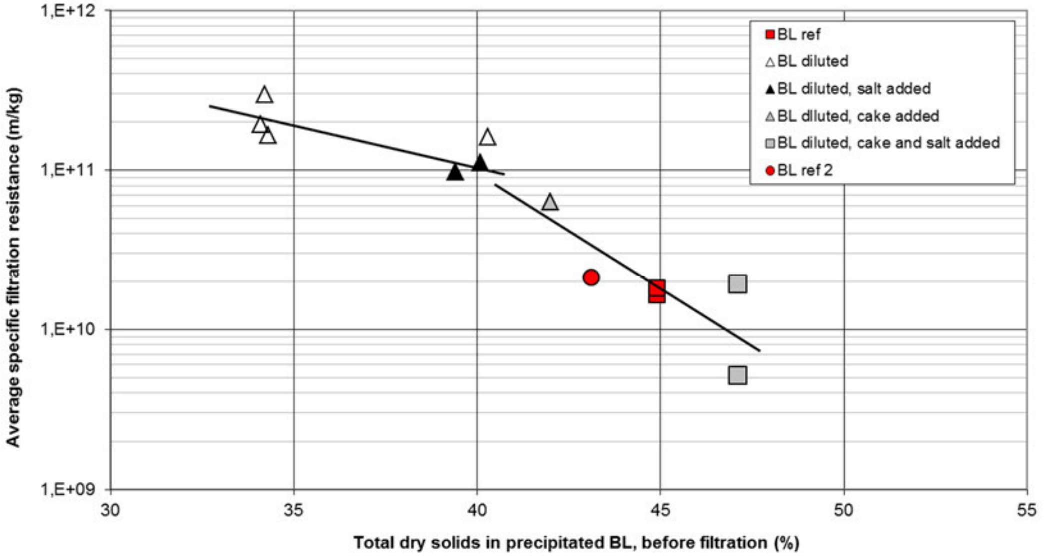
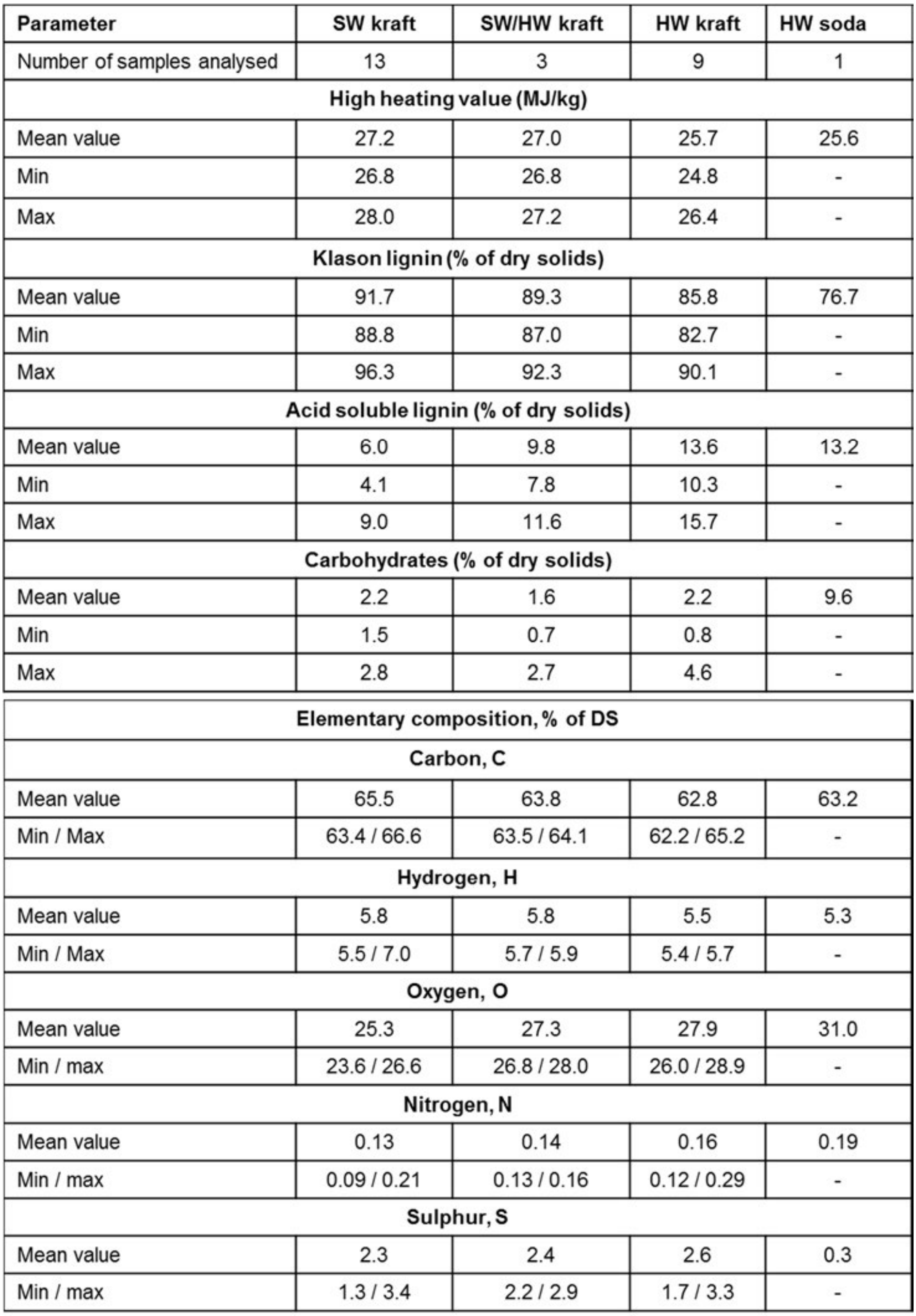


Figure 8. Average specific filtration resistance at different total dry solid content of the incoming black liquor achieved in different ways.

Properties of the produced lignin

Lignin from the kraft process contains more carbon compared to most other bio-fuels (torrefied wood is basically similar) and correspondingly higher heat value. The heating value of lignin fuel samples has been determined as higher heating value (HHV) in a bomb calorimeter. The lower heating value (LHV) is calculated based on the HHV and the elemental analysis. The HHV (mean value) for softwood lignin was in our studies about 27 MJ/ kg dry lignin, Table 2. This should be compared with 18–20 MJ/ kg for wood chips.

Table 2. Characterization of different lignin samples produced by the LignoBoost concept.



Parameter	SW kraft	SW/HW kraft	HW kraft	HW soda
Number of samples analysed	13	3	9	1
High heating value (MJ/kg)				
Mean value	27.2	27.0	25.7	25.6
Min	26.8	26.8	24.8	-
Max	28.0	27.2	26.4	-
Klason lignin (% of dry solids)				
Mean value	91.7	89.3	85.8	76.7
Min	88.8	87.0	82.7	-
Max	96.3	92.3	90.1	-
Acid soluble lignin (% of dry solids)				
Mean value	6.0	9.8	13.6	13.2
Min	4.1	7.8	10.3	-
Max	9.0	11.6	15.7	-
Carbohydrates (% of dry solids)				
Mean value	2.2	1.6	2.2	9.6
Min	1.5	0.7	0.8	-
Max	2.8	2.7	4.6	-
Elementary composition, % of DS				
Carbon, C				
Mean value	65.5	63.8	62.8	63.2
Min / Max	63.4 / 66.6	63.5 / 64.1	62.2 / 65.2	-
Hydrogen, H				
Mean value	5.8	5.8	5.5	5.3
Min / Max	5.5 / 7.0	5.7 / 5.9	5.4 / 5.7	-
Oxygen, O				
Mean value	25.3	27.3	27.9	31.0
Min / max	23.6 / 26.6	26.8 / 28.0	26.0 / 28.9	-
Nitrogen, N				
Mean value	0.13	0.14	0.16	0.19
Min / max	0.09 / 0.21	0.13 / 0.16	0.12 / 0.29	-
Sulphur, S				
Mean value	2.3	2.4	2.6	0.3
Min / max	1.3 / 3.4	2.2 / 2.9	1.7 / 3.3	-

Heating values for hardwood lignin was in our studies just slightly lower (~26 MJ/kg) than for softwood lignin (~27 MJ/kg). Lignin from hardwood seemed to contain more acid soluble lignin. Most hardwood lignin samples in our study contain carbohydrates on the same level as equal to softwood or softwood/hardwood mix. The soda lignin is an exception and 10% carbohydrates are in this specific case amongst the highest value we have seen.

Hardwood lignin seems to have lower amount of carbon, but higher amount of oxygen. Oxygen is not analysed as such, but calculated from what is left after other components. All lignins contains traces of chlorine, but very low levels (0,01–0,02%). Sulphur content in lignin ranges from 1.3 to 3.4 for kraft lignins, with a typical value of 2.4%. Exception is the hardwood soda lignin where the process is sulphur free and by that it result in about 0,3% sulphur in the lignin. The sulphur added in the LignoBoost process (H_2SO_4) is effectively washed out from the lignin before it leaves the final chamber press filter. The sulphur content measured in the kraft lignin is bonded into the lignin structure during the kraft cooking operation and it is with today's knowledge relatively costly and not effective to remove this sulphur.

Summary

- Innventia has a lot of knowledge about lignin removal from many different black liquors
- The LignoBoost concept results in quite pure lignins
- There are some differences in how different black liquors behave in the LignoBoost process. Innventia has tools for handling of these differences.
- Lignin is an excellent bio-fuel and several fuel applications are ready for use already today
- Lignin has a great potential to be converted into higher value products, e.g. to carbon fibers, binders etc.

Acknowledgements

Many people have been involved at Innventia to collect the data for these results. The author wants to acknowledge the whole lignin team at Innventia for their high quality work, great attitude and contribution in many different ways.

The Swedish Energy Agency, Fortum Värme, Metso, Stora Enso and Södra Cell are acknowledged for their funding and engagement in the LignoFuel Program which is one important long-term platform for our work on process development.

Recovery of biobased light carboxylic acids from dilute aqueous solutions

Jukka Hietala
Kemira Oyj

Abstract

Thermal, chemical and biotechnical treatments of biomass can degrade components like hemicellulose, cellulose and starch to smaller molecules that include water soluble carboxylic acids.

These acids are commercially useful but their recovery from biomass processes is generally not considered feasible because they are normally present as complex mixtures in very dilute aqueous solutions.

We have studied liquid-liquid extraction followed by distillation or back extraction as methods to isolate C_1–C_4 acids from dilute aqueous solutions. Many critical parameters were identified. In some cases even 98% recovery yields were obtained from solutions that contain 2–3 wt-% of the desired acid. However, each particular feed is a case of its own. Various technically working, safe and industrially feasible concepts should be developed side by side and at the end let the total costs decide.

Introduction

Biomass as source of light carboxylic acids

During the past years several thermo-chemical biomaterial conversion processes have been developed for renewable fuel and chemical production. In these processes some cellulose, hemicellulose and starch disintegrates to acids. Usually it happens as unwanted side reactions but there are some on-purpose concepts also. One of them is the co-production of formic acid and levulinic acid by acid catalysed decomposition of cellulose. [1] Formic acid has many applications as natural, easily controllable pH regulator or microbial control agent and its salts are used for example as biodegradable anti-icing agents. Levulinic acid is a platform chemical and its esters are renewable fuel oxygenates.

When one ton of pulp is produced in Kraft process, 100–200 kg of light carboxylic acids are formed. [2] This would mean global production of 13–26 million tons of these acids, now burnt as an insignificant contribution to the process heat. In addition to these, potentially valuable sugar acids are formed (10–15% of the dry mater).

A typical fast pyrolysis oil unit produces annually 50–150 kt bio oil for heating and transportation. The composition varies on the feed and process conditions but it includes 4–5 wt-% water soluble carboxylic acids. [3] Selective removal of them would not affect much to the heating value but would decrease corrosivity of the oil.

Many microorganisms are capable of converting low value organic material, even municipal waste, to carboxylic acids. In one of our projects technical glycerol coming from biodiesel production as side stream was converted to a mixture of propionic, acetic and succinic acid. These acids have applications in polymers, and acetates and propionates are also important food preservatives.

Organic acids are also formed during pre-treatment of cellulosic material for bioethanol fermentation. The acids are inhibitors of the fermentation yeast and their removal have shown to boost bioethanol production significantly. [4]

With all these biomass based sources of light carboxylic acids the main technical challenge is the very dilute solutions. Concentration of the desired acid is usually 0.1–5 wt-%. Thermal separation would involve evaporation of lot of water, which is a very energy consuming process. On the other hand, profitable biorefineries should make the best possible use of all chemicals that are formed in the process.

Extractants for liquid-liquid extraction are in this case often either inefficient, poorly separating from water or too strongly binding. Many reactive extractants are also labeled toxic or they are available only as lab chemicals. Accumulation of acids on solid adsorbents from large water volumes, followed by their isolation and purification from the surface is not very efficient. Membranes have difficulties to separate small polar molecules from each other (like formic acid from water) and in continuous operation their fouling by other biomass components is a problem.

Liquid-liquid extraction as the method of recovery

With some earlier experience and teachings of the literature in our mind we set a target to find feasible extraction methods to recover acids from very dilute (ca. 1–3 wt-%) aqueous solutions. The main target processes were formic acid separation from levulinic acid production and recovery of propionic acid and acetic acid from glycerol fermentation. Extraction followed by distillation or alkaline back extraction were selected as the separation methods. Some of the systems were tested also in feeds coming from black liquor and pyrolysis oil fractionation and from sugar fermentation to glycolic acid.

The extractants used in the literature in isolation of organic acids from dilute aqueous solutions can be divided into three groups [5]:

- organic tertiary and quaternary nitrogen compounds
- trialkyl phosphine oxides
- organic oxygen compounds with low reactivity (alcohols, ketones, esters, ethers).

Experimental

Most of the extractions were run in 100–200 ml scale batches in a stirred vessel; all examples here are from these experiments. In addition, some larger trials were done in agitated or fixed bed extraction columns with continuous co-current feeds. Acids were recovered from the extracts by distillation or by back extraction with hot water or with alkaline solution. Some product salts were isolated as precipitates.

Lab grade chemicals were used, except the industrial Alamine solvents from BASF, Cyanex 923 from Cytec and hydrocarbon mixtures from ExxonMobil Chemicals, including Isopar H.

When only one acid component was present, like synthetic formic acid solutions, both extracts and raffinates could by analysed by titration. In many cases excellent mass balances and agreement with HPLC analysis were be obtained. In more complicated cases the acid distributions were based on the raffinate analysis (HPLC and in some cases CE) and on the titration of the total acids in all phases. Water in organic phase was determined by Karl-Fischer titration. FT-IR, NMR (^{1}H, ^{13}C, ^{31}P) and GC-MS were used to characterize other components and the interaction between the extractant and acids.

Results and discussion

Extractant-acid complexes

Figure 1 shows extraction yields of 3 wt-% and 25 wt-% formic acid solution with a hydrocarbon solvent (toluene), an ether, an amine and a mixture of trialkyl phosphine oxides. It can be seen that the solvents from the groups mentioned in the introduction are highly active extractants to formic acid. Interestingly, often more than one molecule of acid can be bound per active site of the extractant. For example in this experiment the more concentrated acid solution was used with the ratio acid (mol)/amine (mol) = 2.8.

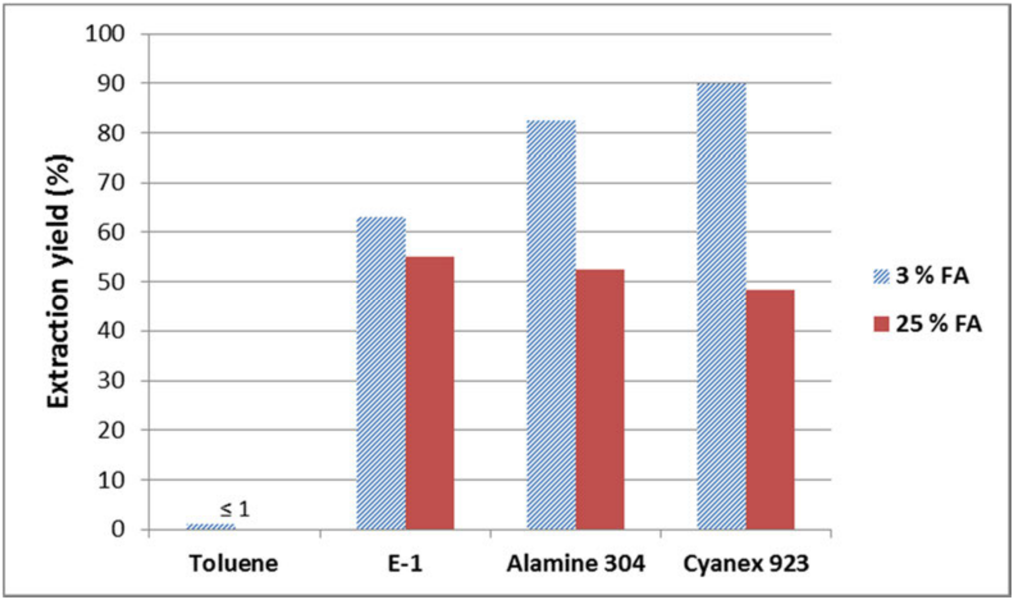


Figure 1. Comparison of the efficiency and capacity of various types of extractants in formic acid (FA) extraction. Feed 3 w-% or 25 wt-% formic acid solution in water, feed (g)/extractant (g) = 1.0 (= w/o), 20°C.

E-1	an ether
Alamine 304	trialkyl amine (tridodecyl amine)
Cyanex 923	trialkyl phosphine oxides ((alkyl = C_6, C_8).

Binding of carboxylic acid to the extractant can be seen as change of C = O absorptions in FT-IR (Figure 2). Depending on the strength of the interaction, various proportion of salt character can be seen. For phosphine oxides, shift in ^{31}P-NMR can be used to compare the strength of binding.

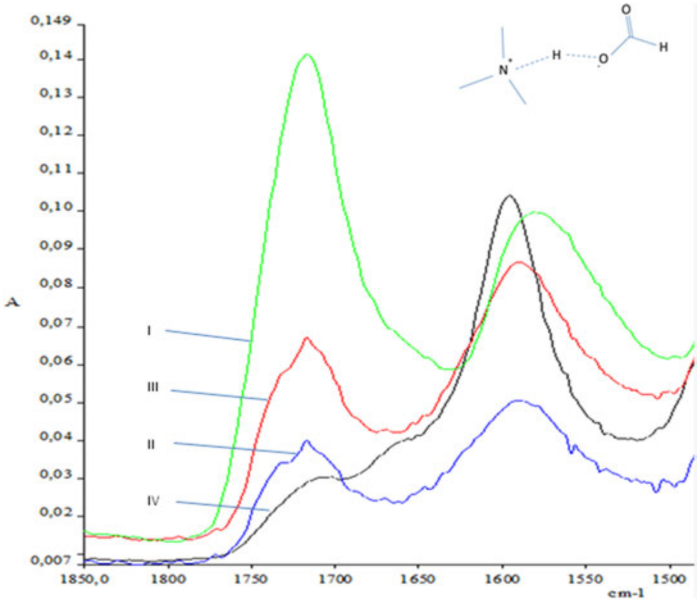


Figure 2. Carbonyl absorptions (A) in FT-IR of some formic acid – amine complexes. The peaks at 1 717 cm^{-1} come from free or loosely bound acid, the peaks at 1595–1580 cm^{-1} are related to formate salts. The samples contained 2 wt-% formic acid and molar equivalent of amine in dichloromethane.

I	Tris(2-ethylhexyl) amine
II	Tris(iso-octyl) amine
III	Trioctyl amine
IV	Dimethyldecyl amine

Strong binding gives high distribution constant (K_D) but can also cause problems in the acid recovery step (Table 1).

Table 1. Correlation of the length and branching of the amine carbon chains to extraction efficiency and behaviour in distillation. Salt character in IR increases I → II → III → IV (see Figure 2). Distillation with 20 wt-% formic acid in amine, the maximum bottom temperature was 140°C in order to avoid formic acid decomposition.

No	Carbon chains in amine	K_D	Distillation
I	3 x CH_3-$(CH_2)_3$-$CH(CH_2CH_3)$-CH_2-	0.19	A part of formic acid distils out at 1 bar, distils fully under vacuum
II	3 x $(CH_3)_2$-CH-$(CH_2)_5$-	3.8	A part of formic acid distils out at 1 bar, distils fully under vacuum
III	3 x CH_3-$(CH_2)_7$-	4.6	Formic acid does not distil out at 1 bar but distils under vacuum
IV	1 x CH_3-$(CH_2)_9$- 2 x CH_3-	syrup	Solidifies, formic acid does not distil out even under vacuum

$K_D = [HCOOH]_{extract}/[HCOOH]_{raffinate}$, $[HCOOH]_{feed} = 0.65$ moldm^{-3} (3 wt-% solution)

The complexes are formed only between free acid and extractant, which means that in most fermentations a separate acidification step is needed before extraction. Fermentations that can be run near or below pKa's of the product acids would have an advantage.

Co-solvents

Extractant-acid complexes can have so strong salt character that they do not dissolve well in the bulk extractant but separate as third liquid phase. Removal of the residual water in distillation can cause formation of solid salt. The organic phases can be homogenized by addition of certain hydrocarbon co-solvents. We have noticed that in formic acid extraction alcohol co-solvents that are often used in literature cause significant ester formation. Formate esters were found to be poor acid extractants.

Co-solvent affects also the extraction selectivity and can be a tool to fine tune the extractant properties in a certain application. For example co-extraction of furfural with acids was be increased by addition of polar cyclohexanone to amine and decreased by addition of non-polar alkanes.

Uptake of water

The solvent system is preferably selected so that minimal amount of extractant is dissolved in the aqueous phase (high purity of the process waste water) and minimal amount of water is dissolved in the extract (isolation and purification of the product with minimal evaporation of water).

We found that formation of acid-extractant complexes introduce some polarity (see Figure 2) that can change the properties of the liquid. Water solubility can increase significantly (Figure 3), as well as extractant solubility to water. This can interfere with phase separation. If the acid is recovered by distillation, it is likely that azeotropes with water changes the distillation pattern in some extent.

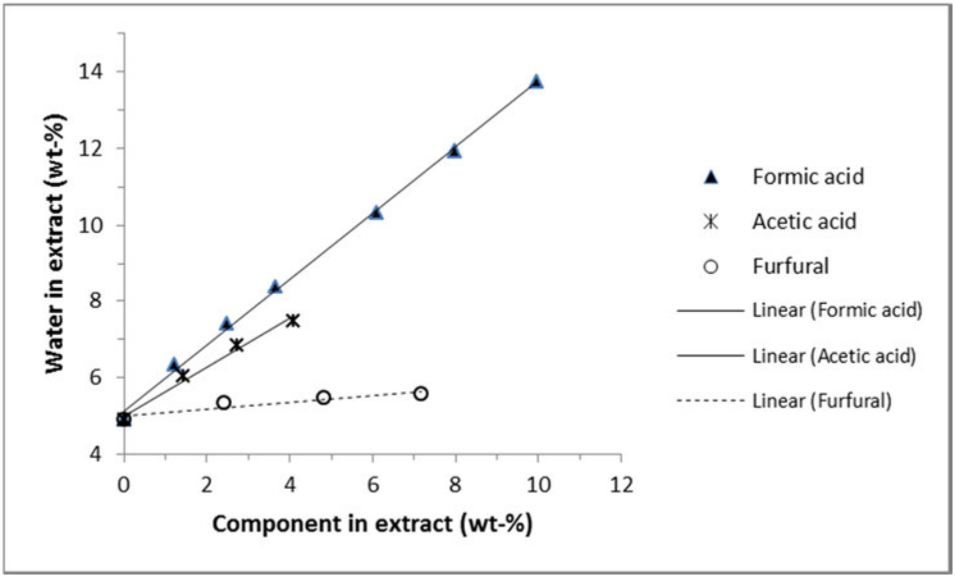


Figure 3. Effect of formic acid, acetic acid and furfural on the dissolvation of water in an ether type of extractant. Individual contributions are additive. Extractions with w/o = 1.1, 45°C.

Recovery of the acid and regeneration of the extractant

There are hardly any low boiling point extractants that would have low enough water solubility, toxicity and flammability to be useful. Thus, in practise the complex forming extractants are usually high boiling point liquids that are not feasible to regenerate by distillation. If the products are hydroxy acids, they are easily decomposed or dimerized during distillation.

All distillations may be avoided if aqueous concentrated base is added to the extract and the acids are back-extracted as salts. This is especially convenient if the acid is also used in salt form in the final application. The remaining organic phase is washed and recycled back to extraction. Success of this procedure depends naturally on the binding of non-acidic impurities.

Interestingly, the base does not need to be very strong or well soluble to be effective. The glycerol fermentation product extracted with amine based solvent contained 5.00 wt-% propionic acid, 0.21 wt-% acetic acid and 0.16 wt-% succinic acid. When back extracted with extremely poorly water and organic solvent soluble calcium bases; $CaCO_3$ and $Ca(OH)_2$ (as aqueous suspensions, w/o = 0.4, 20% Ca excess), calcium propionate yields up to 90% were obtained. Calcium salts of light carboxylic acids are water soluble, so they are easy to separate from the unreacted base. Carbonate and hydroxide have different basicity and so they tend to give different calcium salt distribution from a mixture of acids. In this case the weaker base $Ca(CO)_3$ gave a larger portion of acetate in the product.

Conclusions

Thermal, chemical and biotechnical treatments of biomass can degrade sugar oligomers and polymers to smaller molecules that include water soluble carboxylic acids. In some special cases also fats and oils, lignin, polypeptides etc. could be the starting point in the conversion. These reactions are normally run in aqueous environment and the acids end up usually in very dilute solutions containing many components. Their recovery is challenging.

We have studied liquid-liquid extraction followed by distillation or back extraction as methods to isolate C_1–C_4 acids from biomass based dilute aqueous solutions. Various critical parameters and prerequisites were identified. In some cases even 98% recovery yields were obtained from solutions that contained 2–3 wt-% of the desired acid. However, each particular feed is a case of its own where many variables, not least the composition of the extracting solvent and the method of recovery from the extractant should be carefully optimized. After the screening phase, where the basic understanding of the system is obtained, the work should continue with feed from the real process so that the effect of all the components in actual concentrations can be seen.

After finding technically working arrangements, where all the chemicals are industrially available and safe to use, it is important to include total energy consumption, waste water purification, solvent regeneration, purification of the product etc. in the studies. All flows in the process are modelled. Various concepts should be developed side by side and at the end put the total investment and operation costs to comparison.

In general, our experience has shown that liquid-liquid extraction followed by distillation or back extraction can provide an attractive route for carboxylic acid recovery from industrial side streams.

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References

1. Fitzpatrick, S.W. 2006. A “Bio-Refinery” Concept Based on Thermochemical Conversion of Cellulosic Biomass. Feedstocks for the Future, ACS Symposium Series, 921, Chapter 20, p. 271.

2. Käkölä, J., Alén, R., Pakkanen, H., Matilainen, R., Lahti, K.J. 2007. Quantitative Determination of the Main Aliphatic Carboxylic Acids in Wood Kraft Black Liquors by High-Performance Liquid Chromatography-Mass Spectrometry. Chromatography A 1139(2), p. 263.

3. Oasmaa, A., Peacocke, C. 2010. Properties and Fuel Use of Biomass-derived Fast Pyrolysis Liquids. VTT Publications 731.

4. Alriksson, B., Cavka, A., Jönsson, L.J. 2011. Improving the Fermentability of Enzymatic Hydrolysates of Lignocellulose Through Chemical In-situ Detoxification with Reducing Agents. Bioresour. Technol. 102, p. 1254.

5. Kertes, A.S., King, C.J. 1986. Extraction Chemistry of Fermentation Product Carboxylic Acids. Biotechnol. Bioeng. 28, p. 269.

Some xylan ethers for coating applications

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Abstract

Hemicelluloses and celluloses are the most abundant natural polymers and their availability outranges practically the current volumes of plastic production. This paper demonstrates opportunities of xylan ether derivatives in material applications as developed for wood-based xylan. Routes to chemicals and materials useful for coating and packaging – including barrier materials and coating binders – was demonstrated for white and pure xylan from bleached birch kraft pulp resulting in materials with improved plasticization, processability, and barrier properties. This platform, tailoring of chemicals and materials, enables further development for specific applications.

Introduction

Hemicelluloses are non-crystalline heteropolysaccharides classically defined as alkali soluble material after removal of pectic substances [1]. They are composed of various sugar units and are branched. Hemicelluloses have a degree of polymerization of 80–200. The backbone of hemicelluloses can consist of only one unit e.g. xylose in xylans, or of two or more units in e.g. glucomannans. Hemicelluloses are quite easily hydrolyzed by acids to their monomeric components consisting of D-xylose, L-arabinose, D-glucose, D-galactose, D-mannose, uronic acids and small amounts of other sugar units. Hemicelluloses and in particular xylan can be produced from different kinds of wood or agro-based materials using different kind of extraction methods [2, 3, 4].

For xylan isolation, lignin is usually first removed from pulp followed by bleaching. After that, the xylan is easily extractable from wood and agro-based material in alkaline conditions [6, 7]. Typically, alkaline extraction cleaves the native acetyl substituents of the xylan and markedly affects solubility. Dependent on the source of xylan, the color can vary from brown (lignin-containing) to white.

Xylan isolation from bleached birch kraft pulp

The xylan content in hardwood and hardwood pulps is between 20 and 30 w-% for eucalypt and birch as shown in Figure 1. Due to the higher xylan content, birch is favored over eucalypt as raw material for xylan.

A production process for pure and essentially linear xylan has been developed and upscaled at Keskuslaboratorio (KCL), Finland and VTT Technical Research Centre of Finland. The process includes alkaline extraction of bleached birch kraft pulp and purification by e.g. ultrafiltration, precipitation or a combination of the methods [10, 11, 12]. The xylan extract composition from an industrial bleached kraft pulp is shown in Table 1 showing that the major component is very pure xylan (i.e. free from other hemicellulose components). Only 1–2% of the total sugars are other than xylose. Mannose and galactose contents were below 5 mg/l. The product is a milky, white dispersion after e.g. ultrafiltration (see Figure 2). This xylan is used as dispersion in non-dried form for the further modification.

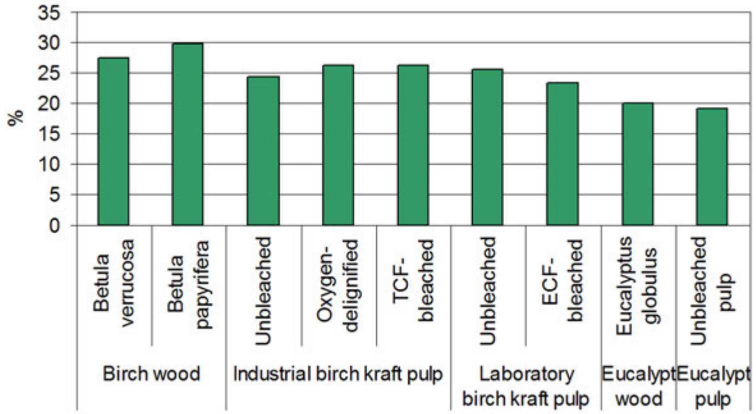


Figure 1. Xylan content, %, in hardwood and hardwood pulp for birch and eucalypt [1, 8, 9].

Table 1. Sugar content as monosaccharides after acid hydrolysis and xylan content of alkaline extract from bleached birch pulp; values of two parallel extractions.

NaOH, mol/l	Xylose, mg/l	Arabinose, mg/l	Glucose, mg/l	Total sugars, mg/l	As xylan, mg/l *	Extracted xylan, % of original pulp
0.5	5 000–6 100	9–10	13–15	5 100–6 200	4 400–5 400	8–9
1.0	9 900–11 000	5	16–25	9 900–11 000	8 710–9 680	15–17

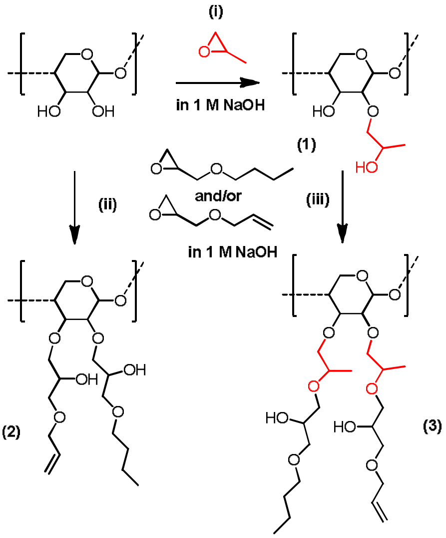
* As acetyl-free, glucuronic acid-free, polymeric xylan.

Modification

The non-dried xylan was etherified in alkaline conditions using epoxide reagents12, 13 to different derivatives as shown in Scheme 1. The products, hydroxypropylated xylan (HPX), butyl-allylated xylan (X-BA) and hydroxypropylated and butyl-allylated xylan (HPX-BA), have thermoplastic properties e.g. film forming properties. Some characteristics and analysis data is collected in Table 2.

Table 2. Characteristics of the xylan ether derivatives HPX, XBA and HPX-BA (see text for abbreviations). The degrees of substitution were calculated from the peak areas after peak integration of 1H-NMR spectra.

Sample code	DS (HP)	DS (A)	DS (B)	Film forming properties	T_g (°C)
HPX	1.5	No	no	Transparent flexible film	66
X-BA	No	0.3	0.5	Transparent flexible film	58
HPX-BA	0.6	0.2	0.3	Slightly opaque film	64



Scheme 1. Etherification routes using epoxy reagents in alkaline conditions. (i) xylan is hydroxypropylated using propylene oxide; (ii) xylan is only etherified using butyl and allyl glycidyl ethers; (iii) hydroxypropylated xylan is further etherified using butyl and allyl glycidyl ethers [1]. Hydroxypropylated (HPX); [2] butyl-allylated (X-BA) and [3] hydroxypropylated and butyl-allylated (HPX-BA) xylans.

Application tests

Barrier coatings on board

The growing demand for replacing existing barriers, such as aluminum and synthetic non-renewable polymers (e.g. polyethylene, polyvinyl alcohol, polyvinylidene chloride etc.) with biobased materials, has led to an accelerated development of biopolymer barrier layers for food packaging systems. Barrier coatings have been designed to protect and preserve the product from harmful external influences. Such external influences can range from oxygen, carbon dioxide and water in consumer commodity packages to trace levels of metal ions in state-of-the-art microelectronic devices. In 2007, the market for barrier coatings for paper and board was 3 778 M€ and is expected to climb to 4 552 M€ by 2014 [14].

The prepared xylan ether derivatives were evaluated as barrier coating materials in packaging for oxygen, water vapor and grease barrier properties. It was found that chemically cross-linked water-soluble xylan derivatives show promising barrier properties on precoated board (Table 3). The non-dried xylan and precoated board coated with HPX are shown in Figure 2 as an example. The key to success lies in the water solubility and particle dimension as well as the structure of the board substrate. The introduced internal plasticization improved film formation of xylan, since unmodified xylan from alkaline extraction of kraft pulp is not film forming. Cross-linking was used as a technique to further improve the barrier properties of the xylan ether derivatives and their coatings. The best oxygen permeability (OP) at 23°C and 0% RH was exhibited by cross-linked hydroxypropylated xylan (HPX 2+CA) and was three times better than the best reference, that being PET-coated board. Water vapor permeabilities of the xylan coatings were 50–100% of that measured for the commercial biopolymer coating. In addition, the barrier coatings showed grease barrier properties.

Table 3. Normalized oxygen permeability (OP), normalized water vapor permeability (WVP) and grease resistance values for xylan derivative coatings on precoated board [12].

Sample	**OP 23°C, 0% RH ($cm^3 \mu m/d,m^2,kPa$)**	**WVP 23°C, 50% RH ($g \mu m/m^2,d,kPa$)**	**Grease barrier**	**KIT grease resistance**
SE Cupforma Classic PE	1 141 ± 37	1.3 ± 0.8	-	12
SE Cupforma Natura Bio	202 ± 22	13 ± 0.3	> 24 h	NA
SE Trayforma Performance PET	41 ± 0.1	2.3 ± 0.9	NA	NA
SB-latex + talc	9 405	8 ± 0.4	NA	NA
Xylan	-	-	-	-
HPX* + 5% CA	15 ± 1	7 ± 1	> 24 h	> 12
X-BA+ 5% CA	150 ± 28	6 ± 1	> 24 h	> 12
X-BA+ 20% G:S 1:1+5% CA	181 ± 8	8 ± 1	> 24 h	> 12
HPX-BA + 20% G:S 1:1	1 487 ± 84	13 ± 2	> 24 h	> 12

SE-Stora Enso; G-Glycerol; S-Sorbitol; CA-Citric acid; *20% solids; ^11% solids; NA-Not Analyzed

Figure 2. Xylan isolated from bleached birch kraft forms a white dispersion after ultrafiltration or precipitation from the alkaline extract (left). Barrier coating of HPX on pre-coated board (right).

Pigment coating binder for offset grade printing grades

Another important converting process is pigment coating which is applied for printing papers as well as board to improve printing properties and the appearance of uncoated paper and board. Coating colors contain mineral pigments, binders, rheology modifiers (thickeners), and water and are applied on the base material. Replacement of oil-based latex binders with bio-based polymers is of interest in the coating color to decrease the dependence synthetic polymers. Currently, synthetic latexes are preferred to commercially available bio-based, soluble starch binders, because the surface strength of the coated paper is normally higher and printing properties are better with latex than with starch formulations. Dispersed xylan acetate has been tested earlier as coating binders [15] but some challenges were observed e.g. in film forming properties. Introduction of internal plasticization to xylan derivatives as performed here is a tool to address these challenges.

Xylan ether derivatives were tested as binders in pigment coating applications for offset grade papers [12]. Good surface strength of coated paper could be demonstrated with butylated and allylated xylan(X-BA) and it performed in the tests almost as well as the reference latex (Figure 3). The performance of hydroxypropylated xylan (HPX) was not as good as that of X-BA. Some development is needed as e.g. shear viscosities of the coating colors with xylan derivative binders were generally considerably higher than that of the latex color.

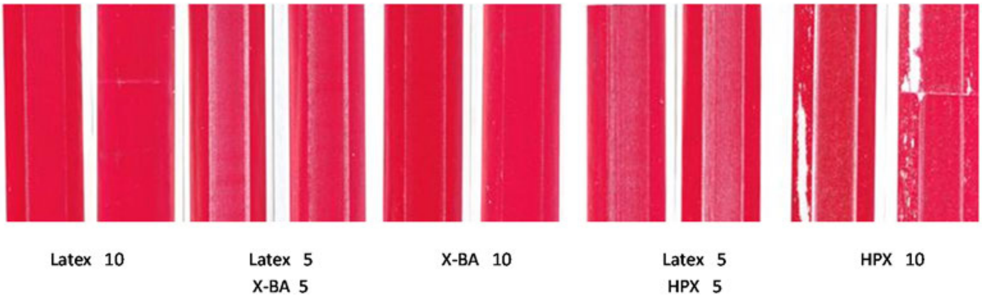


Figure 3. Coated paper samples after Prüfbau wet pick test. The labels describe the binder type and the binder amount (pph) in the coating colors. Also mixtures of binders were tested.

Conclusions

Xylan provides a good starting polymer for modification of potential chemicals in film, coating and barrier applications. Good barrier properties were demonstrated for the xylan ether derivatives in oxygen, water vapor and grease barrier. The tested derivatives demonstrated reasonable performance as pigment coating binders for offset printing papers, as indicated, for example, by the relatively good surface strength. By further optimization and tailoring, even better properties are expected. Currently, there is no industrial production of hemicelluloses for product development. However, xylan and other hemicelluloses may become readily available in case the production of dissolving pulp increases significantly. This would be the case, if the demand to use wood-based fibers to replace e.g. synthetic textile and cotton fibers would grow significantly. In addition, the developed modification routes can be applied and adjusted for new sources of polysaccharides in agricultural or marine biorefineries.

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References

1. Sjöström, E. 1993. Wood chemistry—fundamentals and applications. Academic, London.

2. Ebringerová, A., Heinze, T. 2000. Xylan and xylan derivatives – biopolymers with valuable properties, 1 Naturally occurring xylans structures, isolation procedures and properties. Macromol. Rapid Commun. 21, pp. 542–556.

3. Glasser, W.G., Kaar, W.E., Jain, R.K., Sealey, J.E. 2000. Isolation options for non-cellulose heteropolysaccharides (HetPS). Cellulose 7, pp. 299–317.

4. Willför, S., Rehn, P., Sundberg, A., Sundberg, K., Holmbom, B. 2003. Recovery of water-soluble acetyl-galactoglucomannans from mechanical pulp of spruce. Tappi J. 2, pp. 27–32.

5. Willför, S., Sundberg, A., Pranovich, A., Holmbom, B. 2005. Polysaccharides in some industrially important hardwood species. Wood Sci. Technol. 39, pp. 601–617.

6. Buchanan, C.M., Buchanan, N.L., Debenham, J.S., Shelton, M.C., Wood, M.D. Corn fiber for the production of advanced chemicals and materials: arabinoxylan and arabinoxylan derivatives prepared therefrom. US Patent application 2001020091 A1.

7. Glasser, W.G., Jain, R.K., Sjöstedt, M.A. Thermoplastic pentosan-rich polysaccharides from biomass. US Patent 5430142.

8. Fuhrmann, A., Rautonen, R., Toikkanen, L. 1999. Kartering av en TCF-björkvedssulfatmassafabrik, ‘Survey of a TCF birch kraft mill’, SCAN Forsk report 715. 54 p.

9. Laine, C., Tamminen, T. 2002. Origin of carbohydrates dissolved during oxygen delignification of birch and pine kraft pulp. Nord. Pulp Pap. Res. J. 17(2), pp. 168–171.

10. Pekkala, O. Method of producing paper and cardboard, WO2007065969 A1.

11. Krogerus, B., Fuhrmann, A. 2009. Isolation and use of pure xylan from bleached kraft pulp, The 2nd Nordic Wood Biorefinery Conference, NWBC 2009. Helsinki, Finland, Sep 2–4, Proceedings, Posters, Volume 2. Pp. 198–202.

12. Laine, C., Harlin, A., Hartman, J., Hyvärinen, S., Kammiovirta, K., Krogerus, B., Pajari, H., Rautkoski, H., Setälä, H., Sievänen, J., Uotila, J., Vähä-Nissi, M. Hydroxyalkylated xylans – their synthesis and application in coatings for packaging and paper, Ind. Crop. Prod. (Accepted for publication.)

13. Jain, R.K., Sjöstedt, M., Glasser, W.G. 2001. Thermoplastic xylan derivatives with propylene oxide. Cellulose 7, pp. 319–336.

14. Jenkins, S. 2009. The Future of Functional and Barrier Coatings for Paper and Board, Leatherhead, PIRA International Ltd.

15. Laine, C., Peltonen, S., Hyvärinen, S., Krogerus, B., Mikkonen, H., Pajari, H., Vähä-Nissi, M. Production of novel dispersions based on hemicellulose ester polymer in water, WO 2008145828 A1.

Posters

Activities of IEA bioenergy task 42 “biorefinery” on wood based bioenergy driven biorefineries – classification, sustainability assessment, complexity index and international perspectives until 2025

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IEA Bioenergy Task 42 “Biorefineries” has formulated the following definition: “Biorefining is the sustainable processing of biomass into a spectrum of bio-based products (food, feed, chemicals, materials) and bioenergy (biofuels, power and/or heat)”. “Energy-driven” biorefineries and “product-driven” biorefineries are distinguished. A classification system for biorefinery was developed to describe each biorefinery by the following four features (Figure 1, Figure 2): 1) platform, 2) feedstock, 3) products and 4) processes, e.g. “A 3-platform (lignin, C6&C5 sugar, electricity&heat,) biorefinery using wood chips for bioethanol”. Based on the activities of the 11 participating countries (A, AUS, CA, DK, FR, G, I, IR, NL, T, US) the task identifies and assesses the current status and development potential of “energy-driven” biorefineries and “product-driven” biorefineries based on wood. The assessments are based on a “Full Value Chain Approach”, covering raw material issues, conversion processes and final product use in an integrated approach and assessing economic, socio-economic, environmental and social aspects in comparison to conventional processes and products. As a first step the 6 most interesting “energy-driven” biorefinery concepts based on wood until 2025 and their value chains, including the integration and deployment options in industrial infrastructures, are analysed. These concepts based on wood (e.g. wood chips, saw mill residues) produce road transportation biofuels: bioethanol, FT-biofuels, biomethane and hydrogen (Figure 3):

1. “2-platform (syngas, electricity&heat) biorefinery using wood chips for FT-Biofuels, electricity, heat and waxes with steam gasification”
2. “3-platform (pyrolyses oil, syngas, electricity&heat) biorefinery using straw for FT-biofuels and methanol with oxygen gasification”
3. “3-platform (pulp, syngas, electricity&heat) biorefinery using wood chips for FT-biofuels, electricity, heat and pulp”
4. “3-platform (C6&C5 sugar, lignin, electricity&heat) biorefinery using wood chips for bioethanol, electricity, heat and phenols”
5. “4-platform (hydrogen, biomethane, syngas, electricity&heat) biorefinery using wood chips for biomethane (SNG), hydrogen and carbon dioxide”
6. “4-platform (C6&C5 sugar, lignin&C6 sugar, electricity&heat) biorefinery using saw mill residues, wood chips and sulfite liquor for bioethanol, pulp&paper, electricity and heat”.

In a next step for these selected concepts “Biorefinery Fact Sheets” will be made within the activities of IEA Bioenergy Task 42 “Biorefineries” (Figure 4). Based on the mass and energy balance of these energy driven biorefineries in these “Biorefinery Fact Sheets” a sustainability assessment based on whole value chain including environmental, economic and social aspects will be documented. In addition a so called “Biorefinery Complexity Index” is under development based on the classification, which is developed for these biorefineries similar to the “Nelson`s complexity index” for oil refineries. Further information see: http://www.iea-bioenergy.task42-biorefineries.com/.

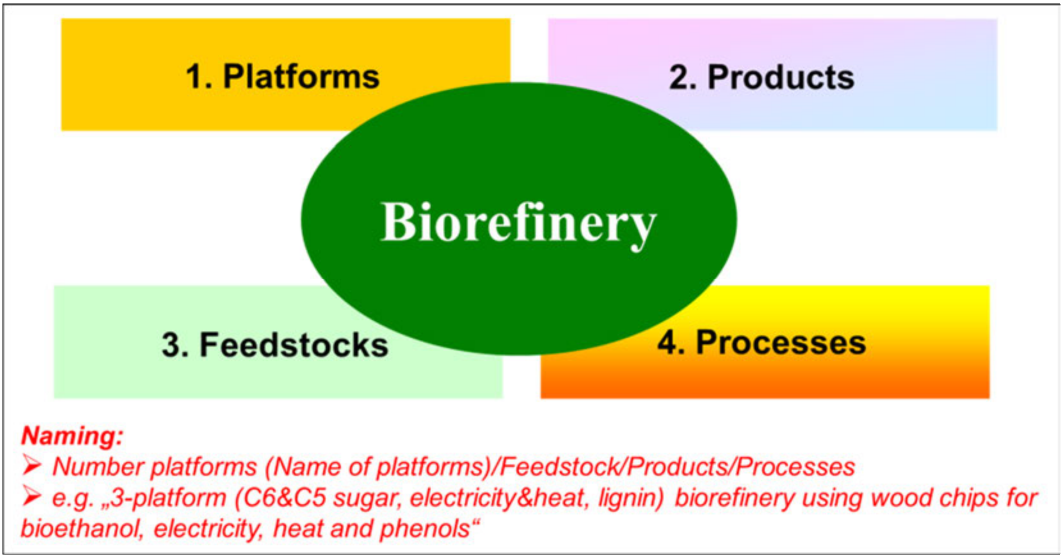


Figure 1. The 4 features to characterise a biorefinery system.

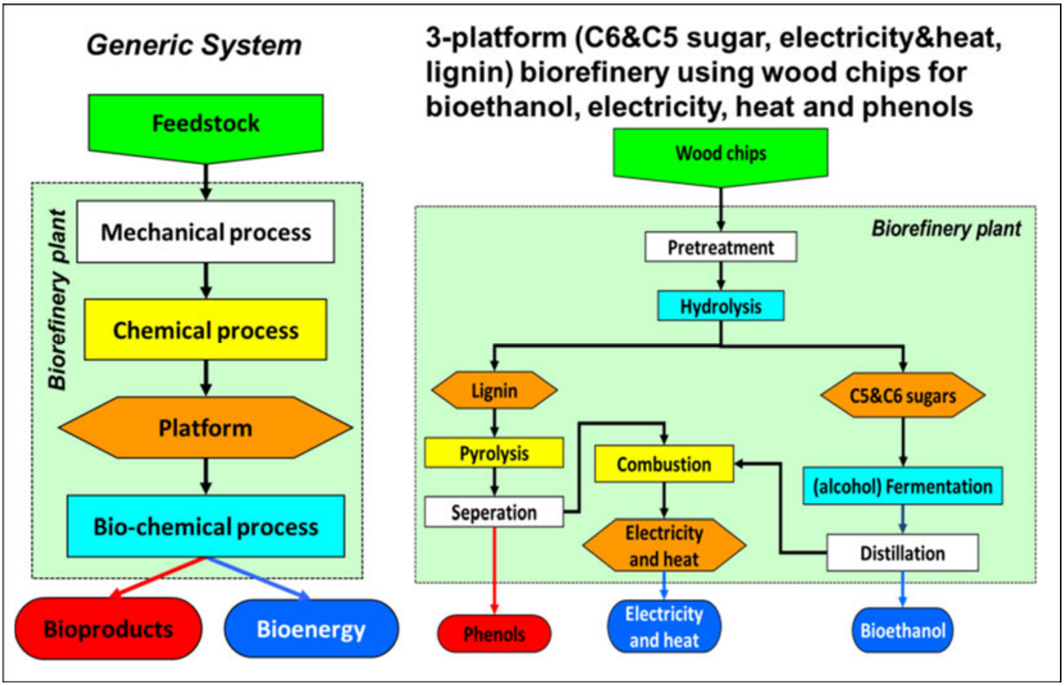


Figure 2. Application of classification system and naming.

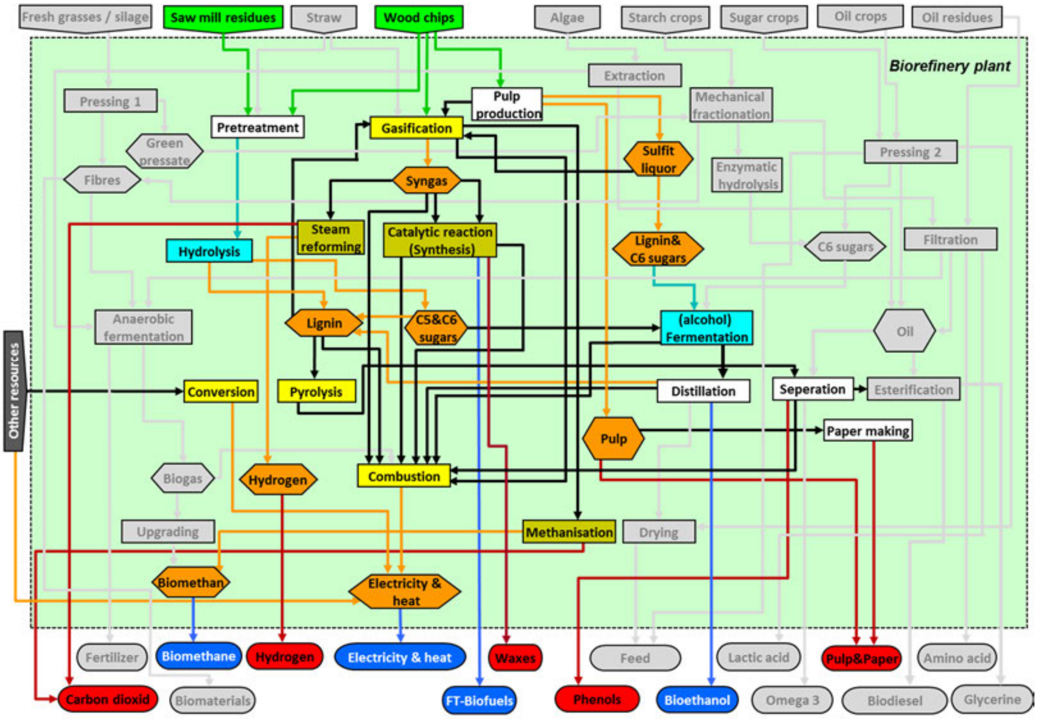
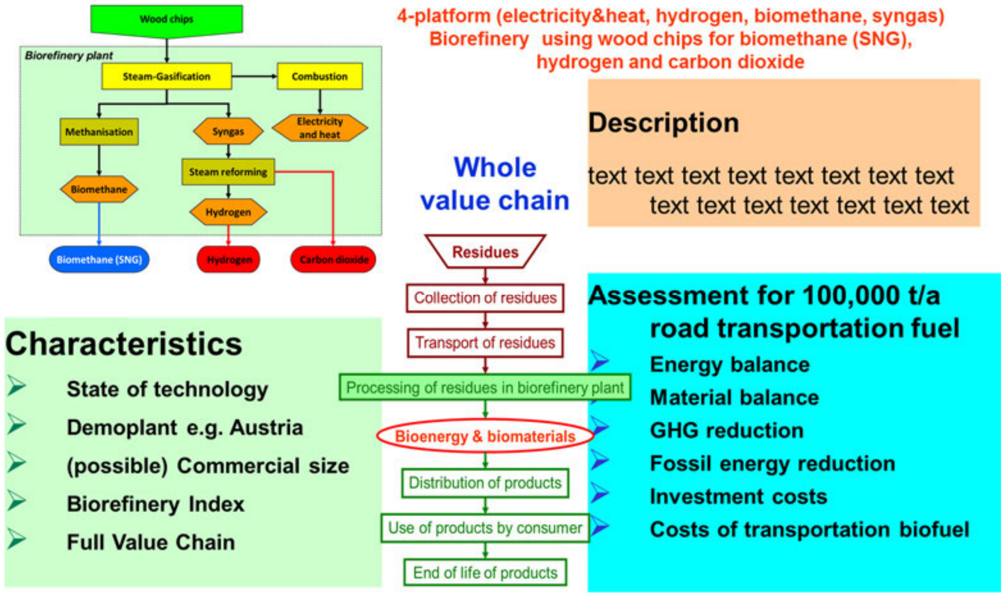


Figure 3. Energy driven biorefineries using wood in context to biorefineries using other feedstocks.



4-platform (electricity&heat, hydrogen, biomethane, syngas) Biorefinery using wood chips for biomethane (SNG), hydrogen and carbon dioxide

Whole value chain

Description

text text text text text text text text text text text text text text

Characteristics

- State of technology
- Demoplant e.g. Austria
- (possible) Commercial size
- Biorefinery Index
- Full Value Chain

Assessment for 100,000 t/a road transportation fuel

- Energy balance
- Material balance
- GHG reduction
- Fossil energy reduction
- Investment costs
- Costs of transportation biofuel

Figure 4. The “Biorefinery Fact Sheet”.

Immobilization of cellulases on magnetic particles enables enzyme re-use during hydrolysis of pretreated spruce

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Introduction

Bioethanol produced from lignocellulosic biomass is currently one of the most promising alternatives due to the great availability and low cost of this raw material. An important step for the production of lignocellulosic derived ethanol is the conversion of cellulose to glucose which can be achieved enzymatically, by the combined action of endoglucanases, exoglucanases and beta-glucosidases. However, enzyme cost is one of the main obstacles for enabling an economically viable large-scale process of lignocellulosic ethanol. Consequently, different approaches for decreasing the cost of the enzymatic step are being considered. Enzyme immobilization could reduce the enzyme cost by improving operational stability of the enzyme and allowing enzyme re-use. Recycling of the enzyme may however be difficult when treating crude particulate containing lignocellulosic feedstocks. One approach to overcome the difficulty in recycling would be to use enzymes immobilized on small magnetically susceptible particles (Figure 1).

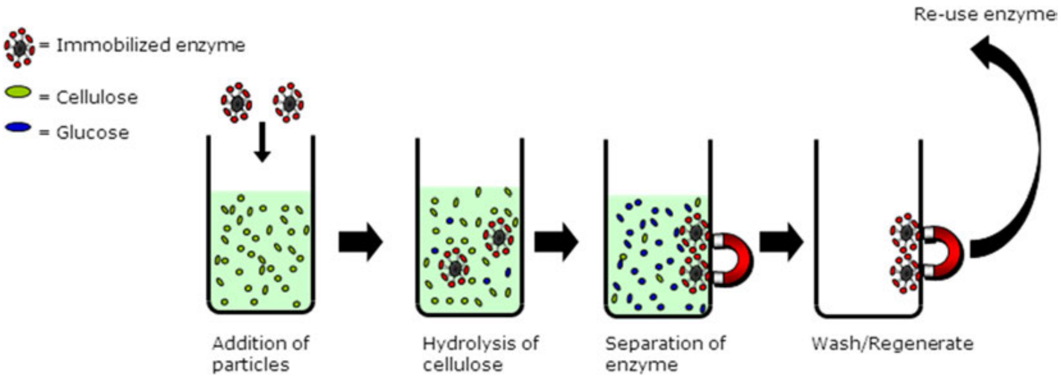

Figure 1. Schematic illustration of cellulose hydrolysis using enzyme immobilized on magnetic particles.

The aim of this study was to evaluate the possibility of covalently immobilizing cellulases on magnetic particles. The magnetic particles used were micron-sized, non-porous silica based ones, activated with polyglutaraldehyde and cyanuric chloride groups. Immobilization was conducted by using one pure β-glucosidase preparation and two different commercial cellulase mixtures from Novozymes; Celluclast 1.5L and Cellic Ctec2.

Results and discussion

The results demonstrate that it is possible to immobilize and retain activity of cellulases on magnetic particles (Table 1). Cellic Ctec2 gave higher immobilized β-glucosidase and cellulase activity compared to Celluclast 1.5L. Purified β-glucosidase resulted in highest immobilized β-glucosidase activity. The bead related activities shown in Table 1 are based on magnetic particles activated by cyanuric chloride. These particles were in all cases superior, in terms of immobilized activity, compared to particles activated with polyglutaraldehyde.

Table 1. Immobilized enzyme activity on magnetic particles using different enzyme preparations. The PNPG-assay was employed for determining β-glucosidase activity. Cellulase activity was determined by measuring liberated reducing sugar using microcrystalline cellulose as substrate (1h, pH4.8 at 50°C).

Enzyme preparation	**β-glucosidase activity (Units / g particles)**	**Cellulase activity µmole reducing sugar / (min*g particles)**
Pure β-glucosidase	104.7	-
Celluclast 1.5L	5.5	18.2
Cellic Ctec2	22.8	61.0

The performance and recyclability of immobilized β-glucosidase (BG) on more complex substrate (pretreated spruce) was studied. It was shown that adding immobilized BG to free cellulases increased the hydrolysis rate of pretreated spruce (Figure 2). Furthermore, it was possible to recycle the immobilized BG and retain activity for at least four hydrolysis campaigns. The immobilized enzyme thus shows promise for lignocellulose hydrolysis.

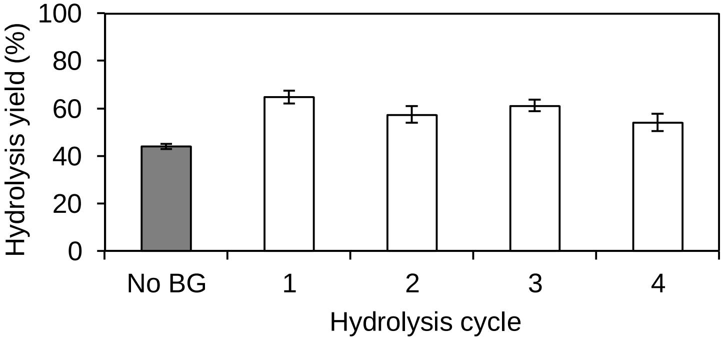

Figure 2. Hydrolysis yield of pretreated spruce using Celluclast 1.5L in combination with immobilized β-glucosidase (BG). No BG = Only Celluclast 1.5L. One hydrolysis cycle was performed for 24 h using 1.5% (w/v) DM spruce, pH4.8 at 50ºC. Amount of added Celluclast 1.5L and immobilized BG was 8 FPU/g DM and 16 U/g DM, respectively.

Contrast of *Escherichia coli KO11* and *Saccharomyces cerevisiae ATCC96581* in fermenting *Pinus patula* hydrolysate pretreated at severe steam explosion conditions

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Abstract

Bioconversion of wood residues to biofuels such as ethanol is one of the feasible initiatives towards production of renewable energy. This work compares the effectiveness of *Escherichia coli KO11* and *Saccharomyces cerevisiae ATCC96581* in fermenting *Pinus patula* (pine) hydrolysate pretreated by acid-catalyzed steam explosion. The results showed no significant difference in terms of the ethanol yield when *E. coli KO11* and *S. cerevisiae ATCC96581* were used. The maximum ethanol concentration obtained in test tubes fermentation was 18.30g/l and 19.41g/l for *E. coli KO11* and *S. cerevisiae ATCC96581* from samples pretreated at 0.5 and 3% SO_2, respectively. The ethanol yields obtained using 3L Applicon fermentors for samples pretreated at 225°C and 0.5% SO_2 for 5min. were 21.30g/l and 19.63g/l for *E. coli* and *S. cerevisiae*, respectively. Overall, ethanol yields were higher in Applicon fermentors than in the test tubes for both strains. In comparison, *S. cerevisiae* consumed the substrate faster than *E. coli*, thus making *S. cerevisiae* the most preferred strain in fermentation of hydrolysates from steam pretreated *P. patula*.

Background

Saccharomyces cerevisiae has been widely used as a fermenting organism. Presence of 5-HMF, levulinic acid and formic acid in fermentation hydrolysate affect cell growth, leading to low ethanol yield. Researchers have developed recombinant organism to ferment sugar substrate that are not fermentable by *S. cerevisiae* and tolerance to lignocellulosic inhibitors. Among other developed strains, *Escherichia coli KO11* has been reported by many researches (Trinh et al., 2010) to ferment both 5-carbon and 6-carbon sugars in lignocellulosic biomass in the presence of inhibitory compounds resulting from steam explosion pretreated processes (Gill et al., 2009).

Material and methods

Pinus patula wood chips were steam pretreated using gaseous sulphur dioxide (SO_2) (0.5–3% on water) as acid catalyst. The acid catalysed steam pretreatment was carried out at extensive conditions by using high (225°C) temperature. The pretreated materials were washed and subjected to enzymatic hydrolysis carried out by enzymes (cellulaclast 1.5L and Novozyme 188) at 50°C and 200 rpm for 72 hours. The enzymatically hydrolysed hydrolysate was filtered using Whatman filter paper (Q 110mm). The supernatant were used as a substrate in preceding fermentation process optimisation experiment. The fermentation experiments were done in test tubes for both three set of pretreated samples while in fermentors only samples pretreated at (0.5% SO_2, 225°C, 5min) were used. The fermentations were performed at inocula level of 10%v/v (test tube) and 30%v/v (fermentors) for both strains but different pH and temperature, for *S. cerevisiae* pH 5.5, temperature 30°C were applied while for *E. coli* pH were 5.5 (test tube) and 6 (fermentors), and 37°C temperature.

Results

The maximum ethanol concentrations obtained were 18.30 g/l (87%) and 19.410 g/l (88%) for *E. coli KO11* and *S. cerevisiae* obtained from the sample pretreated at acid concentration of 0.5% and 3%, respectively (Figure 1). The results indicate that all samples were fermented by the two strains. However, until the termination of the experiment, *E. coli* fermentation broth remained with some amount of glucose. In comparing test tubes and bioreactors, at 0.5% SO_2, 225°C and 5 min, the maximum ethanol concentrations were 18.30 (87%) and 21.30 g/l (91%) for *E. coli KO11*; and 17.29 (82%) and 19.63 g/l (82%) for *S. cerevisiae* respectively. These results indicate that the theoretical maximum ethanol yield is the same for test tubes and bioreactors in case of *S. cerevisiae* but they are not the same in case of *E. coli KO11*.

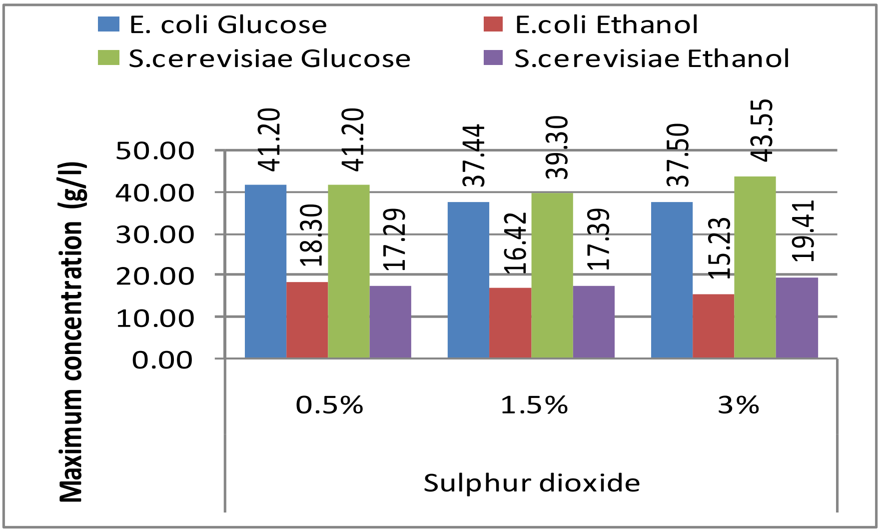

Figure 1. Maximum glucose utilized and ethanol concentration produced by tube fermentation of *S. cerevisiae* and *E. coli* at different SO_2 concentration.

Acknowledgements

The authors acknowledge with gratitude the financial support from the NUFU to the ESEPRIT Project that facilitated this study. PFI and SINTEF, Norway, are thanked for granting permission to use their laboratories to carry out part of the experiments for this work. The departments of Molecular Biology and Biotechnology and Chemical and Mining Engineering at UDSM are acknowledged for logistical support.

References

1. Trinh, C.T., Huffer, S., Clark, M.E., Blanch, H.W., Clark, D.S. 2010. Elucidating Mechanisms of solvent toxicity in ethanologenic Escherichia coli. Biotechnology and Bioengineering 106(5), pp. 721–30.

2. Gill, T.R., Mills, T.Y., Sandoval, N.R. 2009. Cellulosic hydrolysate toxicity and tolerance mechanisms in Escherichia coli. Biotechnol. for biofuels 2(26), pp. 1–11.

Simultaneous production of ethanol and softwood kraft pulp: pretreatments and effects of inhibitors on fermentations

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Introduction

The objective of this project is to develop a process for the parallel production of ethanol and cellulose in the same pulp mill, by applying a prehydrolysis step to softwood chips to extract hexose sugars for their subsequent fermentation in ethanol.

In a previous work it was shown that prehydrolysates from prehydrolysis treatment carried out with the addition of sulphuric acid, could be fermented directly into ethanol (Chirat, 2009). However, the overall yield was significantly lower than the control kraft process, and the final DPv was also significantly decreased. By applying an autohydrolysis treatment, pulps of better properties could be obtained (Chirat et al., 2009, 2011). However, the drawback of the autohydrolysis stage performed at 160°C was that the hydrolysate contained a majority of oligomers, which is not suitable for a direct fermentation into ethanol. The objective of the present study was to compare a prehydrolysis with the addition of 1% sulphuric acid on wood, with an autohydrolysis followed by a posthydrolysis of the hydrolysate, in terms of sugars content and inhibitors concentration. The effect of the inhibitors on ethanol production was studied in a second part.

Results and discussion

Effect of a post-hydrolysis on hydrolysate produced from an autohydrolysis

To increase the rate in monomers after the autohydrolysis treatment, a post acid hydrolysis was performed on the resulting hydrolysate. Figure 1 shows the concentrations in hexoses, HMF, furfural and acetic acid after secondary hydrolysis run under different conditions. Some treatments allowed the hydrolysis of almost all the oligomers into monomers, while minimizing the production of degradation products: 140°C during 30 min with 0.5 and 4% of H_2SO_4 and 120°C during 60 min with 2.25% of H_2SO_4. The final concentrations in hexoses were lower than after an acid hydrolysis (23.6 g/L compared to 33.1 g/L) but with concentrations in acetic acid, HMF and furfural respectively 1.5 times, 4 times and 2 times lower.

Effect of inhibitors on fermentation

The effect of three inhibitors, HMF, furfural and acetic acid was studied on synthetic media of fermentation containing sugars and inhibitors at the same concentrations as those measured after the hydrolysis carried out with 1% sulphuric acid. The fermentations of sugars alone, sugars with one inhibitor and sugars with the simultaneous presence of the three inhibitors were compared.

Gay-Lussac yields of fermentations were calculated from the initial amount of hexoses after 4, 24 and 48 hours of fermentation. The yield after 4 hours gives the productivity of the fermentation before reaching the final yield. The measurement after 24 or 48 hours ensures that the final yields are reached before 24 hours, when no significant difference is observed between 24 and 48 hours (Figure 2). The presence of only one inhibitor had no significant effect compared to the fermentation without any added inhibitor. The simultaneous presence of the three inhibitors however lowered the productivity, but the final yield was not affected. Inhibitors are known to potentially decrease the ethanol yield (Almeida et al., 2007), but can also reduce the productivity.

These results show that the concentrations of inhibitors found in the hydrolysates from the prehydrolysis carried out with 1% of sulphuric acid should not be a problem for ethanol production. This point was verified by carrying out a fermentation of the "real" hydrolysate obtained from wood. Nevertheless, increasing the hydrolysate concentration prior to the fermentation could be necessary to have a profitable distillation. An autohydrolysis would be advantageous in this case, as it was shown that autohydrolysis followed by a post-hydrolysis of the hydrolysate yielded very low concentrations of inhibitors.

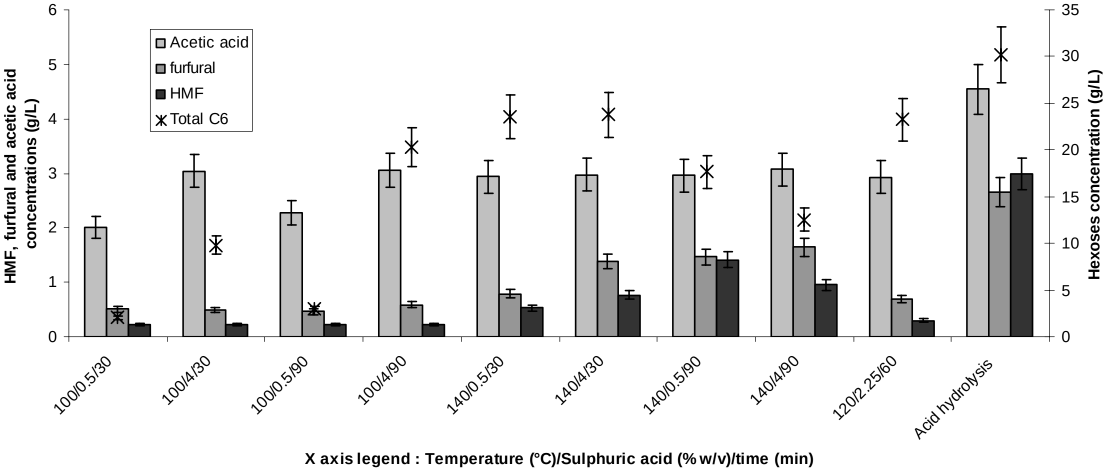

Figure 1. Concentrations in hexoses, acetic acid, furfural and HMF in hydrolysates resulting from secondary hydrolysis. Comparison with the hydrolysate from the prehydrolysis carried out with the addition of 1% of sulphuric acid.

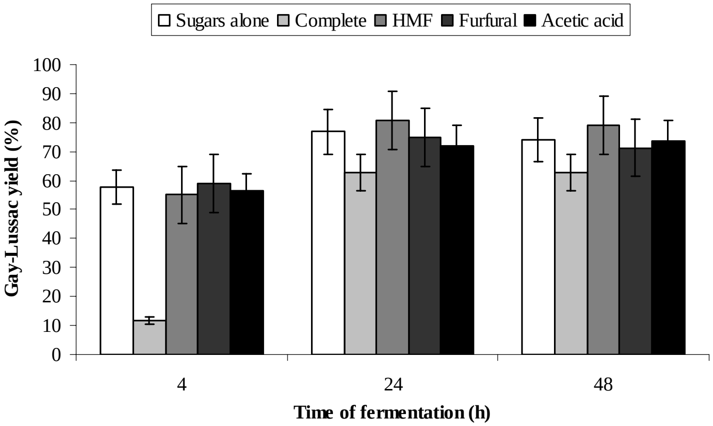

Figure 2. Gay-Lussac yields of fermentations after 4, 24 and 48 hours.

Acknowledgements

The authors wish to thank the TUCK foundation (ENERBIO programme) for the funding of this study.

References

Almeida, J.R.M. et al. 2007. Increased tolerance and conversion of inhibitors in lignocellulosic hydrolysates by *Saccharomyces cerevisiae*. Journal of chemical technology and biotechnology 82, pp. 340–349.

Chirat, C. et al. 2009. Hemicelluloses extraction from eucalyptus and softwood wood chips: pulp properties and ethanol production in ISWFPF, Oslo, Norway.

Chirat, C. et al. 2011. Bleaching ability of pre-hydrolysed pulps in the context of a biorefinery mill, International Pulp Bleaching Conference, Tappi Proceedings, October 5–7, 2011, Portland, USA.

Sustainable biofuel: innovations in bioethanol production technologies (SusBioFuel)

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Abstract

The aim of the project is to develop biochemical technologies for sustainable ethanol production from lignocellulosic material (spruce and straw). Ionic liquid pretreatment indicates a reduction in cellulose crystallinity giving a more effective enzymatic hydrolysis. Immobilized β-glucosidase on cyanuric acid particles has been shown functional after repeated recycling operation. A double mutant of the thermophilic anaerobe *Thermoanaerobacter islandicum* (*ace*$^-$ *lac*$^-$) has been developed with increased ethanol yield and able to ferment pentoses, hexoses and the disaccharide cellobiose.

Introduction

SusBioFuel (2010–2014) is a project in the Top-Level Research Initiative (TRI) partly funded by Nordic Energy Research. Major barriers for biochemical conversion of lignocellulosic materials and to their utilization as biofuels are high costs for physical pretreatment, enzyme hydrolysis of celluloses/hemicelluloses and fermentation of sugars to ethanol. Reductions in cellulose crystallinity and/or lignin content by ionic/organic solvents pretreatment are expected to improve the enzymatic hydrolysis yield of cellulose. A new recycling method for enzymes, based on magnetic particles and immobilization, may reduce the cost of enzymatic hydrolysis. High ethanol yield and high production rate are required for an optimal production of ethanol. Thermophilic anaerobic bacteria are robust microorganisms and wild types are known for direct ethanologenic fermentation of polysaccharides containing both hexoses and pentoses. However, the yields of ethanol for known strains on sugar basis are low and need to be improved by genetic methods. Anaerobic thermophilic strains isolated from geothermal habitats in Iceland, such as *Thermoanaerobacter spp* are used for knock-out mutations to reduce by-product formation and increase yield.

Results

Improved pretreatment process using ionic liquids

Pretreatment process has been optimized for Norway spruce using the ionic liquid EMIM-OAc (1-ethyl-3-methylimidazolium acetate). The spruce raw material used was treated by the newly developed Advanced Thermo Mechanical Pulping (ATMP) process which shows significantly lower energy consumption than traditional TMP processes (up to 40% reduction). The ionic liquid pretreatment process was optimized with respect to time and temperature, using enzymatic saccharification potential of the pretreated biomass as the main optimization parameter. Pretreatment with EMIM-OAc gave effective dissolution of the spruce ATMP, giving 90% enzymatic digestibility of spruce glucans under optimal conditions (100°C, 12 hrs). Lignin dissolution in EMIM-OAc was, however, low at these conditions.

Enzyme recycling process

β-glucosidase has been covalently immobilized on non-porous magnetic particles which were activated by different functional groups. Particles activated with cyanuric chloride and polyglutaraldehyde gave the highest bead related immobilized enzyme activity. Added immobilized β-glucosidase to free cellulases (Celluclast 1.5L) increased the hydrolysis rate of pretreated spruce. In addition, the immobilized β-glucosidase was re-used and the activity retained for at least 4 cycles. In another approach of immobilization, biotin-tagged β-glucosidase has been expressed by using *in vivo* biotinylated in *E. coli* strains. Immobilization of cellulase mixture (Celluclast 1.5 L and Cellic Ctec2) has also been performed. The results showed that the immobilized cellulases could hydrolyse microcrystalline cellulose and pretreated spruce. The next will be to study whether the immobilized cellulases can be recycled and determine how many hydrolysis cycles the cellulases can be used.

Combining ***lac***$^-$ and ***ace***$^-$ mutations in one strain of ***T. islandicum***

The major obstacles to genetic manipulation of thermophilic bacteria are the lack of available functional genetic markers and difficulties with transformation. Insertion of kanamycin and erythromycin resistance genes into *T. islandicum* AK17 was successfully achieved through electrotransformation and both genes conferred antibiotic resistance at 55°C, making it possible to genetically manipulate *T. islandicum*. Two *T. islandicum* mutants were constructed, knocking out a lactate dehydrogenase gene (*lac*$^-$) and acetate kinase and acetaldehyde dehydrogenase genes (*ace*$^-$), respectively, for reduced by-product formation. The *lac*$^-$ mutant produced almost undetectable amounts of lactic acid, while acetic acid production was similar to what was observed in the wild type strain, and ethanol yields were increased. The *ace*$^-$ mutant showed reduced acetic acid production, increased lactic acid production, and reduced ethanol production. The knockouts were subsequently combined into one double mutant (*lac*$^-$ *ace*$^-$) which produced ethanol as the main by-product, and almost undetectable amounts of acetic and lactic acid.

Optimizing of fermentation process for double mutant strain of ***T. islandicum***

The developed double mutant (*lac*$^-$ *ace*$^{-)}$ of *T. islandicum* AK 17 has been characterized for sugar fermentation and product formation. The strain ferments the lignocellulosic hexoses (glucose, galactose and mannose), the pentoses (xylose and arabinose) and the disaccharide cellobiose, but not the polysaccharides cellulose or xylan. As expected, the strains produce ethanol as the main product, and almost undetectable amounts of acetic and lactic acid was observed. In batch fermentation, 17 g ethanol/l was obtained with a yield of 0.41 g/glucose consumed, a specific growth rate of 0.12 h^{-1} in the exponential growth phase, and a volumetric ethanol production rate of 0.34 g/l·h in the main ethanol production period.

Oxidative pretreatment of CCA-treated wood for bioethanol production

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Abstract

The waste management of chromate copper arsenite treated wood is challenging due to the toxic chemicals it contains. Catalytic and alkaline pretreatments are effective methods for separating carbohydrates from lignin in lignocellulosic materials. Here these pretreatments are applied to CCA-treated wood in order to produce easily hydrolysable carbohydrate rich material.

Introduction

Chromated copper arsenite (CCA) has been one of the most widely applied preservative for over 60 years around the world. Although it is not used anymore as preservative the challenge of waste management and recycling continues as the lifetime of CCA-treated wood is approximately 30 years. The waste management is complicated due to the toxic chemicals it contains. Primarily CCA-treated wood is disposed within landfills, but the leaching of copper, chromium and arsenic to the environment is a problem. On the other hand, the possible vaporization of toxic arsenic compounds is a matter of concern in thermal treatment of CCA-treated wood.

Here we present an interesting method that enables the use of treated wood as a raw material for bioethanol production. Earlier studied catalytic (CatOx) and alkaline (AlkOx) oxidation pretreatments can be used to isolate cellulose also from CCA-treated wood. [1, 2] During the treatments lignin is dissolved and some of the metal ions are removed. The obtained material can be enzymatically hydrolyzed.

Experimental

CatOx and AlkOx were carried out at 120°C for 20 hours in alkaline water solution (0.25 M Na_2CO_3) and under 10 bar oxygen pressure. In CatOx 1,10-phenanthroline was used as a catalyst ingredient. The reactions proceeded well; lignin was solubilized and the solid carbohydrate fraction was filtrated. The hydrolysis experiments were done for the carbohydrate rich materials as such and after additional extraction with mild sulfuric acid for 22 hours at room temperature.

Results and discussion

The pretreatments proceeded well; lignin was solubilized and after CatOx 76% of copper, 50% of chromium and 45% of arsenic were removed. After AlkOx the amounts were 82%, 36% and 39% respectively.

The cellulose from CatOx was hydrolyzed slightly better than the cellulose from AlkOx (Figure 1). However both samples when treated also with mild sulfuric acid were almost completely hydrolyzed already in 24 hours.

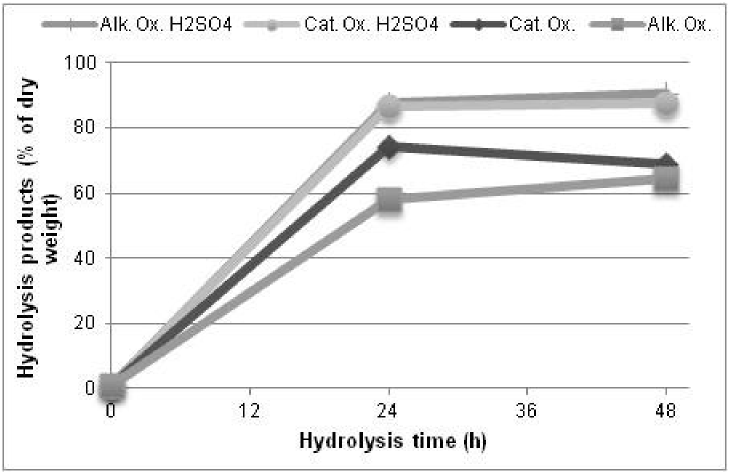

Figure 1. Enzymatic hydrolysis of carbohydrate fraction after catalytic and alkaline oxidation reactions without extraction (CatOx and AlkOx) and after additional sulfuric acid extraction (CatOx H_2SO_4 and AlkOx H_2SO_4).

Conclusions

CatOx and AlkOx together with sulfuric acid extraction are efficient methods for pretreating CCA-treated wood for cellulosic ethanol production. Although some of the metal ions remained in the material the cellulose fraction is well hydrolyzed by enzymes also without additional extraction after the oxidations.

Acknowledgements

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References

1. Hakola, M., Kallioinen, A., Kemell, M., Lahtinen, P., Lankinen, E., Leskelä, M., Repo, T., Riekkola, T., Siika-aho, M., Uusitalo, J., Vuorela, S., von Weymarn, N. 2010. Liberation of Cellulose from the Lignin Cage: A Catalytic Pretreatment Method for the Production of Cellulosic Ethanol. ChemSusChem 3, pp. 1142–1145.

2. Rovio, S., Kallioinen, A., Tamminen, T., Hakola, M., Leskelä, M., Siika-aho, M. 2012. Catalysed Alkaline Oxidation as a Wood Fractionation Technique. BioResources 7(1), pp. 756–776.

Improvement of enzymatic hydrolysis conditions of *Salix viminalis* polysaccharides

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Abstract

Research evaluating the effect of used enzyme preparations on the effectiveness of hydrolysis of *Salix viminalis* polysaccharides is presented. The used enzyme preparations included: two cellulase preparations – Celluclast 1.5L and cellulase from *Trichoderma longibrachiatum*, two xylanase preparations – Pentopan Mono BG and xylanase from *Trichoderma longibrachiatum,* and cellobiase. The highest hydrolysis efficiency was obtained when polysaccharides of pretreated *Salix viminalis* were hydrolyzed using the enzyme complex composed of: cellulase and xylanase from *T. longibrachiatum* and cellobiase.

Introduction

The increasing consumption and decreasing supplies of crude oil have led to a search for alternative energy supports. The abundance and low price of lignocellulosic materials make them attractive as a feedstock for fuel ethanol production [2]. Fast-growing energy crops, such as *Salix* and switchgrass, are considered to be a possible source of bioethanol. A process based on pretreatment of material, enzymatic hydrolysis of polysaccharides and fermentation is regarded as a promising alternative in converting the carbohydrates in lignocellulosic materials into ethanol with high yields and relatively low production costs [1].

Experimental

Salix viminalis biomass ground to a particle size of 1–2 mm was alkali pretreated with the use of experimentally fixed conditions: the proportion of alkali – 0.1 g NaOH/g d.m. of substrate, temperature 121ºC, time 3 h. After pretreatment, the pH of the suspension (10% d.m.) was adjusted to 5.0 and sodium azide was added to avoid microbial contamination. In the next step, numerous attempts at hydrolysis of the pretreated material were performed, with the use of: two cellulase preparations – Celluclast 1.5L and cellulase from *Trichoderma longibrachiatum*, two xylanase preparations – Pentopan Mono BG and xylanase from *Trichoderma longibrachiatum*. In all the hydrolysis experiments, cellobiase (Novozyme 188) was used in order to convert cellobiose to glucose. The effects of 72-hour hydrolysis were established on the basis of the amount of released reducing sugars, measured with DNS reagent. The experiments of hydrolysis of untreated material were also conducted.

Results and discussion

The highest hydrolysis efficiency was obtained when polysaccharides of pretreated *Salix viminalis* were hydrolyzed using the enzyme complex composed of: cellulase and xylanase from *T. longibrachiatum* and cellobiase. Under these conditions, the concentration of released reducing sugars (expressed as glucose) after 72 hour hydrolysis was 48.5 g/dm^3 (69.05% of theoretical value (on the basis of cellulose and hemicellulose content in raw material). The lowest amount of released reducing sugars was obtained for the enzyme complex composed of Celluclast 1.5 L and cellobiase, without xylanase. As is shown in the Figure 1, xylanase from *T. longibrachiatum* is crucial in the process of enzymatic hydrolysis of *Salix* polysaccharides. Furthermore, it was confirmed that the pretreatment step significantly affects the enzymatic hydrolysis yield (approx. a 3-fold increase).

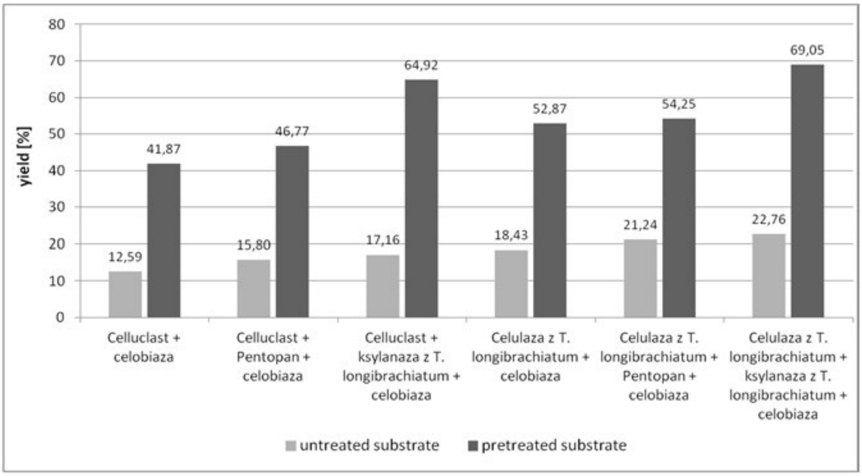

Figure 1. The effects of 72 h hydrolysis of *Salix viminalis* polysaccharides with the use of different compositions of enzymes.

Conclusions

The results of the conducted research show that hydrolysis efficiency is strongly determined by the type of enzyme complex used. Moreover, using a xylanase in combination with cellulase significantly improves process yield. It was also found that pretreatment of lignocellulosic substrate is an essential step in obtaining a high hydrolysis yield.

The strategic program of the National (Polish) Centre for Research and Development (NCBiR):

> “Advanced Technologies for Energy Generation. Task 4: Elaboration of Integrated Technologies for the Production of Fuels and Energy from Biomass, Agricultural Waste and other Waste Materials.”

References

1. Sassner, P., Galbe, M., Zacchi, G. 2008. Techno-economic evaluation of bioethanol production from three different lignocellulosic materials. Biomass Bioenergy 32, pp. 422–430.

2. Stephenson, A.L., Dupree, P., Scott, S.A., Dennis, J.S. 2010. The environmental and economic sustainability of potential bioethanol from willow in the UK. Bioresource Technology 101, pp. 9612–9623.

Production of fermentable sugars by enzymatic hydrolysis of pretreated waste textile

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Abstract

Cellulose (cotton) and polyester based textile with contribution of 27 and 39 million tons per year, respectively, has the highest share of the textile market in the world. Cellulose recovery and degradation to simple sugar in order to use for other applications, such as biofuel production, is the best way to achieve environmental goals at the lowest cost. In this study, NaOH/urea aqueous solution was used for recovery of cellulose from cotton-polyester waste textiles. The treatment with the alkali solvent resulted in efficient separation and purification of polyester and a high yield of glucose recovery out of the highly crystalline cotton after an enzymatic hydrolysis.

Introduction

A huge amount of fibre production creates million tons of waste textiles. On the other hand, one of the serious problems of cloth industry is waste textiles disposal. Environmental problems with landfilling and incineration force us to find procedures for textile recycling and new applications for these recycled textiles [1]. Cotton composes of 88–96% cellulose, therefore it is possible to hydrolyse these textiles and produce fermentable sugars for biofuel production [2]. A separation can be obtained by enzymatic hydrolysis of the cellulose in the textiles. However, the cotton structure is highly crystalline resulting to deprived hydrolysed by the hydrolytic enzymes. The current study, investigate the effect of different treatment procedures for having efficient separation of cotton and lately fermentable sugar production.

Experimental

The waste textile used in this work was 35/65 polyester/cotton blend (Poya Baft factory, Isfahan, Iran). Two enzymes, cellulose (SIGMA, C2730) and β-glucosidase (SIGMA, G0395) were used for enzymatic hydrolyses.

Textile solution (4%) was prepared by mixing 2 g textile with 48 g NaOH/urea aqueous solution (7:12 in wt.%) at different temperatures -20, 0, 20 and 100°C for 1 h and manually mixed every 10 min using a glass rod. The chemically treated fibers were then washed with extensive amounts of distilled water to obtain pH 7 and kept in the refrigerator until hydrolysis. The treated and untreated textiles were subjected to 72 h enzymatic hydrolysis at 45°C and pH 4.8 in 50 mM sodium citrate buffers with 3% (w/v) solid substrates, using 30 FPU cellulase and 60 IU β-glucosidase per gram cellulose. After 72 h hydrolysis, the residual solid (polyester) was separated by centrifugation at 4 000 rpm and 10 min.

Results and discussion

The efficiency of textile disintegration after treatment at -20–100°C was between 95–99%. The best results were obtained at the highest temperature in which cellulose separation achieved by 99%, while efficiency of untreated process was only 54%.

Table 1 shows the results of enzymatic hydrolysis of NaOH/urea treated textile at different treatment conditions. The results indicate a signification improvement in glucose production from the textile after pretreatment compared to untreated sample. The best glucose concentration was gained by 20.5 g/L at the highest temperature (100°C) after 72 h of hydrolysis.

Table 1. Glucose production from the textile by the alkali pretreatment (g/L).

Alkali pretreatment	24h	48h	72h
-20°C	14.4	15.5	19.3
0°C	10.5	12.9	18.7
20°C	17.7	19.2	19.7
100°C	17.6	18.8	20.5
Untreated	6.1	7.4	8.1

Conclusions

NaOH/urea treatment leads to a remarkable enhancement in fiber separation over 90%. Also, temperature rise has a notable effect on the process efficiency after 48 hours while it slightly increases the sugar production after 72 hours.

References

1. Jeihanipour, A., Karimi, K., Niklasson, C., Taherzadeh, M.J. 2010. A novel process for ethanol or biogas production from cellulose in blended-fibers waste textiles. Waste Management 30, pp. 2504–2509.

2. Jeihanipour, A., Taherzadeh, M.J. 2009. Ethanol production from cotton-based waste textiles. Bioresource Technol 100, pp. 1007–1010.

Monosaccharide production from lignocellulosic biomasses via concentrated acid hydrolysis

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Introduction

Monosaccharides are valuable and versatile platform chemicals that can be obtained by hydrolyzing cellulose and hemicelluloses in lignocellulosic biomasses [1, 2, 3]. Hydrolysis with concentrated sulfuric acid as catalyst leads to 80% or higher monosaccharide yield. Only a low amount of by-products is formed [2, 3].

The hydrolysis acid must be removed prior to downstream processing of monosaccharides. Traditionally neutralization with $Ca(OH)_2$ has been used. This results in high chemical consumption and generation of waste gypsum. In addition, fresh sulfuric acid is needed for every hydrolysis [2, 3].

In order to lower the chemical costs of the concentrated acid hydrolysis process, the hydrolysis acid should be recycled. This can be accomplished by using chromatography: the hydrolysates are fractionated into sulfuric acid fraction, monosaccharide fraction, and by-product fractions [2].

In this work, batchwise chromatographic fractionation of wood based concentrated acid lignocellulosic hydrolysates was studied. Effectiveness of the chromatographic purification was evaluated by investigating ethanol production from the purified monosaccharide solutions using *S. cerevisiae*.

Results

Chromatographic fractionation

An elution chromatogram of a batchwise chromatographic fractionation of a concentrated acid spruce hydrolysate using sulfonated strong acid polystyrene–divinylbenzene cation exchange resin in acid form as adsorbent is shown in Figure 1A. Sulfuric acid has a co-operative effect on the sorption of the other components. This co-operation leads to some peculiar shapes of the monosaccharide elution profiles: the profiles have elongated front parts under the sulfuric acid profile and focusing of the monosaccharides occurs at the rear of the sulfuric acid profile (Figure 1A). The co-operative effect of sulfuric acid on the elution of the other components is not clearly seen due to early separation.

The performance of the chromatographic fractionation was investigated by simulations. Both stand alone chromatographic separation and a process consisting of concentrated acid hydrolysis unit, chromatographic fractionation unit, and sulfuric acid concentration unit were investigated.

Column loading and hydrolysis acid concentration have strong effects on the performance of the chromatographic separation. Yield and productivity of the process with respect to the monosaccharides decreases rapidly as hydrolysis acid concentration in the feed solution increases. This is due to stronger overlapping of the sulfuric acid and monosaccharide profiles. Increase in column loading leads to decrease in the monosaccharide yield, while the productivity goes through a maximum.

Strong overlapping of sulfuric acid and monosaccharide profiles results in low monosaccharide yield in the stand alone separation: a large part of the monosaccharides end up to the sulfuric acid fraction. Due to the recycling of the sulfuric acid fraction, the process performance should be evaluated in steady state conditions while taking into account the surrounding unit operations.

In the investigation of the effect of the column loading on the separation, the loading giving the maximum productivity was found to be considerably higher with the recycling (18 vol%) than without it (13 vol %). Also the maximum productivity was found to be 2.6 times larger. However, the recycling has the largest effect on the monosaccharide yield: the yield in stand alone separation with the optimal loading was as low as 32.0% whereas with the recycling it was 90.6%. With recycling of sulfuric acid fraction, less than 10% of fresh sulfuric acid is needed in the hydrolysis.

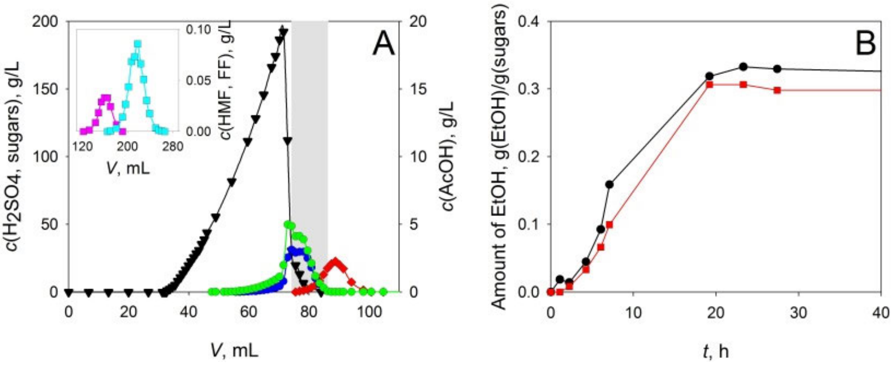

Figure 1. A: Outlet profile of concentrated acid spruce hydrolysate on strong acid PS–DVB resin in acid form (50°C). Colors: black = H_2SO_4; green = glucose; blue = combined xylose galactose, mannose, arabinose; red = acetic acid; pink = HMF; cyan = furfural (FF); shaded area = monosaccharide fraction. B: Fermentation of chromatographically purified (black) and $Ca(OH)_2$ neutralized (red) spruce hydrolysates with *S. cerevisiae*.

Fermentation

Fermentation of chromatographically purified and $Ca(OH)_2$ neutralized concentrated acid hydrolysates was studied using genetically modified *S. cerevisiae*. Ethanol productivity from chromatographically purified and $Ca(OH)_2$ neutralized hydrolysates were comparable (Figure 1B). Chromatographic purification removes all HMF and furfural from the hydrolysates and only a slight amount of acetic acid remains in the purified solution. This is not the case with $Ca(OH)_2$ neutralization. This, however, has a very limited effect on the *S. cerevisiae*. Although the ethanol productivities were comparable, chromatographic separation provides a significant increase for the ethanol yield (74.3% of the theoretical value 0.51 g(EtOH)/g(sugar)) over the $Ca(OH)_2$ neutralization (61.3%).

References

1. Burk, M.J. 2010. Sustainable production of industrial chemicals from sugars. Int. Sugar. J. 112, pp. 30–35.

2. Heinonen, J., Tamminen, A., Uusitalo, J., Sainio, T. 2012. Ethanol production from wood via concentrated acid hydrolysis, chromatographic separation, and fermentation. J. Chem. Technol. Biotechnol. 87, pp. 689–696.

3. Farone, W.A., Cuzens, J.E. 1995. Strong acid hydrolysis of cellulosic and hemicellulosic materials. US Patent No. 5,597,714, June 7.

Process schemes for chromatographic fractionation of lignocellulosic concentrated acid hydrolysates

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Introduction

Chromatography is well suited for difficult large scale biomass hydrolysate fractionations. However, often classical batch process does not give sufficient productivity and may become a bottleneck in a forest biorefinery. In such cases more advanced chromatographic separation process schemes are required.

One advanced process option for chromatographic separations is the steady state recycling chromatography (SSR) which has been shown to provide better process performance than batch chromatography in difficult separation (*e.g.* [1]). In SSR, a recycled (mixed) fraction is fed to the column with fresh feed. Eventually, a periodic steady state is obtained [1].

Simulated moving bed chromatography (SMB) also often provides better performance than the batch process (*e.g.* [2]). However, conventional SMB cannot deliver multiple fractions as is often desired, and more advanced SMB schemes are needed. One option is the Japan Organo SMB (JO-SMB), which is used in sweeteners industry. On the contrary to the basic SMB, the feed to JO-SMB is not continuous which enables the separation of three or even more components already with four column system [2]. A periodic steady state is eventually reached also with JO-SMB.

In this work, SSR and JO-SMB are compared with the classical batch process in the chromatographic fractionation of concentrated acid lignocellulosic hydrolysates. Effective fractionation of these hydrolysates is essential for the production of monosaccharides via concentrated sulfuric acid hydrolysis. The hydrolysates are chromatographically fractionated into sulfuric acid fraction, monosaccharide fraction, and by-product fractions. The sulfuric acid fraction is recycled back to the hydrolysis reactor while the other fractions are led to downstream processing.

Results

Steady state recycling chromatography

Use of steady state recycling chromatography for the fractionation of concentrated acid lignocellulosic hydrolysates was investigated with a binary model system of sulfuric acid and glucose. A large scale system (h_{bed} 3 m, d_{bed} 1 m) was used and both flow rate and column loading (% of resin bed volume) were optimized. Steady state was achieved in six cycles.

Highest productivity of the separation process with respect to the monosaccharides was obtained with a high flow rate of 250 mL/min and 6.5 vol % column loading. The productivity was approximately 33% larger than with the batch process. Minimization of eluent consumption while keeping the productivity constant was also investigated: SSR provided equal productivity as the batch process with almost 50% smaller eluent consumption.

Pareto sets illustrating the process performance for different purity requirements are presented in Figure 1A. Pareto frontiers show the highest productivity that can be achieved with certain eluent consumption. Operation above the lines is not possible, and eluent consumption can be lowered only at the expense of productivity. Decrease in the productivity with increasing purity is greater with the batch process: the benefit of SSR is pronounced when high product purity is desired.

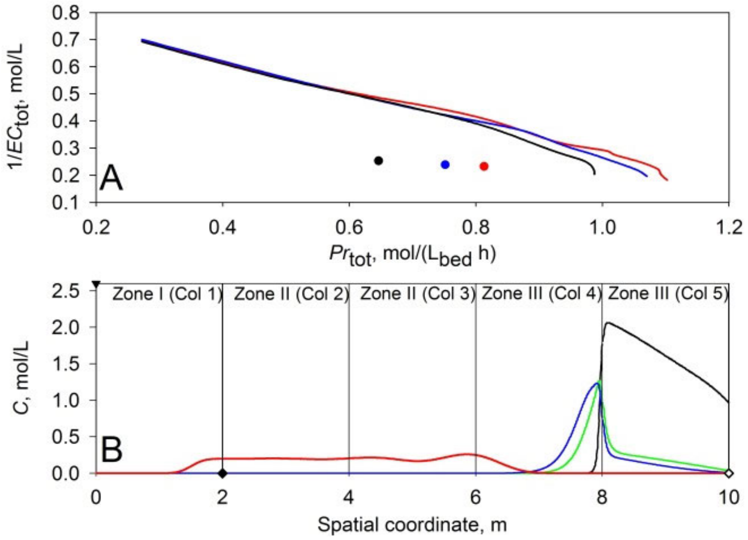

Figure 1. A: Pareto frontiers for sulfuric acid–glucose separation using batch (circles) and SSR (lines) chromatography with various glucose purity constraints: 90% (red), 95% (blue), and 99% (black). Purity of H2SO4 fraction = 98.7%. B: Spatial profiles of H2SO4 (black), glucose (green), xylose (blue), and acetic acid (red) in JO-SMB in steady state at the end of cycle.

Japan Organo SMB chromatography

Ternary fractionation (sulfuric acid, monosaccharide, and acetic acid fractions) using a five column JO-SMB (h_{bed} 2 m, d_{bed} 2 m) was also investigated. Eluent consumption was omitted.

15 cycles were needed for the system to reach periodic steady state. Good separation between monosaccharides and acetic acid was obtained (Figure 1B). However, overlapping of sulfuric acid and monosaccharide profiles was caused by interactions between these components [3]. Due to the interactions, focusing of the monosaccharides was observed at the rear of the sulfuric acid profile. This is beneficial for the productivity of the process.

JO-SMB was found to provide approximately 50% larger productivity than batch process. With the operating conditions giving the maximum productivity the purities of sulfuric acid, monosaccharide, and acetic acid outlet streams were 89.0%, 88.7%, and 100%, respectively. Accordingly, the recoveries were 97.3%, 61.7%, and 93.5%, respectively. The recovery of the monosaccharides is rather low due to overlapping of the sulfuric acid and monosaccharide profiles (Figure 1B). However, the monosaccharides in sulfuric acid outlet stream are not lost product because they are recycled back to the hydrolysis reactor.

References

1. Sainio, T., Kaspereit, M. 2009. Analysis of steady state recycling chromatography using equilibrium theory, Sep. Purif. Technol. 66, pp. 9–18.

2. Kurup, A.S., Hidajat, K., Ray, A.K. 2006. Optimal operation of a pseudo-SMB process for ternary separation under non-ideal conditions, Sep. Purif. Technol. 51, pp. 387–403.

3. Heinonen, J., Sainio, T. 2012. Modelling and performance evaluation of chromatographic monosaccharide recovery from concentrated acid lignocellulosic hydrolysates. J. Chem. Technol. Biotechnol. Doi: 10.1002/jctb.3816.

Potential expansion of second generation Fischer Tropsch biodiesel production in Finland

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Abstract

The Finnish biofuel industry is undergoing a major change in particular second generation Fischer Tropsch (FT) biodiesel production. However, efficient geographical energy planning is essential to optimally allocate the limited natural resources between biomass based industries. Therefore, a decision tool was formulated which includes three different models: (1) a spatial model that estimates the amount of biomass supply and industrial residues available for energy production, (2) an energy demand model calculates the amount of heat and transport fuel that can be delivered to the customers, (3) an optimization model that minimizes the complete costs of biodiesel supply chain from biomass supply to biodiesel delivery at the fuel stations to determine the optimal location, size and configurations of FT biodiesel production plants in Finland. Model results show that five cost-optimal biodiesel production plant locations of 390 $MW_{feedstock}$ are needed to be built to meet the 2020 renewable energy share in transport (25.2 PJ). The unit cost of FT biodiesel produced in Finland could range between 1.1 and 1.4 $€/l_{2011}$ without heat sales.

Optimization modeling

Given a set of feedstock supply points, energy demand regions, existing industrial locations and candidate FT biodiesel production plant sites, the MILP model minimizes the costs of complete supply chain from biomass supply to biodiesel distribution to determine a cost-optimal FT biodiesel plant locations, number, size and configurations (Figure 1). The model solves the optimization problem by allocating the feedstock resources efficiently to new FT biodiesel plants considering the demand from the existing biomass based industries like pulp and paper mills, pellet plants, and Combined Heat and Power (CHP)/District Heating (DH). The model provides solution to which type of feedstock (forest biomass, sawmill residuals and biomass import) can be effectively used and from which region shall it be procured considering the transportation distance, price of feedstock and its availability. Moreover, the model also analyses the potential to sell the produced by-products, heat and electricity to increases the profitability of the plant as a whole. Detailed description of the model can be found in [1, 2].

Plant locations and costs

Five cost-optimal FT biodiesel plant locations selected indicate that the spatial distribution of biomass supply and energy demand plays a dominant role in optimizing the locations of biodiesel

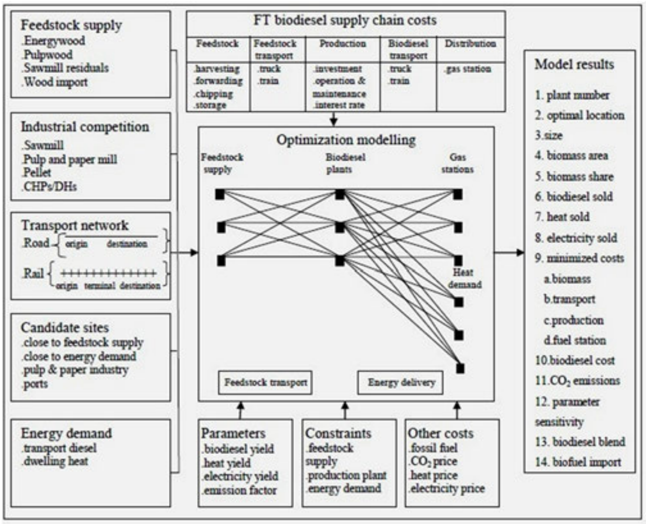

Figure 1. Outline of the optimization model.

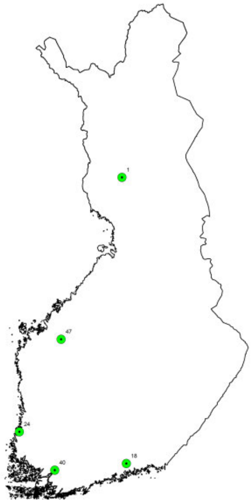

Figure 2. Optimal plant locations.

plants. Out of five, three were located at Rovaniemi, Kauhava and Rauma while the other two were located close to biomass resources. Spatial extension of sawmills which are another potential source of feedstock also play a significant role in determining the biodiesel plant sites. The results of the sensitivity analysis show that the most influencing parameters on the biodiesel cost are found to be investment costs, biodiesel conversion efficiency and operating hours, and then followed by biomass cost and heat price. The biomass availability, biomass transportation and biofuel transportation costs are least influential parameters on the biodiesel cost. This is due to the reason that the given optimal locations are indeed rich in biomass resources and also sited close to high energy demand regions where the excess heat could be sold to potential customers.

The conceptual and mathematical modeling framework contributes greatly to an understanding of the feasibility, constraints, and potential for the expansion of a biodiesel industry in Finland. More recently, renewable transportation fuels have become the top priority for Finnish Government and private investors, and therefore it is imperative to identify the optimal locations for bio-refineries in order to start up the large scale commercial biodiesel production. Thus, this study helps to provide a valuable study for government and private stakeholders to determine the most suitable strategy regarding the cost optimal locations and configuration of new biodiesel plants.

References

1. Leduc, S. 2009. Development of an optimization model for the location of biofuel production plants, Division of Energy Engineering, Department of Applied Physics and Mechanical Engineering, Luleå University of Technology.

2. Natarajan, K., Leduc, S., Pelkonen, P., Tomppo, E., Dotzauer, E. 2012. Optimal Locations for Methanol and CHP Production in Eastern Finland: BioEnergy Research, Doi: 10.1007/s12155-011-9152-4.

Biofuels and chemicals from lignocellulosic materials – a scheme for conditioning SO_2-ethanol-water spent liquor for ABE fermentation

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Abstract

We are presenting a process for conditioning spent liquor produced by SO_2-ethanol-water (SEW) fractionation of different lignocellulosic materials i.e. spruce chips, mixed forest softwood biomass and Empty Fruit Bunches (EFB) for fermentation to biofuels and chemicals by ABE (acetone-butanol-ethanol) fermentation technology utilizing Clostridia bacteria.

Introduction

SEW fractionation is a well proven, lignocellulosic fractionation technology that is herein employed to release hemicellulose derived sugars and cellulosic fibers from different feedstocks in only 30 min at 150°C. However, the dissolved sugars cannot be directly utilized for production of butanol by ABE fermentation, and further processing and conditioning is required. For instance, it is necessary to adjust the pH of SEW spent liquor to neutral levels to avoid killing the bacteria. Moreover, fermentation inhibitors such as ethanol and SO_2 must be fully removed and recovered to obtain an economical and environmentally benign process. Lignin and any other fermentation inhibitors such as furanic compounds and formic acid must also be removed.

Experimental

SEW fractionation for all lignocellulosic materials tested is performed in 30 min at 150°C with a 50% (w/w) ethanol-water solution containing 12% (w/w) SO_2 at a liquor-to-wood ratio of 3:1 L/kg. In addition, only in the case of EFB, the ash content of the feedstock is reduced by leaching before SEW fractionation. The produced pulp after SEW fractionation is efficiently washed to allow for high sugars recovery. Pulp washings are added to SEW spent liquor and the dilute mixture is then evaporated under low pressure to remove the major fermentation inhibitors i.e. SO_2 and ethanol. Ethanol removal is almost complete and any SO_2 left after vacuum evaporation is almost totally removed by subsequent steam stripping. Neutralization by liming with $Ca(OH)_2$ is then employed to bring the solution to a pH level suitable for fermentation by Clostridia bacteria. The liquor is then catalytically oxidized to convert any residual sulfite ions to sulfate. Finally, the liquor is treated with resins to further remove lignin. Figure 1 presents the overall conditioning scheme and clarifies the names of the liquors after each conditioning step.

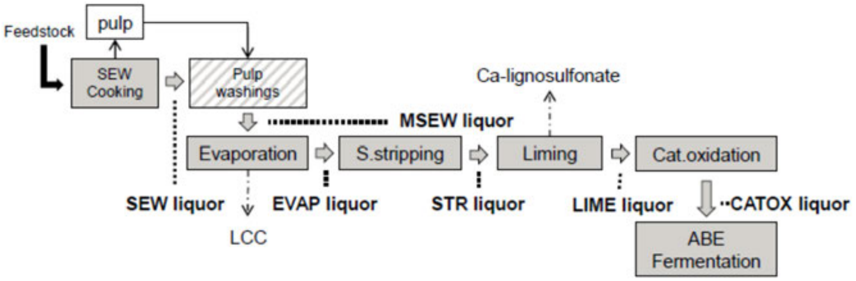
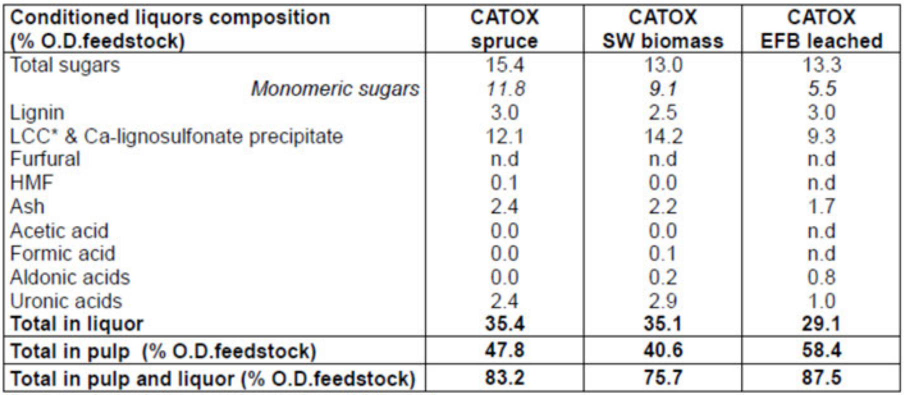


Figure 1. SEW spent liquor conditioning scheme.

Results and discussion

The mass balance in Table 1 shows that 76 to 88% of the mass of the original feedstock is accounted for in the combined CATOX liquor and pulp fibers. The sugars in the CATOX liquor of the Spruce and softwood biomass feedstocks are mostly monomeric in nature, while they are mostly polymeric (total minus monomeric) in the EFB CATOX liquor.

Table 1. Mass balance on solid phase (pulp) and conditioning liquors.



Conditioned liquors composition (% O.D.feedstock)	CATOX spruce	CATOX SW biomass	CATOX EFB leached
Total sugars	15.4	13.0	13.3
Monomeric sugars	*11.8*	*9.1*	*5.5*
Lignin	3.0	2.5	3.0
LCC* & Ca-lignosulfonate precipitate	12.1	14.2	9.3
Furfural	n.d	n.d	n.d
HMF	0.1	0.0	n.d
Ash	2.4	2.2	1.7
Acetic acid	0.0	0.0	n.d
Formic acid	0.0	0.1	n.d
Aldonic acids	0.0	0.2	0.8
Uronic acids	2.4	2.9	1.0
Total in liquor	**35.4**	**35.1**	**29.1**
Total in pulp (% O.D.feedstock)	**47.8**	**40.6**	**58.4**
Total in pulp and liquor (% O.D.feedstock)	**83.2**	**75.7**	**87.5**

*lignin carbohydrate complex, n.d., not detected

IC analysis results show that SO_2 is fully removed from conditioned liquors. Results from fermentation trials confirm that all conditioned liquors are fermentable by Clostridia bacteria.

Conclusions

An effective method to fractionate and condition SEW spent liquor from different lignocellulosics is presented. Further optimization of the conditioning scheme is underway to allow more efficient handling of feedstocks of widely different composition.

References

1. Sklavounos, E., Iakovlev, M., Yamamoto, M., Teräsvuori, L., Jurgens, G., Granström, T., van Heiningen, A. 2011. Conditioning of SO_2-ethanol-water spent liquor from spruce for the production of chemicals by ABE fermentation. Holzforschung 65(4), pp. 551–558.

Opportunities and challenges in emerging bioenergy business: Case of Finnish sawmilling industry

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Abstract

The resources of currently dominant fossil fuels are limited, and their use causes greenhouse gas emissions. Consequently, the public interest within the European Union has changed toward using renewable energy. Finland's forest industry is one of the world leaders in producing and utilizing wood-based bioenergy. Hence, it is of interest to evaluate new value-creation opportunities and the consequent challenges that face the Finnish sawmill industry. In order to identify the strategic resources that enable developing competitive advantages in the emerging bioenergy field, we applied the natural resource-based view of strategy to the sawmill industry. In the empirical part, qualitative semi-structured interviews with managers of 23 sawmills based on the Delphi methodology were conducted in two phases. We identified partnerships with local community heat plants as a strategic resource for providing new business opportunities, apart from raw material availability and existing technologies. Although the Finnish sawmills have a long tradition in energy production, most energy-related investments have been made only during the past decade, and the sawmills would be keenly interested in increasing the efficiency of using their by-products through new investments. In conclusion, the Finnish sawmill industry being the local producer of wood-based bioenergy can support meeting the ambitious national target for renewable energy production for 2020. However, the volatile bioenergy policy changes act as a major factor of uncertainty in predicting the future development of the business environment and further increase the risk level for future investments.

Keywords: Opportunities, challenges, bioenergy, Finnish sawmill industry

Introduction

Driven by globalization, industrialization, economic growth, and expanding population, the demand for global energy has grown rapidly. Since the resources of currently dominant fossil fuels are limited and their use causes greenhouse gas emissions, renewable energy usage has gained popularity as a way to address these concerns. Biofuels have been regarded as the most viable alternative to fossil fuels (Bauen et al., 2009).

Finland's forest industry is one of the world leaders in producing and utilizing wood-based bioenergy, and sawmilling is the oldest industry in the Finnish forest-based sector. To create a sustainable competitive advantage (SCA), the Finnish sawmill industry needs to develop new value-creation strategies (Lähtinen and Toppinen, 2008), for example, by using their by-products to produce bioenergy. The purpose of this study is to explore the sources of SCA, the value-creation opportunities and the consequent managerial challenges that face the Finnish sawmill industry.

Theoretical background

In the theoretical background, we applied natural resource-based view to the sawmill industry to identify the strategic resources that enable maintaining and developing SCA in the emerging bioenergy business.

Materials and methods

In this study, the focus in data gathering was on the Finnish non-integrated medium-sized sawmills whose core business is sawn wood manufacturing, and the focus in data analysis was on the managerial perceptions of the main resources for bioenergy businesses of the Finnish sawmills and the factors that facilitate or hinder future development in bioenergy production of sawmills. In the empirical part, qualitative semi-structured interviews with managers of 23 sawmills based on the Delphi questionnaire methodology were conducted in two phases.

Results

According to the two-rounds of interviews, the share of bioenergy in the Finnish sawmill value creation ranged from 0 to 10%. The interviewed sawmill managers uniformly stated that raw materials, technological know-how, personnel know-how, collaboration and services were the most important resources for bioenergy production, and sufficient and stable demand for bioenergy, governmental energy policies and financial support were the most important factors that affect the future of bioenergy business for the Finnish sawmills. In addition, prices of raw materials, prices and subsidies of bioenergy, prices and taxation of fossil fuels, vicinity of potential markets, quality of customer relationships and available outbound logistics also played important roles in developing the bioenergy business.

Based on the results mentioned above, we summarized the most promising value-creation opportunities and the consequent managerial challenges for developing bioenergy business at the Finnish sawmills, as shown in Table 1.

Table 1. Opportunities and challenges for bioenergy business of the Finnish sawmills.

Industry factors	**Opportunities**	**Challenges**
Market demand	1) A boom in renewable energy demand; 2) Potentially fruitful opportunities for sawmills for initiating value-creation businesses by producing bioenergy in collaboration with the energy industry.	Due to the cyclicality of the sawmill industry, reliance of the bioenergy production on sawmills as raw material suppliers implies that the bioenergy business also becomes vulnerable to downturns in demand in business cycles.
Policies	1) Renewable energy policy is the main driver of the growth in renew-able energy use; 2) Finland's long-standing government policy support for bioenergy (environmental taxes, investment support and subsidies); 3) A new feed-in scheme introduced in Finland in 2011 supports the wood-based power generation (MEE, 2011).	1) In Finland, environmental taxes on fossil fuels are levied only in the heating sector; 2) Finland's political decision, such as "renewable energy package", is a factor of distorting the competition among energy producers; 3) The volatile bioenergy policy changes would pose challenges for predicting the development of the business environment and increase the risk of investments.
Availability of raw material	1) Internal supply of wood fuels for sawmills at a competitive price will facilitate processing into energy products (Mäkelä et al., 2011); 2) The structural change of the forest industry in reducing the demand for sawmill by-products in traditional applications could promote the use of by-products in bioenergy production and thus open up collaboration opportunities between the sawmill industry and the energy industry.	1) Uncertainty in the sawn wood markets has increased due to Russia's political decision to limit its round wood exports; 2) Uncertainty of pellet prices prevents the expansion of the traditional sawmill industry into Finland's pellet markets (Mäkelä et al., 2011).

Technological know-how	Finland is one of the world leaders in using wood-based fuels in energy production, with globally recognized technological and logistical know-how.	The same technological and logistical solutions might be replicated by competitors outside Finland;
Forms of collaboration	Partnerships with district heating plants of the local community were emphasized as a strategic resource to create competitive advantages for bioenergy business of sawmills.	A similar collaboration form might be replicated by competitors outside Finland.
Impacts on profits	Although the share of bioenergy in Finnish sawmill value creation is small, it will affect the financial performance of sawmills overall.	Low share of bioenergy might make some sawmills lose their interest in increasing bioenergy production.
Investments	1) The Finnish forest industry has invested heavily in bioenergy, and the share of bioenergy is projected to increase (Kallio et al., 2007); 2) Finnish municipalities have a long tradition in investing in wood fuel plants; 3) The Finnish non-integrated sawmills have made large investments in bioenergy production. Some sawmill managers are interested in investing in new bioenergy branches and enlarging bioenergy business by using by-products to increase efficiency and profitability.	1) Investments in bioenergy are risky and capital intensive; 2) Relatively high investment costs are an obstacle for small-scale CHP and pellet production

Discussion and conclusion

Producing wood-based bioenergy is regarded in both the long term and the short term as a sustainable energy provision alternative. Finland is one of the leading countries for utilizing wood-based bioenergy, and the forest industry is the largest producer of wood-based bioenergy in Finland. Some Finnish sawmills have invested in bioenergy production to diversify their business and increase the firm-level value added. Although it is commonplace that producing bioenergy is emphasized as a new business option for sawmills in discussions, it is not a new issue for the Finnish sawmills and there are already many unutilized value-creation opportunities in this emerging bioenergy business.

Faced with the ambitious national targets for renewable energy for 2020, the Finnish sawmill industry could strongly support meeting this target by providing a local-level contribution for renewable energy production. Nevertheless, increasing bioenergy production to meet larger demands in the energy markets and managing both internal resources and external investment risks also brings new challenges for management. For instance, as raw material suppliers for bioenergy production, sawmills have an internal supply of wood fuels, but uncertainty in the sawn wood markets and the cyclicality of the sawmill industry makes the bioenergy business vulnerable to sawmill business cycles. Moreover, the volatile bioenergy policy changes were considered a major factor of uncertainty that poses challenges for forecasting the future development of the business environment and further increases the risk levels of investments in bioenergy capacity.

References

1. Bauen, A., Berndes, G., Junginger, M., Londo, M., Vuille, F. 2009. Bioenergy – a sustainable and reliable energy source. Executive Summary. IEA Bioenergy: ExCo: 2009:05. Retrieved December 23, 2011, from http://www.ieabioenergy.com/MediaItem.aspx?id=6360.

2. Kallio, K., Erkkilä, A., Raitila, J. 2007. Finnish firewood markets (D2). Jyväskylä. VTT. Quality Wood Project Report WP2.1/2007, Project EIE/06/178/SI2.444403.

3. Lähtinen, K., Toppinen, A. 2008. Financial performance in Finnish large- and medium-sized sawmills: the effects of value-added creation and cost-efficiency seeking. J. Forest Econ. 14(4), pp. 289–305.

4. Mäkelä, M., Lintunen, J., Kangas, H.-L., Uusivuori, J. 2011. Pellet promotion in the sawmill industry: the cost-effectiveness of different policy instruments. J. Forest Econ. 17(2), pp. 185–196.

5. Ministry of Employment and the Economy (MEE) 2011. Finland takes concrete steps to promote renewable energy. Retrieved December 23, 2011, from http://www.energy-enviro.fi/index.php?PAGE=2&PRINT=yes&ID=3475.

Preliminary spectral characterization of the calorific value of pyrolitic products from wood biomass

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Abstract

Heats of combustion of pine, spruce, birch and aspen pyrolitically produced oils correlate well with proton type abundances given by their NMR spectra in the aliphatic (0.6–3.5 ppm), unsaturated and oxygenated (3.5–6.0 ppm) and aromatic (6.1–8.0 ppm) regions. Preliminary results using the pitch (highest boiling) fractions show a correlation R value of 0.999 for predicted vs. measured heats of combustion, the latter determined by oxygen bomb calorimetry. The equation Q = Aa + Bb + Cc was used for various oils, where Q was the measured heat of combustion, the A, B, and C were "sensitivity factors" determined by least squares fitting procedures using the NMR integrals a, b, and c for the three proton regions.

Introduction

Since fossil fuels are growing increasingly scarce, biologically renewable fuels such as pyrolitic oils based on waste wood have received increasingly more attention. Traditionally such oils have been divided into fractions based upon their boiling points – summary oil (low and middle boiling fractions), middle boiling fraction, and pitch, the highest boiling fraction. Each fraction contains several hundred compounds, with 95% of the oils composed of at least 50 compounds, many partially oxygenated. For the purpose optimizing the energy yields of these fractions and their sub-fractions, it is convenient to correlate their overall heat of combustion (Q) as a complex mixture with a straightforward set of indices, much as the Dulong formula is based on elemental composition: Q = 340.6(%C) + 1431(%H – (%O/8)) [kJ/kg]. An alternative possibility could relate Q to the integrated intensities of NMR signals in the mixtures in the aliphatic, unsaturated and aromatic proton regions, corresponding to C-H bonds of different energies.

Experimental

Several 10–30 g samples of mature pine, birch, aspen and spruce were dried at 115°C for 24 hrs and pyrolyzed in a closed reactor with an exit stream passing through a jacketed water collecting condenser and burn off vapor exhaust in a fume hood. The process required 2.5 hours in a temperature-controlled oven heated at a 2.0°C/min temperature ramp terminating at a final temperature near 600°C. The boiling point range for the summary oils was 125–220, the middle fractions 160–220, and the pitch from 220–260°C.

Once the NMR data were acquired (Bruker Advance III 400 MHz at YSU) the spectra were integrated in the 0.3–3.0, 3.0–6.0 and 6.0–10.0 ppm regions (vs TMS) and normalized so the total proton area was 1.0 and the fractional areas are a, b and c.

Results and discussion

The set of equations $Q_i = Aa_i + Bb_i + Cc_i$ for the four pitch samples was solved for using the measured heats of combustion Q_i by standard linear regression techniques to yield the optimal values of

A, B and C. Once these sensitivities were determined, a predicted Q_{calc} from the normalized integrated areas was calculated to see if there was a correlation between Q_{calc} and Q_{msd}. Figure 1 shows the results of this correlation, and Table 1 contains the relevant values. Further work continues with other fractions and oils to find more widely applicable sensitivity values.

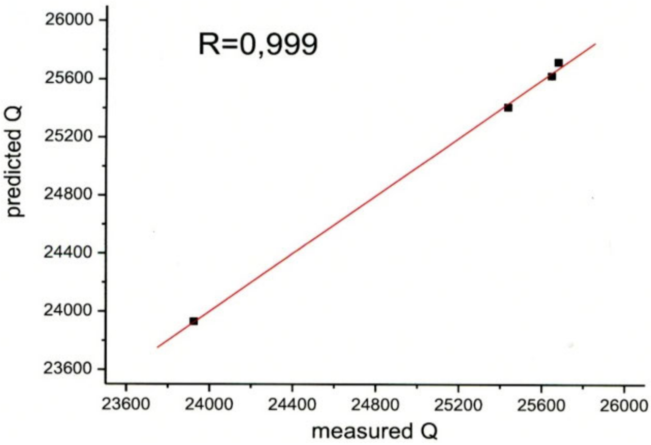

Figure 1. Correlation of measured and calculated heats of combustion of four pitches. Units: kJ/kg.

Table 1. Experimental and calculated heats of combustion for pitch fractions of four pyrolitic oils with their ^{1}H NMR area fractions (a, b, c) and calculated sensitivity coefficients (A, B, C).

Pitch(i)	Q_{exp}(kJ/kg)	Q_{calc}(kJ/kg)	a_i	b_i	c_i	Sensitivity Coeff.
Pine	23925±56	23930	0.7533	0.2054	0.0413	A = 22656±144
Spruce	25646±46	25629	0.6371	0.2279	0.1351	B = 25351±495
Birch	25679±92	25740	0.5729	0.2961	0.1310	C = 40106±818
Aspen	25436±23	25408	0.5645	0.3285	0.1070	

Conclusion

From the reasonable correlation above the conclusion could be drawn that the calorific values of pitches from various wood species strongly depend on the chemical structure of their constituents. For other fractions their characteristics could be obtained from their NMR spectra.

Acknowledgements

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An industrial plant (25,000 m^3/yr) for wood ultraoxypyrolysis by the formed layer process

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Introduction

A technology for obtaining bio-oils is presented here which is based on the ultraoxypyrolysis of waste wood biomass. Presently the quantity of this biomass exceeds 700 M m^3 per year in the Russian Federation. We have developed a resource conserving, ecologically clean thermochemical technology for the conversion of waste wood biomass, which includes waste forest cuttings, chopped waste, sawdust, and processed wood, into liquid boiler fuels (some of which may be used as diesel fuel) and energetic biocharcoal.

Technology

The perspective technology for the boiler fuels and biocharcoal according to our design employs the technique of “formed layers” of wood chips in counter-current flow with hot gases consisting of air and recycled pyrolysis gases in the pyrolitic reactor. The method is characterized by thermally equilibrated material balances and a minimal apparatus size for various feedstock processing. Our liquid products have high energy density (30–32 GJ/m^3) consistent with a bioboiler fuel. The small size means that these thermochemical conversions can be produced by mobile units at the points of wastewood production, rather than by collecting the waste wood and processing it at a central location, thereby saving both transportation costs for the waste wood and alternative fuel costs for plant operation.

Distinguishing features

The speed of advancement of the raw materials along the auger bed and reactor length is strictly controlled so as to permit the appropriate product distribution of uniform quality and quantity. Compact formed layers of waste wood chips still permit a significant increase in feedstock permeability by hot gases, thus allowing for a more rapid increase in the pyrolitic temperature and mass in the reacting zone. This increased coefficient of filling the reactor results in the ability to decrease its dimensions and its massiveness, thus giving the unit its added mobility. The formed layer structure also increases the utilization of heat and thus the efficiency of thermochemical conversion, which in turn strongly increases the specific production of the apparatus.

Mobile installation

Following the research results on the smaller unit, a technical-economic analysis was performed. This evaluation showed the most prominent (profitable) operational features of the unit are: (1) its mobility (saves fuel transportation costs); (2) it is ecologically clean (recycled exhaust gases are combusted eventually to CO_2 and H_2O); (3) it produces 3 200 t/y boiler fuels and 3 800 t/y energetic biocharcoal; and (4) its produces derived specialty products, including domestic and industrial briquettes (for cooking and smelting of silica to semiconductor quality silicon) and road surface coatings. We are in the final stages of construction of this larger installation.

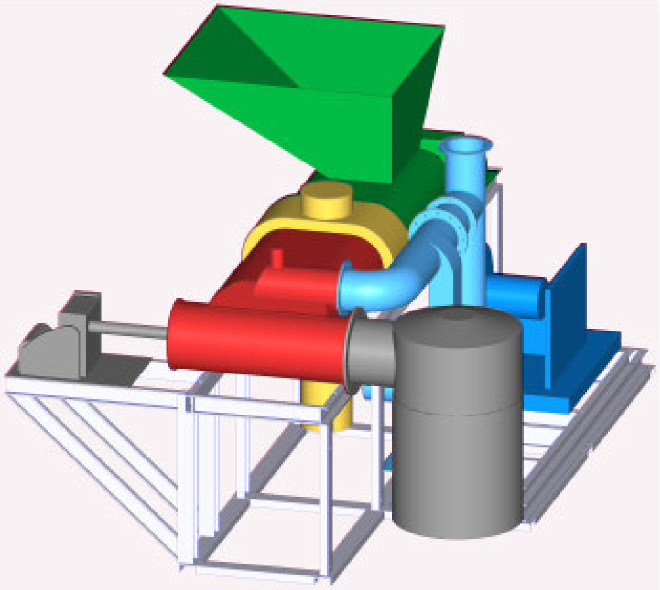

Figure 1. The current model for the mobile ultraoxypyrolysis production unit set for 1,5 t/hr from dry wood chips.

Conclusions

We consider the practical pyrolitic conversion of waste wood chips into boiler fuels and biocharcoal in a process that is ecologically clean and economically efficient. Additional applications include lowering the toxicity of gasoline and diesel exhaust, reducing fuel transportation costs to worksites, smokehouse food preparations, and food flavoring agents. Energetic biochar may be used to prepare air and water filters as well as briquettes for everyday life and industrial semiconductor silicon.

List of patents and sponsors

1. Charcoal production unit Patent RF N2001127158/20 (Russia) 08.10.2001;
2. Retort for continuous thermal processing of wood chips Patent RF N 75657 (Russia) 20.08.2008;
3. Method for wood chips processing into bio-oils and charcoal; a drying module designed for wood chips processing into bio-oils and charcoal Patent RF N 2338770 (Russia) 20.11.2008;
4. Method of purification of polluted water Patent RF N 2344997 (Russia) 27.01.2009;
5. The adsorbent for lead ions Patent RF N 2351390 (Russia) 10.04.2009;
6. Continuous thermal processing of chipped wood Patent RF N 2351390 (Russia) 22.05.2009.

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Measurement methods for physical properties of the pyrolysis oil components

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Abstract

Fast wood pyrolysis oils are considered as an alternative energy resource for fossil fuels. Thermodynamic data of the components of the oils are needed to model their behaviour in processes and biorefineries. This data includes vapour pressure and heat of combustion, which can be measured with Knudsen effusion and bomb calorimeter, respectively. A new Knudsen effusion apparatus has been assembled and tested with organic chemicals having a vapour pressures of 0.1–1 Pa. A commercial high precision combustion calorimeter Parr-6200 is tested and used for measuring the heat of combustion.

Background

The inevitable prospect of the depletion of fossil fuel resources has incited the research for alternative and renewable sources of oils and fuels. Especially oil recovered from fast wood pyrolysis is seen as one of the most potent alternatives to satisfy the ever increasing global demand for energy and fuel. [1]

The production and upgrading processes of pyrolysis oils are rather new techniques and they are not yet completely understood. The profound understanding of the processes and subsequent optimization of biorefineries require accurate thermodynamic models of the compounds formed during pyrolysis. These models rely on the accurate data of the physical properties of the pyrolysis oils components. Also, the stability and storability of pyrolysis oils is a matter of interest. Our review of the thermodynamic data available in literature revealed a large gap on experimental data of physical properties such as vapour pressure and enthalpies of vaporization. The vapour pressure of the pyrolysis oil components has an influence to the separating process, storability, transport, distribution, impact on the environment, and safe use of the product.

Measurement of physical properties

Our research concentrates on measuring reliable physical properties, including vapour pressure and energy of combustion, of the components most commonly found in bio-oils. These data sets will be used to create reliable predictive thermodynamic models, which are needed to design production and upgrading processes of pyrolysis oils. The Knudsen effusion is used to obtain enthalpy of vaporization and heats of combustion can be measured using bomb calorimeter. High purity of the compounds is essential to obtain reliable physical properties data. The purity should lie in the 99.9 % range and compounds of such a high purity are commercially scarce. Thus the compounds must be purified onsite before the measurements. For this purpose we have built a sublimation apparatus with six cells.

Knudsen effusion

The Knudsen effusion method is one of the best ways to evaluate vapour pressures of solid organic compounds having vapour pressure below 1 Pa. [2–4] Also, the Knudsen effusion method allows the measurements to take place in low temperatures thus avoiding the decomposition of thermally labile pyrolysis oil components.

A new Knudsen effusion apparatus has been built in our laboratory and has been tested with basic organic compounds such as anthracene and benzoic acid with temperature ranges 340–360 K and 299–317 K, respectively.

Bomb calorimetry

A commercial bomb calorimeter Parr-6200 has been tested and used for measuring the heat of combustion of solid and liquid organic compounds. In literature there are plenty of data about the high accuracy of commercial bomb calorimeters. [5–7] Benzoic acid has been used to determine the energy equivalent of the calorimeter and to test precision and accuracy of the equipment. The heat of combustion of anthracene has been measured. From the value of the standard specific energy of combustion the standard molar enthalpy of combustion and the standard molar enthalpy of formation in the liquid state can be derived.

Future measurements

The work on establishing the vapour pressures and heats of combustion of pyrolysis oil components is expected to get underway in immediate future.

References

1. Mohan, D., Pittman, Jr., C.U., Steele, P.H. 2006. Pyrolysis of wood/biomass for bio-oil: a critical review. Energy & Fuels 20, pp. 848–889.

2. Knudsen, M. 1909. The law of the molecular flow and viscosity of gases moving through tubes. Ann. Phys. 28, p. 75.

3. Knudsen, M. 1909. Effusion and the molecular flow of gases through openings. Ann. Phys. 28, p. 999.

4. Knudsen, M. 1909. Experimental determination of the vapor pressure of mercury at 0° and at Higher Temperatures. Ann. Phys. 29, p. 179.

5. Verevkin, S.P., Emel'yanenko, V.N., Heintz, A. 2009. 1,2-Propanediol. Comprehensive experimental and theoretical study. J. Chem. Thermodynamics 41, pp. 1125–1131.

6. Ferrão, M.L.C.C.H., Pilcher, J. 1987. Enthalpies of combustion of the three bromobenzoic acids by rotating-bomb calorimetry. J. Chem. Thermodyn. 19, pp. 543– 548.

7. Ribeiro da Silva, M.A.V., Ferrão, M.L.C.C.H., Lopes, A.J.M. 1993. Enthalpies of combustion of each of the two bromonaphthalenes. J. Chem. Thermodyn. 25, pp. 229– 235.

Effect of plastics on the co-liquefaction of cellulosic biomass and plastics to liquid fuel

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Abstract

Co-liquefaction of cellulosic biomass and polypropylene(PP) in the presence of solvent at 400°C was carried out. It was confirmed that the co-liquefaction of cellulosic biomass and PP gave the higher conversion than the cases of cellulosic biomass or of PP. Oil was also obtained in the co-liquefaction with various plastics (Polystyrene(PS), Polyethylene terephthalate(PET)) and the acceleration of decomposition of plastics by cellulosic biomass was observed.

Introduction

Development of an efficient technology for converting cellulosic biomass to liquid fuel is an important research area. New technology for converting cellulosic biomass and waste plastics to high quality light oil at low pressure and low temperature using a solvent with liquefying plants of small and simple process is being developed. The effects of plastics on the yield and on the quality of the liquefied oil in the co-liquefaction of cellulosic biomass and waste plastics were investigated.

Experimental

Co-liquefaction of cellulosic biomass and plastics in the presence of solvent was conducted by 300mL-autoclve or by a small extruder with two axes (25 kg/h) at 678–693K for 15–60 min. Cellulosic biomass(Japan cedar pulverized and dried) was used and pellet of polypropylene(PP) or of polystyrene(PS), flake of Polyethylene Phthalate(PET) were used as plastics. Mineral oil and wood tar were used as a solvent. The ratio of solvent to biomass and the ratio of plastics to biomass were 1/3 to 1/6 and 2/8 to 5/5, respectively.

Results and discussion

Co-liquefaction of cellulosic biomass and plastics in the presence of mineral oil conducted by 300mL-autoclve at 678K for 60 min. gave liquefied oil of 60 wt% along with gas and water. It was found that the co-liquefaction of cellulosic biomass and PP gave higher conversion (73 wt%) than the cases of cellulosic biomass or of polypropylene, which was ascribed to the acceleration of decomposition of plastics by radicals derived from the decomposition of cellulosic biomass. In the co-liquefaction by a small extruder with two axes designed as liquefaction plants of small and simple process, liquefied oil was obtained with a similar conversion of cellulosic biomass with the case of the autoclave. It was also found that the liquefied oil was obtained in the co-liquefaction with various plastics (PP, PS, PET), and the acceleration of decomposition of plastics in the presence of cellulosic biomass occurred.

The adaptability of the liquefied oil as an alternative fuel for diesel engines was clarified by the analysis of the liquefied oil prepared by the co-liquefaction. Analysis of three kinds of oil (fraction 190 to 290°C divided by fractional distillation) prepared by the co-liquefaction of PP, PP/PS, PS with cellulosic biomass showed that the oil prepared by the co-liquefaction with plastics had better properties for diesel engines than that with the liquefaction of cellulosic biomass.

Conclusions

It was found that the co-liquefaction of cellulosic biomass and plastics gave liquefied oil, which was ascribed to the acceleration of decomposition of plastics by radicals derived from the decomposition of cellulosic biomass.

Acknowledgement

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AFORE – Forest Biorefineries: Added-value from chemicals and polymers by new, integrated separation, fractionation and upgrading methods

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Abstract

A large EU project AFORE develops new sustainable technologies for the separation, fractionation and primary upgrading of wood-based polymers and valuable low molecular weight compounds present in forest residues and process side streams. These technologies can be applied by the wood processing mills of today and the future wood biorefineries to turn side streams into profitable business.

Background of the AFORE project

Today, only part of the valuable wood biomass ends up in high-value applications (paper and cardboard), whilst a significant part is channeled into different “side-streams”, such as logging residues, debarking residues and pulping liquors. All of these side-streams contain chemically appealing and reactive constituents that could be further refined to value-added chemicals, polymers, materials, and fuels alongside with the sustainable forestry and paper fibre production. The utilization of the wood refining side-streams has been widely studied during the past century. Now, along with the market challenges in the pulp and paper industry and rising oil prices, the interest towards efficient exploitation of process side-stream components has raised again.

During the past 100 years, tall oil and turpentine have become well-established main by-products isolated during kraft pulping of wood raw materials. Recently, lignin separated from the kraft black liquor has also gain interest primarily as an energy component. Substantial amounts of other unharnessed, potentially useful by-products including hemicellulose, hydroxy acids and certain low molecular mass compounds are, however, also known to be formed to side-streams at all wood kraft pulp mills. Furthermore, wood residues and alternative pulping processes as well as totally new wood matrix opening methods are potential sources for valuable wood based polymers and chemicals.

AFORE project

The main aim of the AFORE project is to develop new, industrially adaptable and techno-economically viable and sustainable methods and technologies for the separation, fractionation, and primary upgrading of wood polymers and low molecular mass compounds from forest residue or process side-streams. AFORE strongly targets to demonstration of most potential separation, fractionation and upgrading technologies while concurrently novel process and product openings are search for. The research supports the European wood processing industry and its industrial value chain in their aim of developing new business from forest biorefineries according to the principles of sustainable development.

The AFORE project is a large European Commission Framework program FP7 NMP area funded project. It will run for four years and it has a budget of EUR 10.9 million. The project will end in 2013. There are 19 participants in total: VTT as the coordinator, 17 other European participants and one participant from the USA. Corporations (8 in total), research institutions and universities form the multidisciplinary consortium to achieve the challenging targets of this project.

AFORE research examples

Please visit AFORE web site www.eu-afore.fi to learn more about the project and to see the research examples from the recent newsletter.

Bioconversion of primary sludge from Portuguese pulp and paper mills to fermentable sugars

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Primary sludge, generated in pulp and paper mills, consists of cellulosic fibers lost along the pulping and papermaking process and ash (mostly $CaCO_3$). This lignocellulosic waste is a potential attractive raw material for the biosynthesis of fermentation products. However, primary sludge bioconversion is challenging because cellulose is tough to chemical and biological degradation, and moreover, the high ash content affects negatively the production of fermentable monosaccharides from the carbohydrate fraction of the primary sludge. $CaCO_3$ is responsible for the alkaline pH of primary sludge [7–10] and it also may limit the solid loading capacity in the bioreactor, thus affecting enzymatic hydrolysis pH and yield [1, 2]. A previous treatment may be necessary to remove the existing ash in order to ensure good yields of sugars from both cellulose and hemicellulose. The aim of this research is to study the biochemical processes to convert the primary sludge to fermentable sugars to be used as substrate to produce bioethanol, as a case study, by fermentation. Primary sludge and unbleached pulp (clean reference material) were collected from a Portuguese Kraft pulp mill, which uses *Eucalyptus globulus* as raw-material. Table 1 shows the organic, ash (total inorganics) and $CaCO_3$ contents for both materials. Untreated primary sludge and unbleached pulp were submitted to enzymatic hydrolysis with cellulase Cellic® CTec2, from Novozymes, using an initial carbohydrate (CH) content of c.a. 2.5% w/v and an enzymatic dosage of 35 FPU per gram of carbohydrate (FPU g_{CH}^{-1}). After 24 h of hydrolysis, 90% of the carbohydrates from the unbleached pulp were converted to glucose and xylose, whilst sugar yields reached only 20% for primary sludge with no treatment [3]. Several acids were used to neutralize $CaCO_3$ in the primary sludge (H_2SO_4, HCl, HNO_3 and CH_3COOH). HCl was the most efficient acid to treat primary sludge as shown in Table 1. To avoid the undesirable CO_2 release in the acid neutralization, alternative techniques consisted in washing primary sludge with distilled water for several times (results from 2, 6 and 12 washing cycles are shown in Table 1) were also tested. According to Table 1, $CaCO_3$ was efficiently removed when primary sludge was washed for 6 or more times. These water-based techniques may be a good substitute to acid neutralization in the pre-treatment of primary sludge. Initial carbohydrate concentrations of c.a. 2.5% and 5% w/v of primary sludge pre-treated with HCl were used in enzymatic hydrolysis experiments. The sugar yields obtained after 24 h of reaction are shown in Table 2. Hydrolysis yields of 79% and 88% were reached when using initial carbohydrate concentrations of 2.5% and 5% w/v, respectively (Table 2); it confirms the hydrolysis improvement when a pre-treatment is applied. The enzymatic extracts from the digestibility of primary sludge with an initial 5% w/v carbohydrate content comprised 82% of glucose and 18% of xylose and were used as culture media in ethanolic fermentation processes with *Pichia stipitis* (co-ferments glucose and xylose) and *Saccharomyces cerevisiae* (ferments chiefly glucose). In general, *P. stipitis* showed a better overall performance, producing bioethanol with higher ethanol yield and production rate, according to Table 2. Primary sludge, previously treated, represents a potential resource to be used in order to obtain value-added products by fermentation.

Table 1. Composition of unbleached pulp (reference) and primary sludge (untreated and pre-treated).

Lignocellulose/Treatment		**Content, % w/w (dry weight basis)**		
		Organic	Ash	$CaCO_3$
Unbleached pulp		98.9	1.1	0.9
Primary sludge		65.2	34.8	26.7
Pre-treated primary sludge	H_2SO_4	89.2	10.8	0.7
	HCl	98.2	1.8	0.5
	HNO_3	97.9	2.1	1.9
	CH_3COOH	98.1	1.9	1.9
	2 washing cycles	86.5	13.5	6.9
	6 washing cycles	95.9	4.1	0.1
	12 washing cycles	96.2	3.8	0.5

Table 2. Enzymatic hydrolysis and ethanolic fermentation of primary sludge pre-treated with HCl.

Enzymatic hydrolysis Cellic® CTec2		Initial CH conc., % w/v	2.5	5.0
		Sugar yield, %	79	88
		Sugar conc.*, g_{sug} L^{-1}	20.3	40.4
Ethanolic Fermentation	*P. stipitis*	EtOH conc., g_{EtOH} L^{-1}	-	11.1
		EtOH Yield, g_{EtOH} g_{sug}^{-1}		0.49
		Productivity, g_{EtOH} L^{-1} h^{-1}		0.24
	S. cerevisiae	EtOH conc., g_{EtOH} L^{-1}	-	8.3
		EtOH Yield, g_{EtOH} g_{sug}^{-1}		0.48
		Productivity, g_{EtOH} L^{-1} h^{-1}		0.18

*Sugar concentration in the enzymatic extracts before sterilization; (-) Not performed.

References

1. Kang, L., Wang, W., Lee, Y.Y. 2010. Bioconversion of kraft paper mill sludges to ethanol by SSF and SSCF. Appl. Biochem. Biotechnol. 161, pp. 53–66.

2. Wang, X., Song, A., Li, L., Li, X., Zhang, R., Bao, J. 2011. Effect of calcium carbonate in waste office paper on enzymatic hydrolysis efficiency and enhancement procedures. Korean J. Chem. Eng. 28, pp. 550–556.

3. Mendes, C.V.T., Rocha, J.M.S., Carvalho, M.G.S.V. Enzymatic hydrolysis of pretreated primary sludge from a Portuguese pulp and paper mill. 11th Int. Chemical and Biological Engineering Conference, Lisbon, Portugal, 2011.

Investigating anaerobic digestion of pulp washing effluent using bench-scale UASB reactors

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Abstract

Pulp mill wastewater streams such as pulp washing effluent often contain high concentrations of compounds, such as resin acids (RAs) and fatty acids (FAs) that adversely affect the anaerobic digestion process (see refs in Rintala and Puhakka, 1994). The impact may include diminished biogas production and disintegration of anaerobic sludge granules. Two bench-scale upflow anaerobic sludge bed reactors have been constructed to investigate the mechanisms behind those processes, which ultimately will assist in developing strategies to minimize the adverse impact of pulp washing effluent and other recalcitrant in-mill streams on anaerobic sludge granulation and digester performance. After an adaptation phase of two months, one reactor (test reactor) has been fed with a slowly increasing fraction of pulp washing effluent (PEW) obtained from a sulphite pulp mill. The other reactor (control reactor) is being fed with artificial and easily digestible wastewater. The microbial community, the RA/FA composition, as well as the physical properties of the granules in the reactors are closely monitored using pyrosequencing technology, liquid chromatography – mass spectrometry (LC-MS), and granule analysis methods. So far, the test reactor fed with PEW exhibits significantly lower chemical oxygen demand (COD) removal rates as well as biogas production rates, compared to the control reactor.

Methods

The anaerobic reactors were made from acrylic and each has a working volume of 5.4 L (Figure 1). Mesophilic conditions with a temperature of 37°C within the reactor are ensured by means of a water jacket and a circulating pump. The biogas production is measured using a bubble counter setup. Mixing, necessary to maintain well functioning sludge granules, is provided by recirculating headspace gas into the bottom of the reactor through a porous ceramic disc. The generated fine bubbles provide uplift and turbulence of the granules. Granular seed sludge for both reactors was taken from a full-scale anaerobic IC reactor at a sulphite pulp mill in Canada. The PEW used to feed the test reactor contains approximately 19 g L^{-1} COD, 100 $mg \cdot L^{-1}$ RAs and 20 $mg \cdot L^{-1}$ FAs, and is generated during high alpha specialty pulps production at the mill, where it is for the most part excluded from anaerobic treatment because of its detrimental impact on process performance. The control reactor is being fed with artificial wastewater, which resembles the composition of easily digestible pulp mill wastewater and contains substrate and mineral nutrients. The feed COD of the control reactor consists of acetate, methanol, ethanol, xylose, glucose, and sodium carboxymethyl cellulose. Over the course of the experiment the organic loading rate has been kept at approximately 25 g COD per Litre of reactor per day, and the hydraulic retention time is approximately 12 hours. Frequent, routine analysis includes measurements of effluent pH, oxidation-reduction potential, biogas production, volatile acids – alkalinity ratio, volatile suspended solids / total suspended solids, COD, as well as granule strength and size. For most of these analyses, effluent samples are collected several times per week. Furthermore, weekly sampled effluent is stored at -20°C for later analysis using time-resolved LC-MS. Samples of digester sludge are taken every 3 to 4 weeks from sludge sampling ports in order to analyze granule strength and size. Additional sludge samples have been stored at -80°C for subsequent DNA extraction and community composition analysis by 454 pyrosequencing of amplified 16SrRNA genes.

Figure 1. Bench-scale reactors.

Results and discussion

The test reactor influent currently contains 60 mg·L^{-1} RAs and 15 mg·L^{-1} FAs. The removal rate of soluble COD in the test reactor is diminished by approximately 30% compared to the control reactor. The biogas production rate is also lower in the test reactor by a similar percentage. Preliminary results from LC-MS analyses indicate that of all the investigated chemicals, dehydroabietic acid is the least degradable compound. At the same time this RA is one of the most abundant and inhibitory substances present in pulp mill effluents (Sierra-Alvarez and Lettinga, 1990; Rintala and Puhakka, 1994). The results of this study are expected to notably enhance our understanding on how RAs and FAs influence the anaerobic community dynamics as well as the physico-chemical properties of anaerobic sludge granules.

References

1. Rintala, J.A., Puhakka, J.A. 1994. Anaerobic treatment in pulp- and paper-mill waste management: a review. Biores. Technol. 47, p. 1.

2. Sierra-Alvarez, R., Lettinga, G. 1990. The methanogenic toxicity of wood resin constituents. Biol. Wastes 33, p. 211.

From birch to Soda-AQ pulps, pure xylan and fractions thereof – HemiEx project overview

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Abstract

In this research project hemicellulose-isolating pretreatments and pulping operations were optimised and the papermaking properties and suitability for viscose process of the resulting pulps were evaluated. Alkaline pre-extraction process produced high molecular weight xylan (20kDa) and paper pulp with excellent papermaking properties. Prehydrolysis pulps had inferior strength, however, the samples with more extensive xylan removal were well suited for viscose production.

Introduction

The HemiEx project aimed at selectively extracting hemicelluloses from birch wood in the course of soda-anthraquinone (SAQ) fractionation, following the biorefinery principle. Three different methods for separating xylan were investigated, including water (AH) and oxalic acid (PH(OA)) prehydrolysis as well as alkaline extraction (E) prior to alkaline pulping.

Results and discussion

Optimisation experiments demonstrated that at different pretreatment intensities desired amounts of xylan could be isolated by both acidic and alkaline pretreatments [1, 2]. Simultaneously, small amounts of lignin were co-extracted while cellulose remained largely preserved (Figure 1). Optimal pretreatment conditions selected for further experiments are listed below.

AH P200 150 °C, L:S=4 L/kg, 90 min

AH P1000 170 °C, L:S=4 L/kg, 94 min

PH(OA) 120 °C, L:S=4 L/kg, 0.05 M OA, 70 min

E 95 °C, L:S=9.3 L/kg, 2.4 M NaOH, 60 min

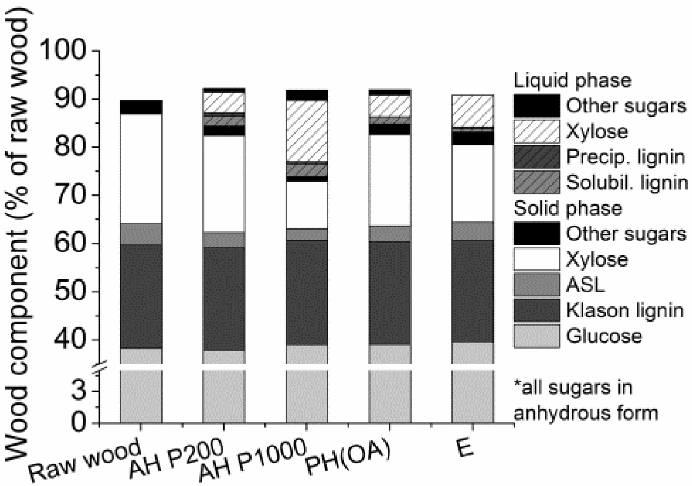

Figure 1. Mass balances of the selected pretreatments.

The weight-average molar masses of the extracted xylans were 20 kDa, 2.1 kDa and 0.4 kDa for E, AH P200 and AH P1000 pretreatments, respectively. As expected, adding oxalic acid as a catalyst in prehydrolysis considerably increased the share of monomeric xylose in the hydrolysate with a 50% share after 0.05 M OA treatment at 120°C for 70 min.

Alkaline pulping after reinforced autohydrolysis as well as mild oxalic acid prehydrolysis and strong alkaline pre-extraction was targeted towards dissolving and paper-grade pulp production, respectively. Pulping of pre-treated birch chips (EA 22%, AQ 0.1% L:S=3.5) required lower pulping intensities as compared to the SAQ reference (Table 1). The yields of the pretreated paper pulps were notably lower (up to 4% and 7% losses based on raw wood for alkaline pre-extraction and pre-hydrolysis, respectively) compared to the reference pulp. This is due to the lower hemicelluloses content and, in the case of acidic prehydrolysis, to susceptibility towards peeling reactions in alkaline pulping due to increased content of carbohydrate reducing end groups. Attempted stabilisation of carbohydrates against alkaline peeling with sodium borohydride (B), AQ and anthraquinone monosulfonate (AQS) resulted in a yield gain of 1–4% based on raw wood. It was observed, however, that not only cellulose but also hemicelluloses were stabilised by oxidative and reductive additives, which is beneficial for paper pulps but is not desired for highly pure dissolving pulps.

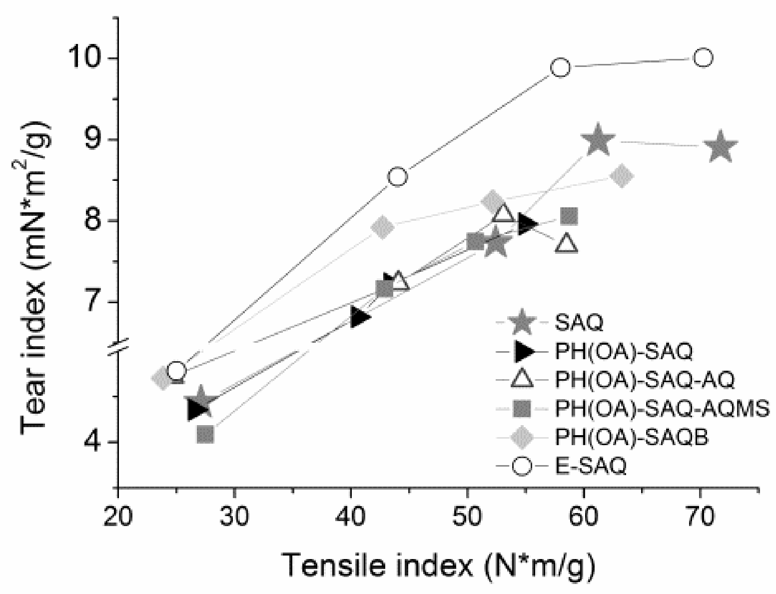

Figure 2. Papermaking properties.

Figure 2 reveals excellent papermaking properties of alkali pre-extracted paper pulps. Prehydrolysis pulps had inferior strength, but stabilisation with BH, resulted in acceptable strength properties. The samples with more extensive xylan removal had high alkali resistance (Table 1) and were well suited for viscose production, having filter values of 417 and 332 for AH P1000-SAQ and AH P1000-SAQ BH, respectively.

Table 1. Properties of pulps obtained by SAQ pulping.

	SAQ pulp	**E-SAQ**	**PH(OA)-SAQ**	**PH(OA)-SAQ-AQ**	**PH(OA)-SAQ-AQMS**	**PH(OA)-SAQ BH**	**AH P1000-SAQ**	**AH P1000-SAQBH**
	Unbleached							
H-factor	800	550	400	350	450	700	350	300
Yield, % of o.d. wood	50.4	46.6	42.7	44.3	45.5	46.3	36.9	38.3
Kappa number	19.8	17.9	19.8	15.6	16.0	16.1	8.3	8.2
Intr. viscosity, mL/g	1051	1123	1321	1342	1291	1221	1305	1309
	Oxygen delignified						***Bleached***	
Yield, % of o.d. wood	49.6	44.7	41.9	43.3	44.6	46.0	34.1	36.2
Kappa number	14.0	12.1	12.9	10.6	11.3	9.0	0.78	0.80
Intr. viscosity, mL/g	945	878	1147	1112	1153	1014	507	572
Zero-span index, N·m/g	0.63	0.54	0.55	0.55	0.55	0.57	-	-
Xylan content, %	21.0	17.5	13.3	14.0	13.8	15.6	4.5	5.7
Alkali resistance R18, %	-	-	-	-	-	-	95.8	95.5

Conclusions

Alkaline and acidic hemicelluloses-isolating pretreatments were best suited for producing paper and dissolving-grade pulps, respectively. However, the economic feasibility of the studied processes is highly dependent on the added value of the products derived from hemicelluloses to compensate for the loss of pulp yield.

References

1. Testova, L., Vilonen, K., Pynnönen, H., Tenkanen, M., Sixta, H. 2009. Isolation of hemicelluloses from birch wood: distribution of wood components and preliminary trials in dehydration of hemicelluloses. Lenz. Ber. 87, pp. 58–65.

2. Costabel, L., Testova, L., Alekhina, M., Ruuttunen, K., Sixta, H. 2011. Alkaline pre-extraction of birch wood prior to alkaline pulping. 3rd NWBC. Stockholm, Sweden. Pp. 305–306.

Implementation of lignin-based biorefinery within a Canadian kraft mill: Impact on utility system and solutions toward optimal operation

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Introduction

Kraft pulping mills continue to explore biorefinery opportunities that create bioenergy, biochemicals and biomaterials. One of theses opportunities offers supplementary revenues through the recovery of lignin contained in the black liquor stream and the increase of pulp production by debottlenecking the recovery boiler. However, implementing such a market transformative solution affects significantly the resources demand (i.e., wood biomass, process energy, utility, water and chemical reactants). To identify and minimize such impacts, several technical and economic challenges need to be addressed via a site-wide approach identifying the complex interactions between the processes of lignin recovery and kraft pulping. This should prioritize efficient use of the resources and optimal strategy design for utility system. Thus, an assessment of exploited resources is performed on a Canadian softwood kraft pulping mill producing up to 400 tonne/day (dry basis). The maximum lignin recovery rate is fixed at 50 tonne/day (dry basis) while the higher heating value of black liquor varies from 13.8 GJ/tonne to 12.7 GJ/tonne during lignin recovery process. The evaluation of the utility system focuses on the potential pathways to generate and distribute the steam from the fuel system and supply it to the end user. The optimal operating conditions are established to minimize the total cost within certain technical and operational constraints. To establish the optimal operating conditions for the existing utility system, a modelling, simulation and optimization of the mill utility system has been developed using a GAMS platform [1]. Three scenarios have been considered: **scenario #1** as a reference case in which the utility system is optimised for baseline load conditions of the mill; **scenario #2** corresponds to the integrated lignin recovery within the mill; **scenario #3** conforms to the integrated lignin recovery within the mill, including process integration measures.

Methodology

The utility system is mainly composed of five boilers (one biomass boiler burning hog fuel and bunker oil, three natural gas power boilers and a black liquor recovery boiler) that generate medium pressure steam. This steam is then distributed to several users at both low and medium pressures. Low pressure steam is obtained through letdown expansion valves considering that there is no power generation capability on the mill site. A reference scenario was first modelled, simulated and optimised with respect to the mill energy demands and related costs. Afterwards, the impact of the lignin-based biorefinery implementation on the utility system operation was evaluated. The influence of energy savings projects on the optimal utility system was also assessed. The economic viability of all scenarios has been established based on one major operating constraint: the minimum black liquor flow rate for steam generation was set at 346 tonne/day (dry basis).

Results and discussion

Table 1 shows the optimal conditions for **scenario #1**. The recovery boiler was set at its current baseline load. Due to high cost of biomass and bunker oil, the biomass boiler should operate at its minimum load. The power boilers burning natural gas are making-up for the remaining difference in steam demands. As there is enough installed power boilers capacity, about 32% total cost savings could be achieved if the kraft mill shuts down the biomass boiler.

Table 1. Optimal conditions for scenario #1.

Item	**Fuel consumption, MW**		**Steam generation, tonne/h**	**Operating Costs, M$/year**
Biomass Boiler	Biomass	8.8	13.7	1.69
	Bunker Oil	5.0		2.47
Power Boilers	Natural Gas	54.9	70.6	5.53
Recovery Boiler	Black Liquor	89.1	67.3	0
Total cost, M$/year				9.84

Table 2 presents the optimal conditions for **scenario #2** in which the cost of chemical reactants required for efficient lignin recovery are included.

Table 2. Optimal conditions for scenario #2.

Item	**Fuel consumption, MW**		**Steam generation, tonne/h**	**Operating Costs, M$/year**
Biomass Boiler	Biomass	8.8	13.7	1.69
	Bunker Oil	5.0		2.47
Power Boilers	Natural Gas	95.5	122.4	9.62
Recovery Boiler	Black Liquor	62.2	46.8	0
Lignin recovery process, 50 tonne/day				
Chemicals				2.13
Annualised Investment				1.91
Revenues				12.50
Total cost, M$/year				5.51

The current average selling price is considered as 750 $/tonne for both lignin and bleached kraft pulp [2]. As illustrated in Figure 1, it is more profitable to increase the pulp production to the maximum allowable limit and use all excess black liquor for lignin recovery. Figure 1 provides optimal conditions for lignin recovery rate, total cost and payback period (PBP) as a function of pulp production increase. The PBP is shorter than one year for all optimal conditions. As expected for **scenario #3**, the PBP is shifted up by about 11% due to extra capital investment corresponding to the increased heat exchange area needed for all energy saving projects (i.e., cumulative savings of 11.3 MW). **Scenario #3** is economically viable since the PBP remains about one year. The potential to produce power was assessed and was in the order of 0.7 MW for the current utility topology. Thus, it was not included in the optimal conditions for all scenarios.

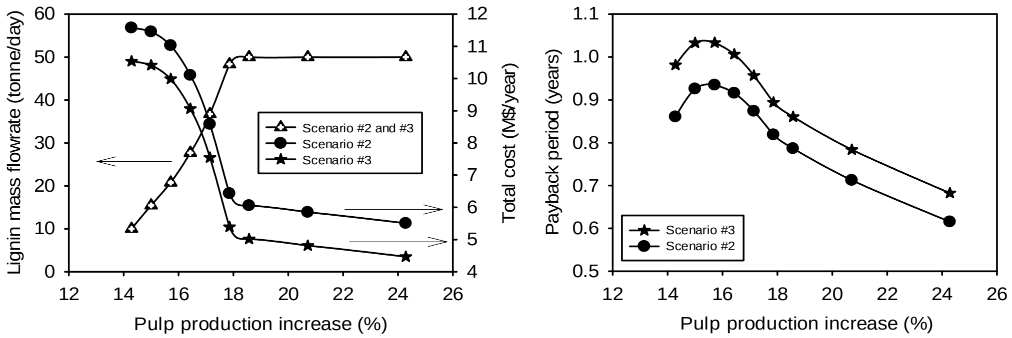

Figure 1. Optimal conditions for scenarios #2 and #3 with their corresponding PBP.

Conclusion

A real kraft mill utility system was assessed for optimal management in the context of an integrated lignin-based biorefinery. For this case study, the optimal implementation is achieved with a reduced total cost by up to 55% using process integration measures. The PBP, which is in the order of one year, points towards the economic viability of the lignin recovery process. The extra revenues from lignin and bleached kraft pulp exceed the capital expenses associated with the lignin recovery technology and the process integration measures.

References

1. Rosenthal, R.E. 20129.GAMS – A user's guide; GAMS Development Corporation: Washington. http://www.gams.com/dd/docs/bigdocs/GAMSUsersGuide.pdf.

2. Périn-Levasseur, Z., Savulescu, L., Benali, M. 2012. Techno-economic evaluation of a lignin-based biorefinery implementation within a Canadian Kraft pulp mill, 2nd International Forest Biorefinery Symposium, PaperWeek Canada, Montreal, Quebec, Canada.

Opportunities for energy upgrading by means of an absorption heat pump in an integrated forest biorefinery

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Abstract

The purpose of this study is to evaluate the technical feasibility of implementing an absorption heat pump (AHP) into an integrated forest biorefinery for furfural production in order to reduce its energy requirement. An AHP configuration is proposed for integration into the main distillation column of the biorefinery. The results show that the heating requirement of the biorefinery is reduced by 4.2 MW (31%) and the cooling requirement by 9.9 MW (24%). This will facilitate the implementation of the biorefinery unit into a Kraft pulping mill without requiring added steam and hot water production capacity.

Introduction

The main process steps of the furfural biorefinery are illustrated in Figure 1 with heating (Q_H) and cooling (Q_C) requirements for each operation. About 65% of the total heating requirement for producing 58 t/d of furfural comes from the separation and purification of furfural by distillation. This requirement can be reduced by means of heat pumping between the reflux condenser and the reboiler of the main distillation column. AHPs are heat driven devices that upgrade free heat available from a process to a higher temperature. In an AHP (Figure 2), driving heat is supplied to the evaporator (E) and generator (G), at an intermediate temperature level, while useful heat is liberated by the absorber (A) at a higher temperature and by the condenser (C) at a lower temperature [1, 2]. The objective of this work is to evaluate the potential for energy reduction from an AHP implementation in a biorefinery process.

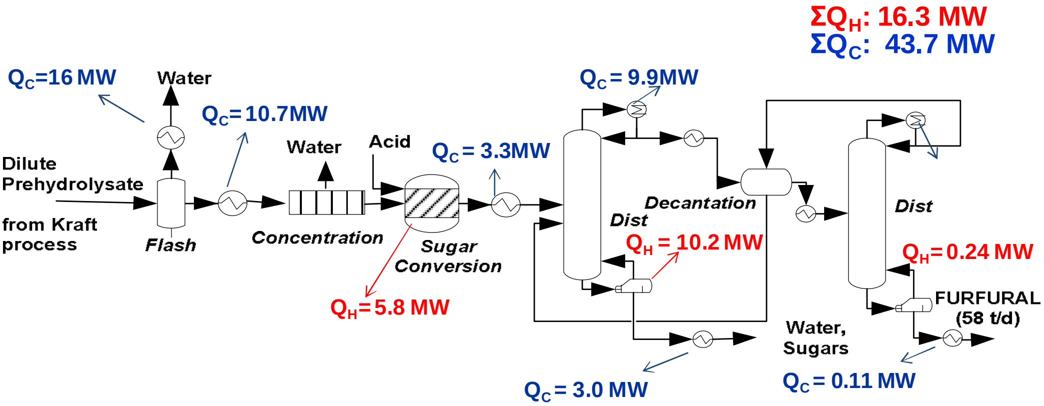

Figure 1. Process diagram of the furfural biorefinery.

Methodology

Operating parameters for the heat pump (temperature, pressure and LiBr concentration) were determined by plotting the cycle on a H_2O/LiBr phase diagram (Figure 2). The work was supported by

Aspen Plus® simulations of the biorefinery and AHP to determine the energy loads and coefficient of performance (COP). An optimized heat exchanger network was developed by pinch analysis before the AHP installation producing a heat requirement and cooling requirement reduction of 15 and 6% respectively. The methodology for positioning an AHP is described by Bakhtiari et al. [2].

Results and conclusion

A single stage AHP with H_2O/LiBr as working fluid was selected and implemented as shown in Figure 3. The selected concentration of the H_2O/LiBr strong solution (0.4/0.6) and the operating pressures (4.5 kPa / 65 kPa) prevent crystallization in the heat pump cycle. The operating temperatures ensure a minimum difference (ΔT_{MIN}) of 10°C between the column and the AHP; the COP of the heat pump is 0.42.

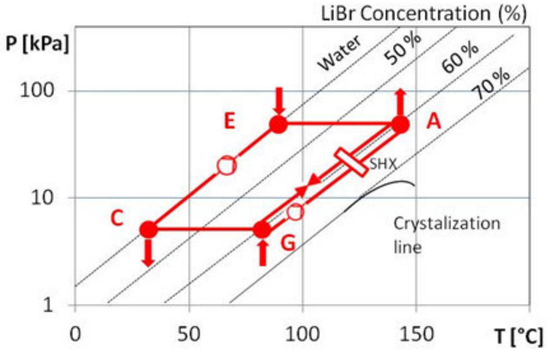

Figure 2. AHP representation in H_2O/LiBr phase diagram.

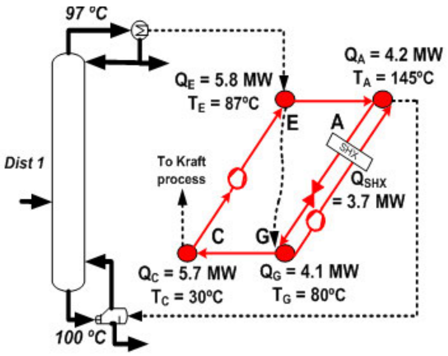

Figure 3. AHP integration.

The condenser duty of the column is completely satisfied as 9.9 MW is transferred to the AHP via the evaporator-generator pair. Useful heat is recovered at a higher temperature from the AHP absorber and fed to the column reboiler; this reduces the heating requirement by 4.2 MW (41%). The reboiler duty is partially satisfied leaving a heating requirement (Q_H) of 6 MW. The heat from the AHP's condenser is suitable for preheating freshwater streams in the receptor mill.

Implementing an absorption heat pump in the integrated biorefinery is technically feasible. The AHP upgrades heat from the distillation column condenser to be used at a higher temperature in the reboiler, thus reducing the steam and cooling water requirement. However, installing an AHP will require the development of an adapted control strategy for efficient operation of the distillation column with the integrated heat pump [3].

References

1. Costa, A., Bakhtiari, B., Schuster, S., Paris, J. 2009. Integration of absorption heat pumps in a Kraft pulp process for enhanced energy efficiency. Energy 34(3), p. 254–260.

2. Bakhtiari, B., Fradette, L., Legros, R., Paris, J. 2010. Retrofit of absorption heat pumps into manufacturing processes: Implementation guidelines. Can. J. Chem. Eng. 88(5), p. 839–848.

3. Alarcón-Padilla, D.C., García-Rodríguez, L., Blanco-Gálvez, J. 2010. Experimental assessment of connection of an absorption heat pump to a multi-effect distillation unit. Desalination 250(2), pp. 500–505.

The LignoForce System™ for the recovery of lignin from black liquor

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Abstract

To improve lignin filterability, FPInnovations developed a patent-pending process called *LignoForce* in which the black liquor (BL) is oxidized under controlled conditions prior to the acidification step. Based on the data obtained, BL oxidation was found to improve the filterability of the acid-precipitated lignin by providing suitable conditions with respect to pH, and temperature for the formation of particles that are easy to filter and wash. In addition, BL liquor oxidation was found to minimize or eliminate the total reduced sulphur (TRS) compounds in BL thereby leading to reduced TRS emissions during all steps associated with all processing steps. Furthermore, BL oxidation led to reduced acid requirements during lignin precipitation from BL by oxidizing sulfide to sulfate and organics to organic acids, which consume the residual effective alkali (sodium hydroxide) in BL.

Introduction

Lignin can be recovered from kraft black liquor through the addition of an acidifying agent such as carbon dioxide, followed by coagulation, filtration and washing. During this process, however, several researchers have previously observed a high filtration resistance which, ultimately, affects lignin purity, productivity and cost. One approach for addressing this problem is a process developed by STFI (now called Innventia) and licensed to Metso [1] which employs a first filter for the filtration of lignin in the sodium form followed by suspension of the lignin cake in dilute sulphuric acid before filtration in a second filter. Another approach for addressing this problem is a patent-pending process developed by FPInnovations and currently commercialized by NORAM under the trade name "*LignoForce Systems*™" [2] (Figure 1). The purpose of this paper is to describe this new process.

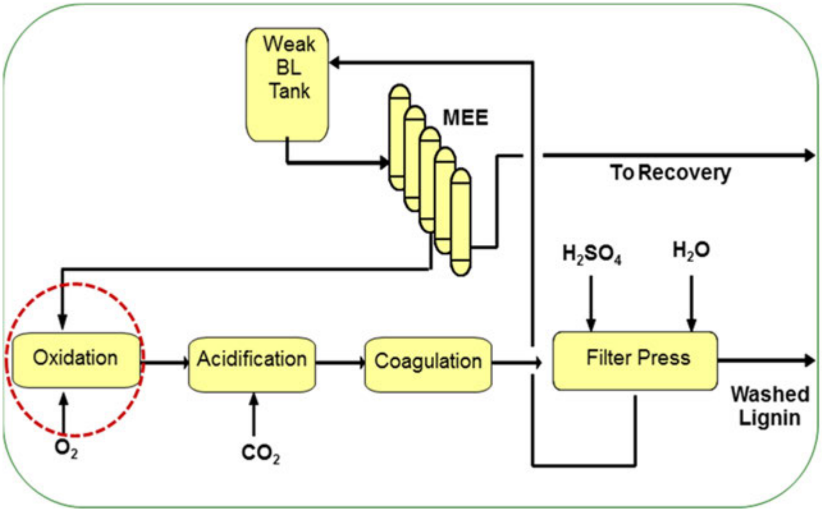

Figure 1. LignoForce system for lignin recovery from black liquor.

Experimental

For the purpose of improving the lignin filtration properties, the BL was oxidized under controlled conditions. The oxidized BL was then acidified, coagulated, filtered, and the lignin washed and dried almost in the same way as in other processes. Since the *LignoForce* process improves lignin filterability, only one filter press was required.

Results and discussion

The filtration rate was measured as the number of kilograms of recovered lignin filtered per unit surface area per hour. The recovered lignin samples were analyzed for dry solids, UV-lignin, and ash content. The results are presented in Table 1.

Table 1. Filtration rate and lignin characterization in the case of oxidized & unoxidized BL.

	Without oxidation	**With oxidation**
Filtration rates (kg of lignin/h.m^2)	0–80	100–200
Total solids (%)	30–58	60–62
Ash content (%)	0.2–15	0.1–0.7
UV lignin (%)	50–98	97–98
Lignin particle size (µm)	0.2–1	5–10

Table 1 shows that higher filtration rates, higher purity, higher lignin solids content and larger lignin particle size were obtained when the BL was oxidized using the *LignoForce* process compared to the absence of BL oxidation.

During the oxidation step, sugars are converted to organic acids and total reduced sulfur (TRS) compounds are oxidized to non-volatile compounds such as sulphuric acid, methane sulphonic acid and dimethyl sulphone, thereby: 1) reducing odour during all subsequent processing steps, 2) generating and distributing heat in a homogeneous fashion, and 3) reducing the pH of BL by consuming the residual sodium hydroxide. The extent of pH reduction was found to be related to the extent of BL oxidation and the rate of pH decline was found to slow down significantly as the carbonate-bicarbonate buffering effect became significant [3]. At the high pH of typical BLs, the repulsive forces between the ionized hydrophilic groups (mainly phenolic hydroxyl and carboxylate groups), stabilize the colloidal lignin and keep it in solution, thereby preventing lignin agglomeration and precipitation [3]. However, as the pH of the BL declines (as a result of the oxidation of sugars to organic acids and the TRS to non-volatile compounds), the dissociated phenolic hydroxyl groups on the lignin begin to accept protons resulting in a decline in the repulsive forces and the agglomeration of lignin to larger particles [3]. As shown in Table 1, the larger lignin particles were found to filter much faster than the smaller lignin particles obtained during acid precipitation of unoxidized black liquor.

Conclusions

The *LignoForce* system was shown to increase the filtration rate, the purity, and the solids content of lignin during its separation from BL. This system was also found to reduce the acid requirements of the process by oxidizing sulfide to sulfate and organics to organic acids which consume the residual effective alkali in black liquor.

Acknowledgements

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References

1. Öhman, F., Theliander, H., Tomani, P., Axegård, P. 2012. Method for separating lignin from black liquor. European Patent, EP1794363B1.

2. Kouisni, L., Paleologou, M. 2011. Method for separating lignin from black liquor. US Patent Application 2011/0297340A1.

3 Hermans, M.A. 1984. High intensity black liquor oxidation. PhD. Thesis, Lawrence University, 1984.

Influence of the use of high shear rate module in membrane filtration performance in ultrafiltration of black liquor

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Introduction

It has been shown that the use of high shear rate modules decreases fouling and increases filtration capacity in treatment of pulp and paper mill process and waste waters [1, 2]. Fouling and decline of filtration capacity are challenges also in ultrafiltration of black liquor and these phenomena are widely studied. However, the research has been mainly focused on the influence of membrane choice on fouling or on the influence of operational conditions on fouling and filtration capacity in one module type. The aim of this study is to find out if the use of high shear rate modules is advantageous in ultrafiltration of black liquor.

Experimental

The high shear rate modules used in the experiments were the cross-rotational module CR-250 from Metso Paper and the vibration enhanced module (VSEP) from New Logic Inc. The results achieved with these modules were compared with the results achieved with the low shear rate module DSS LabStak® (Alfa Laval). The filtration experiments were performed with soft wood black liquor with two different polyether sulphone (PES) membranes: 1000 g/mol (NP010 Nadir) and 10 000 g/mol (UP010 Nadir) ultrafiltration membranes.

Results and discussion

The results clearly demonstrated that the increased shear rate improves filtration capacity in the treatment of black liquor. Significantly higher filtration capacities were measured with the high shear rate modules than with the low shear rate modules (Figure 1., NP010 membrane). The magnitude of the high shear rate on the filtration capacity could be noticed especially at lower recovery values.

The highest filtration capacity was achieved with the CR-filter, in which turbulence is caused on the membrane surface by rotors (Figure 1.). Filtration capacity increased clearly when rotation speed of the rotors increased from 600 to 1200 RPM. The increase of rotation speed to the values higher than 1200 RPM seemed to have relatively small influence on filtration capacity. Compared to the low shear rate DSS filter, higher filtration capacity could also be achieved with the VSEP filter, in which the turbulence on membrane surface is caused by vibrating the filter cell. The results showed the importance of the vibration amplitude choice. The VSEP filter produced clearly higher filtration capacity than the DSS filter only when the higher vibration amplitude (3.8 cm) was used.

The lignin retentions achieved with the different filter modules were between 67 and 84%. It seemed that module type had a significant influence on retention. The lowest retention values were measured with the CR-filter.

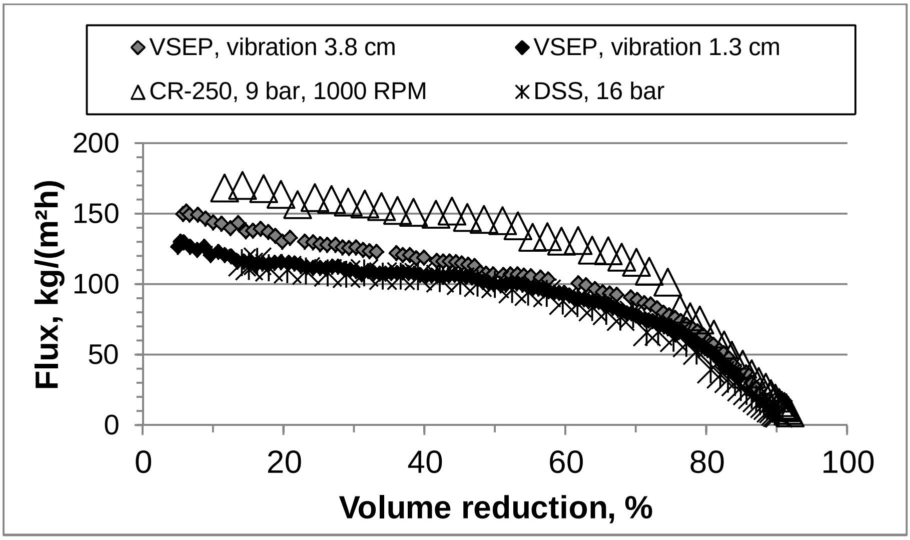

Figure 1. Permeate flux when the low shear (DSS) and high shear rate (CR & VSEP) filtration modules have been used to concentrate lignin from 10 w% black liquor with the NP010 membrane (1 000 g/mol). Filtration temperature was 60°C and pressure in the VSEP experiments 19 bar.

Conclusions

The comparison of the high and low shear rate filtration modules in the treatment of soft wood black liquor revealed that significantly higher filtration capacities can be achieved when the high shear rate modules are used. However, at high recovery values the differences in the capacities were decreasing. Based on the results lignin retention seemed to be affected by the used module type. Thus it can be concluded that advantageous of the use of the high shear rate filter modules depends on the application and its requirements for the permeate quality and volume reduction needs.

Acknowledgements

The authors are grateful to the Future Biorefinery Research Program FuBio 2 for financial support.

References

1. Huuhilo, T., Väisänen, P., Nuortila-Jokinen, J., Nyström, M. 2001. Influence of shear on flux in membrane filtration of integrated pulp and paper mill circulation water. Desalination 141(3), pp. 245–258.

2. Jönsson, A.S. 1993. Influence of shear rate on the flux during ultrafiltration of colloidal substances. J. Membr. Sci. 79(1), p. 93–99.

Impact of lignin extraction on the recovery loop of the Kraft process: Measures to minimize the consumption of chemicals

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Abstract

Impacts of lignin extraction by acid precipitation on Kraft mill chemical recovery cycle have been quantified in this study. Evaporator demand increase, recovery boiler steam production decrease and disruption of Na and S balance have been evaluated according to two scenarios related to spent liquor and washing filtrates recycle. The consumption of make-up caustic was minimized when spent liquor and first 25% of washing filtrates are recycled back to the process.

Introduction

Lignin, a major component of the black liquor which is currently burnt in the recovery boiler of the Kraft process, can be extracted and converted into a broad spectrum of bio-based products. An acid precipitation process is used to recover lignin. In this process, black liquor is extracted from the evaporator train and treated with CO_2 to reduce the pH and precipitate lignin. Precipitated lignin is then washed with dilute H_2SO_4 to remove the remaining impurities. Spent black liquor and washing filtrates have to be recycled back to the chemical recovery loop of the Kraft mill in order to recover organic and inorganic materials that they contain [1, 2]. Lignin extraction and recycle flows change the composition and flow rates of the chemical recovery cycle and disrupts its Na and S balance. In this study these impacts are quantified and mitigation measures are proposed.

Methodology

The studied mill is a representative Canadian Kraft pulp mill which has a pulp production capacity of 750 adt/d. Mass and energy balances have been performed for chemical recovery cycle using Cadsim Plus process simulator. Na and S balance of model mill has been estimated. Lignin extraction process requires 0.21 kg CO_2, 0.2 kg H_2SO_4 and 8 kg water per kg of lignin output. It was modelled in Aspen Plus platform using electrolyte approach to predict the ionic composition changes. In order to exchange data between the two simulators a common excel link has been used. Acid precipitation was implemented in the model mill and spent liquor and washing filtrates were recycled according to the following two scenarios. [1]. Only the spent liquor after filtration is recycled back to the Kraft mill; [2]. Spent liquor and filtrates from washing step are recycled back to the Kraft mill as well. Changes in evaporator steam demand and recovery boiler steam production have been estimated. Disrupted Na and S balance was brought to original values by varying the amounts of salt cake and caustic addition and precipitator dust purge.

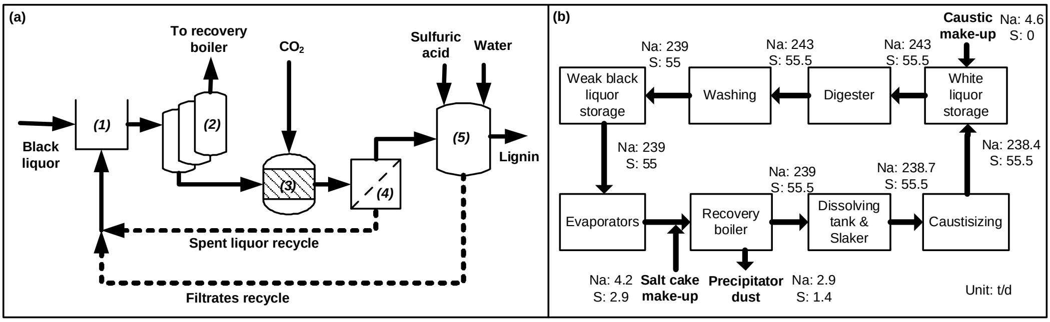

Figure 1. (a) Lignin extraction implementation scenarios: (1) – Weak black liquor tank, (2) – Evaporator train, (3) – Precipitator, (4) – Filter and (5) – Washer. Figure 1(b) – Na and S balance of the reference mill (without lignin extraction).

Results and conclusions

Table 1. Impacts on evaporators, recovery boiler and chemical make-up and purges.

Parameter	Reference mill (No lignin extraction)	With lignin extraction	
		Scenario 1	Scenario 2
Evaporator steam demand	25 MW	28 MW	36 MW
Recovery boiler steam production	88 MW	72 MW	78 MW
Salt cake addition	13 t/d	24 t/d	0
Caustic addition	8 t/d	12 t/d	26 t/d
Precipitator dust purge	8 t/d	0	30.5 t/d

According to Table 1 evaporator steam demand is significantly increased for scenario 2 due to the recycle of water used in washing. On the other hand, the recovery boiler steam production is decreased for the scenario 1 as the organic components of filtrates are lost. The Na and S balance can be maintained by increasing salt cake addition to make-up Na lost with lignin and filtrates. In scenario 2, where additional S is brought into the cycle by H_2SO_4, increasing amounts of precipitator dust have to be purged to maintain S balance. This, however, increases the caustic requirement up to 26 t/d. Excess S addition can be controlled by recycling only the first 25% of filtrates, which results in minimization of make-up caustic required.

References

1. Tomani, P., Axegard, P., Berglin, N., Lovel, A., Nordgren, D. 2011. Integration of lignin removal into a Kraft pulp mill and use of lignin as a biofuel. Cellulose Chemistry and Technology 45(7–8), pp. 533–540.

2. Kouisni, L., Fang, Y., Paleologou, M., Ahvazi, B., Hawari, J., Zhang, Y., Wang, X.. 2011. Kraft lignin recovery and its use in the preparation of lignin-based phenol formaldehyde resins for plywood. Cellulose Chemistry and Technology 45(7–8), pp. 515–520.

Bio-methanol production from kraft pulp mill condensates

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Abstract

Kraft pulp mills have the potential of producing and recovering a considerable amount of methanol. We demonstrated the technical feasibility of removing TRS compounds from the foul condensate feed to the steam stripper or from steam stripper off gas (SOG) condensates using hollow fiber contactor (HFC) technology. HFCs, which are excellent mass transfer devices, can remove TRS compounds from condensate at high efficiency by using a gas stream as a stripping medium. We have shown that the main TRS compounds can be removed from condensates with an efficiency as high as 99% with negligible methanol and terpene losses. We also demonstrated the technical feasibility of using the sulfur-free, methanol-rich SOG condensate as a reducing agent in the chlorine dioxide generator. Any excess bio-methanol in the SOG condensate has to be further purified and concentrated using distillation in order to produce high grade bio-methanol for the market.

Introduction

Evaporator and digester condensates generated at kraft pulp mills contain several volatile organic compounds (VOCs), total reduced sulphur (TRS) compounds, and traces of black liquor. The main total reduced sulphur (TRS) compounds reported are hydrogen sulphide (H_2S), methyl mercaptan (CH_3SH), dimethyl sulphide (CH_3SCH_3), and dimethyl disulphide (CH_3SSCH_3) [1, 2]. The TRS compounds have an offensive odour and their direct discharge to the ambient air or to an effluent treatment system can raise odour concerns from the communities near the mill and/or may cause the mill to exceed its emission limits with respect to these compounds. A kraft hardwood mill can generate 10–15 kg/tp of methanol while a softwood mill typically generates 7–10 kg/tp [3]. The amount of methanol generated depends on the pulping time, temperature, and hydroxide concentration.

Approach

Steam stripping is the dominant condensate treatment approach in the pulp and paper industry. A significant amount of methanol can be present in the foul condensate which ends up in the (SOGs. These gases are commonly burned in the recovery boiler, power boiler, lime kiln, or in a dedicated incinerator. No major attempt has previously been made to recover or to further purify the methanol content in these streams for use within the mill or for sale for specific applications. The objective of this work was to devise a cost-effective approach to purify the foul condensate and to recover methanol for use on site (e.g., in the chlorine dioxide generator as a reducing agent). This will allow kraft pulp mills to stop purchasing methanol from external sources. Mills without steam strippers can use this technology to reduce odour around the mill resulting from the sewering of the untreated condensate. The proposed approach is based upon the use of (HFC technology to remove TRS compounds from condensate ahead of the steam stripper. These contactors contain several hollow fibers. The condensate is allowed to flow around the fibers while an acceptor fluid, or a stripping agent, for example another aqueous solution or a gaseous carrier, is allowed to flow on the inside of the fibers. These contactors can provide fast mass transfer without flooding or loading since the acceptor fluid and the aqueous feed solution flow on different sides of the hollow fiber thereby allowing better control. The HFC unit used in this work had a diameter of about 100 mm, a height of about 330 mm (4 by 13 inches) and a membrane surface area of about 8.1 m^2. Since these fibers are hydrophobic, only hydrophobic compounds can diffuse into the hollow fiber membrane pores. Water molecules as well as other hydrophilic compounds are mostly excluded. The condensate at

50°C was first filtered to remove suspended solids and then passed through the HFC unit at a flow rate of about 5 L/min. The air or nitrogen flow rate was about 16 L/min.

Results

Using this technology, as much as 99% of the TRS compounds in pulp mill foul condensates was removed. The contaminated gas stream generated from the HFC system can be burned in the recovery boiler or in a power boiler. The loss of methanol and terpenes during foul condensate treatment was quite low (about 5%). Once the TRS compounds are removed, the condensate can be fed to a steam stripper thereby obtaining a sulphur- free SOG condensate composed mostly of methanol and water (40–70% methanol solution). The terpene phase can easily be separated from the SOG condensate using a decanter. Alternatively, the SOG condensate which represents a much lower volume than the foul condensate can be treated using an HFC to remove TRS compounds.

The recovered methanol can be used for instance as a reducing agent in the chlorine dioxide generator or sold for some specific applications. For hardwood pulp mills, a terpene-free methanol stream can be generated. To produce pure methanol for sale, the SOG condensate will have to be distilled. The use of methanol-rich solutions in the generator was evaluated using the FPInnovations pilot plant. A solution containing 20–40% methanol and traces of TRS compounds was employed. The terpene content was less than 1.0 g/L and most of the terpenes were terpene alcohols. Preliminary results indicated that the treated SOG condensate generated as much chlorine dioxide as the control solution (20–40% pure methanol solution). No issues with the contaminants present in the methanol-rich solution were observed during the run.

References

1. Blackwell, B.R., Mackay, W.B., Murray, F.E., Oldham, W.K. 1970. Review of kraft foul condensates. Tappi J. 62(10), p. 33.

2. Niemelä, K. 2004. Sulfur and nitrogen compounds in rectified methanol from foul condensate stripping, TAPPI International Chemical recovery Conference, TAPPI Press, Atlanta, pp. 471–482.

3. Zhu, J.Y., Yoon, S.H., Liu, P.H., Chai, X.S. 2000. Methanol formation during alkaline wood pulping. Tappi J. 83(7), pp. 65–78.

Utilization of byproduct streams treated by wet oxidation

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Abstract

In this work a two stage process for recovery of fuel gas components from black liquor is presented. Treated black liquor decomposed into a vapor phase and a solid residue. The vapor phase contains valuable organic components such as methane, acetone, carbon monoxide, besides steam and carbon dioxide. The solids contains sodium carbonate and some char residue. According to material balance for treated black liquor and carboxylic acid salts mixture valuable fuel components such as carbon monoxide, acetone, methanol, methane etc. are produced. In the experiment the yield of fuel components for treated black liquor was fairly low.

Introduction

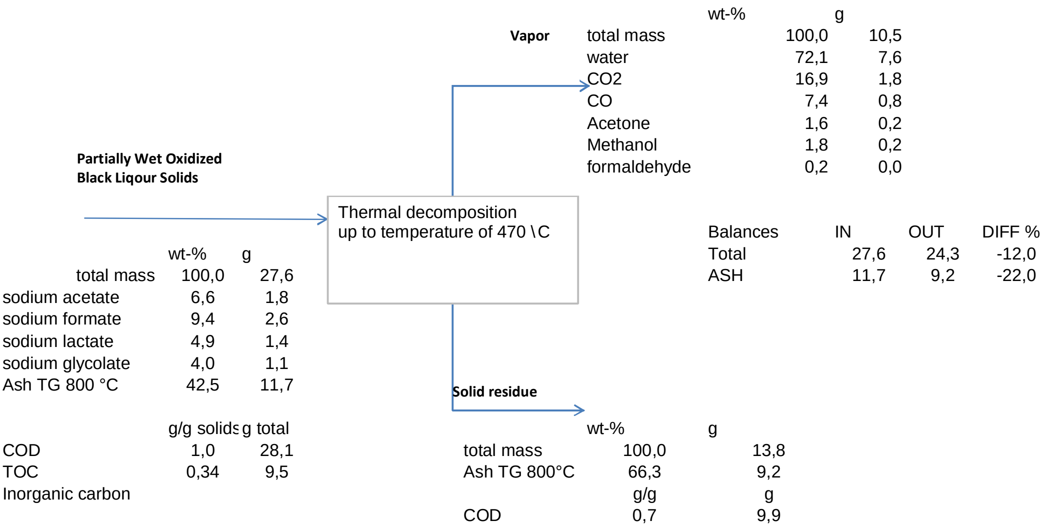
Byproduct streams such as black liquor or other byproduct streams containing a high amount of organic material are attractive due to low cost. Both in the Nordic countries and Asian non wood pulp mills black liquor is available in huge amounts. Normally the byproducts are only for energy production. Fuels or chemicals are usually more valuable products than energy. The process of wet oxidation was at first employed in pulp and paper industry in order to oxidize waste lignin present in black liquor into carbon dioxide and water (Strehlenert, 1915). When the conversion is not complete carboxylic acid salts such as acetates, formates and lactates are obtained. In addition lignin might precipitate due to lower solubility of lignin at lower pH (Devlin and Harris, 1984). The acids salts can be decomposed when heated to approximately 300–500°C. Either as solids or in aqueous solution at high pressure into fuel gas containing for example methane, hydrogen and other volatile organic components (Jude and Paul, 2010). Also a solid carbonate residue and some char are obtained.

Experimental

Sulphur free black liquor evaporated to approximately 30 w-% solid conc. was wet oxidized in a micro reactor to convert sugars and lignin to carboxylic acid salts which decompose at a lower temperature than lignin. The partially wet oxidized black liquor was dried and heated in the micro reactor from room temperature up to a temperature of 470°C without stirring. The formed gases were analysed using FTIR analysis each 20 seconds. Based on the analysed gas composition in the apparatus the average gas composition during the run was calculated. For comparison a carboxylic acid sample with composition shown in Figure 2 was decomposed with the same procedure.

Results and discussion

The gas compositions, chemical oxygen demand etc. are shown in Figure 1 and 2.



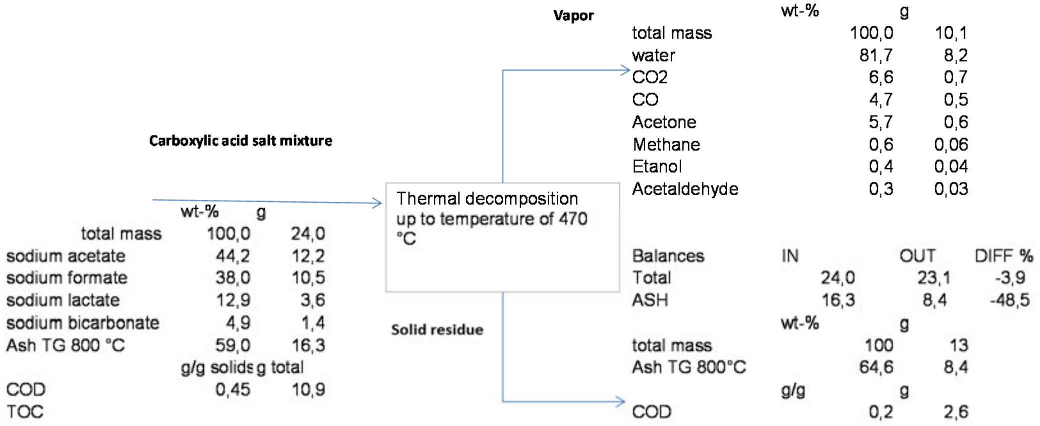
	wt-%	g
total mass	100,0	10,5
water	72,1	7,6
CO2	16,9	1,8
CO	7,4	0,8
Acetone	1,6	0,2
Methanol	1,8	0,2
formaldehyde	0,2	0,0

Balances	IN	OUT	DIFF %
Total	27,6	24,3	-12,0
ASH	11,7	9,2	-22,0

	wt-%	g
total mass	100,0	27,6
sodium acetate	6,6	1,8
sodium formate	9,4	2,6
sodium lactate	4,9	1,4
sodium glycolate	4,0	1,1
Ash TG 800 °C	42,5	11,7
	g/g solids	g total
COD	1,0	28,1
TOC	0,34	9,5
Inorganic carbon		

	wt-%	g
total mass	100,0	13,8
Ash TG 800°C	66,3	9,2
	g/g	g
COD	0,7	9,9

Figure 1. Thermal decomposition material balance for partially wet oxidized black liquor.



	wt-%	g
total mass	100,0	10,1
water	81,7	8,2
CO2	6,6	0,7
CO	4,7	0,5
Acetone	5,7	0,6
Methane	0,6	0,06
Etanol	0,4	0,04
Acetaldehyde	0,3	0,03

	wt-%	g
total mass	100,0	24,0
sodium acetate	44,2	12,2
sodium formate	38,0	10,5
sodium lactate	12,9	3,6
sodium bicarbonate	4,9	1,4
Ash TG 800 °C	59,0	16,3
	g/g solids	g total
COD	0,45	10,9
TOC		

Balances	IN	OUT	DIFF %
Total	24,0	23,1	-3,9
ASH	16,3	8,4	-48,5

	wt-%	g
total mass	100	13
Ash TG 800°C	64,6	8,4
	g/g	g
COD	0,2	2,6

Figure 2. Thermal decomposition material balances for the carboxylic acid mixture.

Conclusions

The chemical oxygen demand has been significantly reduced and useful fuel components are formed. However for the black liquor case the yields of fuel components are low and char remains in the solid residue. All the gaseous components (hydrogen and some hydrocarbons could not be quantified so fuel components yields might be underestimated.

Acknowledgements

Tekes, Aalto University, Fortum's and Gasum's foundations are acknowledged for funding.

References

1. Devlin, H.R., Harris, I.J. 1984. Mechanism of the oxidation of aqueous phenol with dissolved oxygen, Ind. Eng. Chem. Fundam. 23(4), pp. 387–392.

2. Jude, A.O., Paul, T.W. 2010. Hydrothermal reactions of sodium formate and sodium acetate as model intermediate products of the sodium hydroxide-promoted hydrothermal gasification of biomass, Green Chem. 12, pp. 2214–2224.

3. Strehlenert, R.W., U.S: Patent No. 1,149,420, Aug, 1915.

Biorefinery and energy savings

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Abstract

Finland is a country of very high energy consumption per capita and lack of natural resources. Because of rapid increase of fuel price, the electricity price is growing too. Therefore, Finland has strong energy politics forcing adoption of energy saving technologies. Improvement of technology, pollution monitoring, fuel consumption development and regular control from responsible organizations could be mechanisms to achieve stability, independence and profit.

Environmental-oriented governmental programs force research to be focused on transportation fuels. Growing oil prices affect sustainability of economics. Fossil resources from outside of Finland could be partly replaced in near future with own second generation biofuels.

Biorefineries based on existing pulp and paper mills is obvious decision for Finland. UPM-company is going to build a biorefinery in South Carelia, Finland. Innovations used in UPM plant build scientific platform and methodology for other projects in this field. Ongoing research should be able to solve various problems.

Introduction

Finnish main industrial energy consumers are paper and forest companies. There are several ways to improve production processes and decrease energy costs. First is energy monitoring – complex procedure to detect all types of possible losses. Second is proper wastes utilization – biorefinery installation.

Transportation needs, developed paper mill's infrastructure and available resources are main factors resulting possible intensive biofuel production. In Lappeenranta at Kaukas Pulp and Paper mill 2nd generation biodiesel refinery will be installed by 2014 (100 000 tons annually). Raw material is softwood. Technology used in process is hydrotreatment of crude tall oil. 2020 targets for Finland would cover one fourth of total biofuel need if biorefinery in Lappeenranta would be installed.

Energy observation tests present all energy flows, measure their amount and illustrate location. Conclusions describing detailed energy consumption situation, methods and ways to increase energy efficiency are illustrative base for decision-making on biorefinery construction.

Experimental

Energy audit is Complex system of technical, economical, organizational and other activities focused on identifying opportunities to optimize the cost-effective use of energy resources. Measurements and experiments are done using number of equipment, such as thermal image sensors, gas analysers, flow/pressure/volume/temperature detectors, pyrometers and others. Engineers and personnel of factory are involved into the process. There are many types of energy audits:

1. Preliminary audit
2. General audit
3. Infrared thermography audit
4. Investment-grade audit
5. Pollution audit.

Pulp and paper mills as well as refineries are intensive consumers of water, electricity and heat. Hence, energy audit takes quite long time and requires experienced auditors. Remarkable, that energy saving potential in pulp and paper industry is still very high and for some part requires no significant investments.

Discussion

Problems related to research on adoption of biorefineries:

- Amount and constant composition of raw material suitable for certain process
- Technology development (as long as biorefinery concept is under development technologies could be improved and applied for different industries/companies)
- Financial aspects (cost of technology varies due to many factors)
- Lack of educated specialist with experience in both-biorefineries and pulp and paper industries.

Conclusions

Combined solutions for two or more industrial objects require huge amount of work and research. If those two industries are intensive energy consumers it is needed to find out ways to decrease amount of resources used. Instead of manufacturing more and more power plants it is necessary to think about current energy consumption.

Energy observation is perfect option for both-pulp and paper mill and chemical refining. Energy consumption report provides useful information for construction and design. Finally by-products (or even wastes) from paper factory and forestry start innovation opportunities in energy sector and transportation.

References

1. UPM press-release, Pirkko Harrela, The Paper Times, 1 p. http://news.paperindex.com/NewProjects_MillClosures/UPM_to_Build_the_Worldrsquos_First_Biorefinery_Producing_Wood-based_Biodiesel/.

Towards optimal treatment procedure upon fractionation of Nordic lignocelluloses using novel alkanol amine – superbase ionic liquid system

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Introduction

Fractionation of lignocellulosic material using Switchable Ionic liquids (SILs) as solvents was successfully demonstrated. The recovery and reuse for more than one fractionation cycle [1, 2]. Furthermore, selective fractionation of lignocellulosic material was illustrated, incorporation of different acid gases upon formation of the SIL. SILs can easily be synthesized by passing an acid gas, such as SO_2 and CO_2 through a mixture of a super-base such as, 1,8-diazabicyclo-[5.4.0]-undec-7-ene, (DBU) and an OH-containing compound like glycerol (an affordable benign molecule also obtained as a by-product of biodiesel synthesis). The carbonate/sulfonate form can simply be switched back to its starting materials by purging the SIL inert gas (N_2) [3, 4].

Experimental

In order to determine the actual dissolution kinetics (i.e. the rate of dissolution), a series of experiments was conducted (4, 8, 12, 16 and 24 hours, respectively). The parameters affecting the wood components will be discussed. Novel DBU-based $MEASO_2$ SIL was used as fractation solvent at 100°C, Wood to SIL ratio was 1:5, without any mechanical agitation. Fresh Wood Chips (*Betula pendula)* (3x3x0.2 cm)

Results and discussion

SIL treatment of wood resulted in 37% weight reduction in 4 hours, the weight reduction remain the same until. The weight of the chips was reduced to 44% of their initial weight by 24 h with fresh SIL under similar conditions as stated earlier. The total wood lignin amount was reduced to 4% from 20% after 24 h treatment. Furthermore, the total amount of glucose (originating from cellulose hydrolysis in line with the analysis procedure) of the undissolved fraction after SIL treatment increased from 42% (native wood) to 60% after the 24 h treatment (Figures 1 and 2). The undissolved material after 24 h was efficiently fibrillated as seen in the SEM image Figure 3.

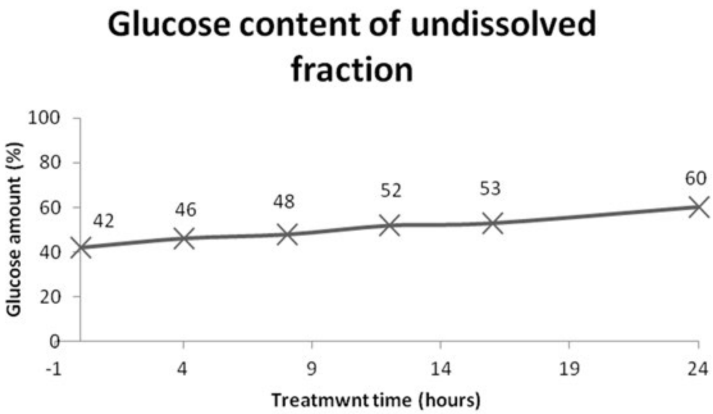

Figure 1. Glucose content of the undissolved treated birch chip.

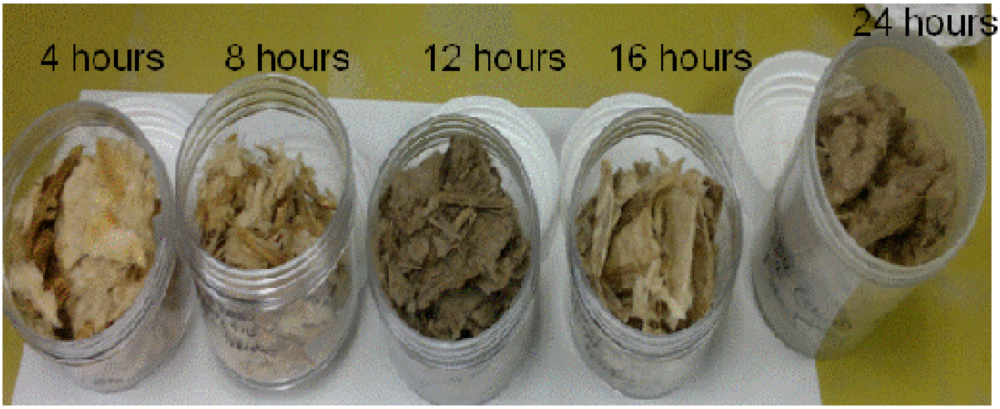

Figure 2. Kinetic study of SIL treatment of birch using the following Treatment conditions 100°C, no stirring, SIL: Wood (5:1), chips (3 x 3 cm).

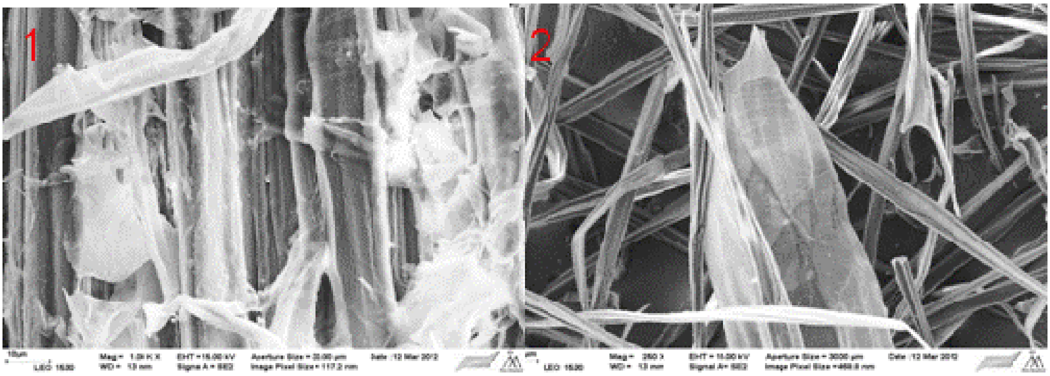

Figure 3. SEM image of 1) native birch and undissolved fraction after 24 h SIL treatment of native birch.

Acknowledgements

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References

1. Anugwom, I., Mäki-Arvela, P., Virtanen, P., Sjöholm, R., Willför, S., Mikkola, J.-P. 2005. Carbohydrate Polymers 87, pp. 2005–2011.

2. Anugwom, I., Mäki-Arvela, P., Virtanen, P., Damlin, P., Hedenström, M., Mikkola, J.-P., Holzforschung. Online Doi: 10.1515/hf-2011-0226.

3. Anugwom, I., Mäki-Arvela, P., Virtanen, P., Damlin, P., Sjöholm, R., Mikkola, J.-P. 2011. Advances 1, pp. 452–457.

4. Anugwom, I., Mäki-Arvela, P., Virtanen, P., Mikkola, J.-P. PCT/FI2011/050959.

Sustainable Resource Technology (SuReTech)

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Abstract

We all need to contribute to a more sustainable development – a fact that has become quite clear observing extreme weathers and diminishing fossil fuel sources. In line with the 12 Principles of Green Chemistry [1], (recommending the use of safer solvents, catalysed reactions, energy efficient processes and renewable feedstocks), research within the SuReTech program aims at developing technologies for the recovery of high-value compounds from forestry and agricultural byproducts. The idea is to create value addition, by adding products to already utilized resources in line with biorefinery concepts. Extractions of antioxidizing compounds from byproducts are thus made by use of carbon dioxide and water as sustainable solvents and combined with biocatalytic conversions for the creation of compounds with desired properties. The byproducts, used as starting materials, are selected based on annual volumes from the Swedish agricultural, food and forestry industry. Substituents on the compounds are modified by biocatalysis, *e.g.* using thermostable carbohydrate converting enzymes selected to fit the conditions in the extraction step. The importance of combining different scientific fields to enable creativity in sustainable development is highlighted.

Value added processing of byproducts from forestry

To minimize the resources necessary to produce solvents as well as the need of destruction of the solvents after use, guidelines for selection with respect to environmental, health and safety properties have been presented [2]. In line with the guidelines, pressurised hot water mixed with ethanol was selected to extract antioxidants from forestry byproducts (bark of spruce [3] and birch [4] (Figure 1). Other bark-resources of interest originate from pine, shown to be rich in catechin, but also containing quercetin [5], which we in previous work have extracted from agricultural (onion) waste in a procedure involving hot pressurized water followed by an enzymatic step [6], used to obtain a uniform aglycone product. In this case, deglycosylation also increases the antioxidizing power. Moreover, addition or subtraction of substituents (glycosylation or acylation, by glycosidases/glycosyltransferases and lipases, respectively) affects solubility-allowing use in different solvents (hydrophilic or hydrophobic – and in the longer perspective a broader use).

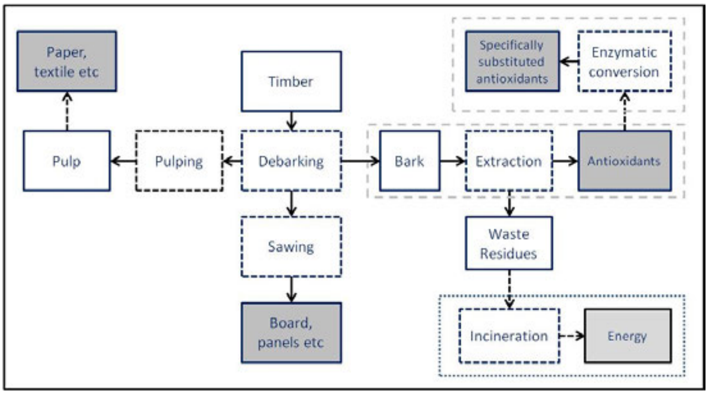

Figure 1. Flowchart showing processing of forestry residues. Value added steps are boxed (grey dashed line). Extraction and enzymatic conversion can be either on-line or independent steps. Waste residues after the added processing are still applicable for energy production (dotted box).

The interdisciplinary approach

Biorefinery concepts are predicted to give environmental and socio-economic benefits in the long term. However, analyses are necessary to find biomass feedstocks/applications with the lowest opportunity costs and best environmental performance. In our project we have seen environmental benefits of new processes for added value products [7]. Socioeconomic analysis is ongoing.

Acknowledgement

We wish to acknowledge financial support from the Swedish Research Council Formas for funding.

References

1. Anastas, P., Warner, J. 1998. Green chemistry: theory and practice, Oxford University Press.

2. Capello, C., Fischer, U., Hungerbühler, K. 2007. What is a green solvent? A comprehensive framework for the environmental assessment of solvents. Green Chem 9, p. 927.

3. Co, M., Fagerlund, A., Sjoberg, P., Sunnerheim, K., Engman, L., Turner, C. 2012. Extraction of antioxidants from spruce (Picea abies) bark using eco-friendly solvents. Phytochem Anal 23, p. 1.

4. Co, M., Koskela, P., Eklund-Akergren, P., King, J.W., Sjoberg, P., Turner, C. 2009. Pressurized liquid extraction of betulin and antioxidants from birch bark. Green Chem 11, p. 668.

5. Bocalandro, C., Sanhueza, V., Gomez-Caravaca, A.M., Gonzalez-Alvarez, J., Fernandez K, Roeckel, M., Rodriguez-Estrada, M.T. 2012. Comparison of the composition of *Pinus radiata* bark extracts obtained at bench- and pilot-scales. Ind Crops Prod 38, p. 21.

6. Turner, C., Turner, P., Jacobson, G., Waldeback, M., Sjoberg, P., Nordberg Karlsson, E., Markides, K. 2006. Subcritical water extraction and β-glucosidase-catalyzed hydrolysis of quercetin in onion waste. Green Chem 8, p. 949.

7. Lindahl, S., Ekman, A., Khan, S., Wennerberg, C., Börjesson, P., Sjöberg, P., Nordberg Karlsson, E., Turner, C. 2010. Exploring the possibilities of using a thermostable mutant of β–glucosidase for rapid hydrolysis of quercetin glucosides in hot water. Green Chem. 1, p. 159.

Identification of degradation products from birch wood in water extracts

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Introduction

Hot water treatment of wood prior to pulping operations is recognized as a potential method to extract the hemicelluloses and convert them into value-added products. In addition to oligo- and monosaccharides originating from the carbohydrates, lignin fractions and organic acids such as acetic acid can be typically found in the water extract [1]. Under intense extraction conditions, considerable amounts of other degradation products are also formed [2]. The goal of this study was to identify low-molar mass degradation products from birch wood in water extracts produced at various extraction intensities.

Experimental

Birch wood chips were extracted with hot water in a 10 L batch reactor, with a liquid-to-wood ratio of 3:1 g/g. A high-pressure pump was used to continuously re-circulate the water through the chip bed. The temperature in the reactor was raised to the setup temperature (180°C, 200°C or 220°C), and after an isothermal treatment time, the water extract was drained through a bottom valve. The intensity of any hot water extraction was determined by the well-known P-factor. The water extracts were analyzed for mono- and oligosaccharides, furfural, 5-hydroxymethylfurfural (HMF) and acetic acid by HPLC, and for aromatic compounds and polar hydroxy acids by GC-MS. The analytical procedures will be described in more detail elsewhere.

Results and discussion

The water extracts produced at the lowest extraction intensities (up to a P-factor ~ 1000) were rich in xylose monomers and xylo-oligosaccharides (Table 1). Increasing extraction intensity led to partial degradation of cellulose in wood, although only small amounts of dissolved glucose mono- and oligomers were found in the extracts. Increasing amounts of degradation products from carbohydrates, such as furfural, HMF and aliphatic acids were also formed. In addition to acetic acid, the GC-MS analyses revealed numerous polar hydroxy acids (Figure 1). The most abundant hydroxy acids included glycolic and 3-deoxypentonic acids, apparently mainly derived from xylose.

More than 30–40 aromatic monomers and up to 30 aromatic dimers, originating from the lignin, were found in the water extracts (Figure 1). A higher amount of aromatic compounds derived from syringyl units, as compared to those derived from guaiacyl units, were detected. The most abundant monomers typically included syringaldehyde, syringol, syringylacetone and 1-hydroxy-3-syringylacetone, whereas syringaresinol was the main dimer. A detailed identification of degradation products will follow in an extended publication. Such identifications may provide useful information for assessing the suitability of water extracts for further applications.

Table 1. Concentration (g/L) of sugars, furfural, HMF, acetic acid and hydroxy acids in the water extracts. Sample name indicates extraction temperature and isothermal extraction time. XOS = xylo-oligosaccharides; COS = cello-oligosaccharides.

Sample	P-factor	Xylose	XOS	Glucose	COS	Furfural	HMF	Acetic acid	Hydroxy acids
180.10	262	1.43	14.97	0.08	0.56	0.46	0.04	1.35	0.24
180.30	766	11.17	16.94	0.28	0.92	3.79	0.19	5.27	0.66
200.10	1057	10.50	11.59	0.33	0.81	5.00	0.22	6.23	0.98
220.2	1322	11.36	7.79	0.56	0.90	7.64	0.31	10.39	1.88
200.30	3600	2.74	0.22	2.05	0.64	18.52	1.98	20.01	2.54
220.25	8166	0.18	0.03	1.94	0.44	16.11	3.51	21.20	2.84

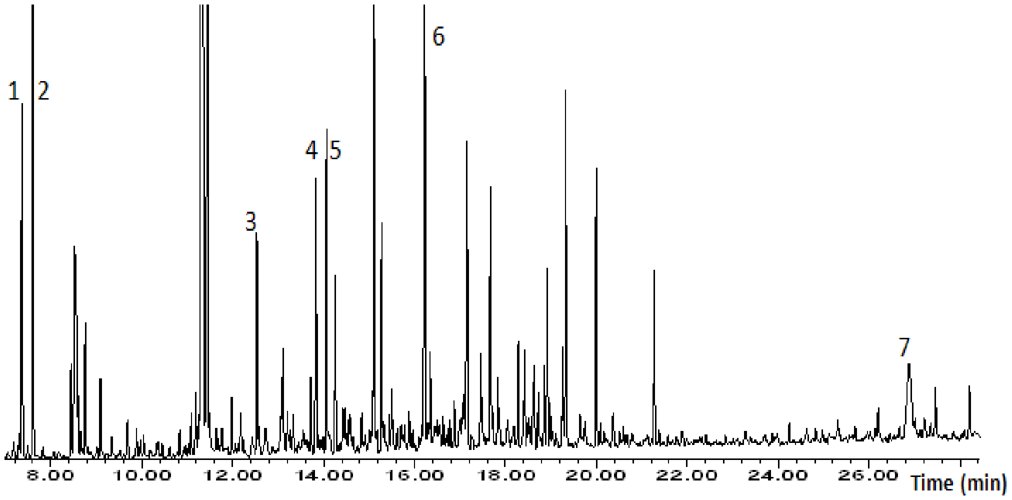

Figure 1. GC-MS chromatogram of sample 220.25, with selected identifications: 1, lactic acid; 2, glycolic acid; 3, syringol; 4 and 5, 3-deoxy-erythro- and threo-pentonic acids (lactones); 6, syringaldehyde; and 7, syringaresinol.

Acknowledgements

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References

1. Garrote, G., Domínguez, H., Parajó, J.C. 1999. Hydrothermal processing of lignocellulosic materials. Holz Roh. Werkst. 57, pp. 191–202.

2. Borrega, M., Nieminen, K., Sixta, H. 2011. Degradation kinetics of the main carbohydrates in birch wood during hot water extraction in a batch reactor at elevated temperatures. Bioresour. Technol. 102, pp. 10724–10732.

Alkaline oxidation pretreatment of wood materials to produce ethanol

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Abstract

Alkaline oxidative fractionation of woody materials and sugarcane bagasse was developed. The enzymatic hydrolysis of alkaline oxidised materials worked well even with low enzyme dosages and at high dry matter conditions. The resulting ethanol yield was on a high overall level. Process concepts were developed based on the results and the estimates of the feasibility of the process were calculated. The results clearly showed the promise of the new fractionation method, but also indicated the key challenges in scaling up the technology to full industrial scale.

Introduction

Plant biomass is the major readily available renewable source to substitute oil as raw material in production e.g. liquid fuels and chemicals. Feasible utilization of the cell wall components by the sugar route requires efficient methods to fractionate woody raw materials into utilizable non-carbohydrate fractions and readily hydrolysable cellulose fraction for hydrolysis. Alkaline oxidation is a method, which fractionates efficiently woody biomass using simple chemicals and mild process conditions, giving carbohydrates with high enzymatic hydrolysability and low inhibitor content and a lignin fraction with interesting technical properties.

Earlier developed catalytic oxidation method for pretreating lignocellulosic material was optimized and an alkaline oxidation pretreatment method was developed and optimized (1, 2). Various reaction conditions (liquid volume, solid content and particle size) were studied with spruce and sugar cane bagasse.

Results and discussion

Alkaline oxidation pretreatment, with or without catalyst, was shown to be an efficient and high yielding method to separate cellulose from lignin, as compared to steam explosion (Figure 1). Oxidation at higher solid contents and volumes needs further development and advanced reactor systems. The alkaline oxidation pretreatment allowed shorter hydrolysis times and clearly lower enzyme dosages in enzyme hydrolysis, as compared to steam explosion pretreatment. The alkaline oxidised materials worked well in processing at high dry matter content and showed no inhibition in ethanol fermentation, whereas enzymatic hydrolysis and fermentation of steam exploded materials were slower in higher dry matter content (Figure 1). High ethanol yields in short fermentation were obtained with alkaline oxidation although the applied yeast was not able to use pentoses present in the raw materials. A maximum ethanol end concentration of 49 g/l was obtained by spruce at 12% dry matter content.

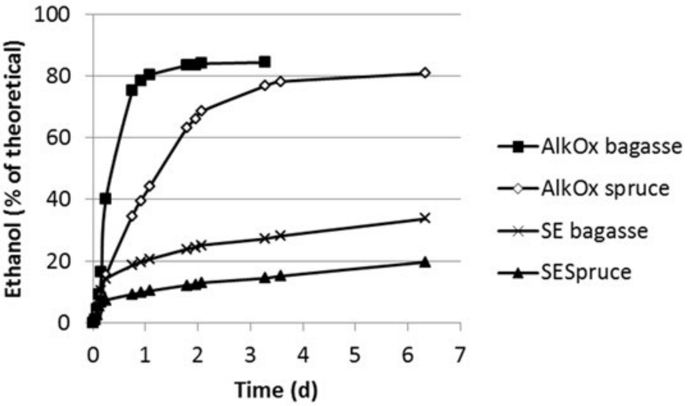

Figure 1. Fermentation of alkaline oxidised spruce and bagasse and steam exploded spruce and bagasse at 12% d.w. at 35°C with commercial yeast Red Star. 6 hours prehydrolysis with Cellic Ctec2+Htec enzyme mixture (enzyme ratio was 90:10; total dosage 15mg/g) at 50°C, pH 5.

First estimates of profitability of a few different developed ethanol production concepts based on alkaline oxidation pretreatment were also calculated. Production costs exceed the assumed ethanol sales price (0.6 €/L) in most of the studied cases. Key variable cost items were feedstock and enzymes, as well as electricity in the integrated sugarcane juice and bagasse ethanol cases. Total capital investment in the ethanol production processes were estimated to be high especially due to the pre-treatment, solid-liquid separation and required chemical recovery equipment. Another very interesting concept giving significant cost savings would be the repurposing of closed mills.

Conclusions

Very good enzymatic hydrolysability and high ethanol yields in short fermentation time were obtained with the alkaline oxidation pretreatment. Further research is needed for obtaining more reliable information for process scale-up and process equipment dimensioning and selection.

Acknowledgements

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References

1. Hakola, M., Kallioinen, A., Kemell, M., Lahtinen, P., Lankinen, E., Leskelä, M., Repo, T., Riekkola, T., Siika-aho, M., Uusitalo, J., Vuorela, S., von Weymarn, N. 2010. Liberation of cellulose from the lignin cage: A catalytic pretreatment method for the production of cellulosic ethanol. ChemSusChem 3, pp. 1142–1145.

2. Rovio, S., Kallioinen, A., Tamminen, T., Hakola, M., Leskelä, M., Siika-aho, M. 2012. Catalysed alkaline oxidation as a wood fractionation technique. BioResources 7, pp. 756–776.

Enzymes – tools to upgrade biomass to high-value products

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The natural resources both on land and in water are subject to steadily increasing demands on a global level due to the growing world population, climate change, depletion of fossil raw materials and increasing environmental load. The urge to ensure optimal, cascaded use of biomass resources has been the driving force for various existing biorefinery and bioeconomy initiatives. In biorefineries biomass is processed in a sustainable manner to various marketable products and energy. Bioeconomy can be seen as an expansion of the biorefinery concept as it includes also the exploitation of biological phenomena in processing of non-biological raw materials or production of non-bio products exploiting certain biological principles.

Biotechnical processing by enzymes offers a possibility to selectively and efficiently turn biomass residues and side streams into new materials, chemicals, energy, food and feed in a sustainable and affordable manner (Figure 1). Due to their specify enzymes are powerful tools to solve the challenges related to the utilisation of biomass in new ways. Compared to traditional manufacturing systems, industrial processes can be performed by enzymes or microbes with significantly less energy, water and without the need of aggressive chemicals. Thus, as a result of industrial biotechnology a more efficient use of natural resources as well as reduced energy and water consumption is obtained.

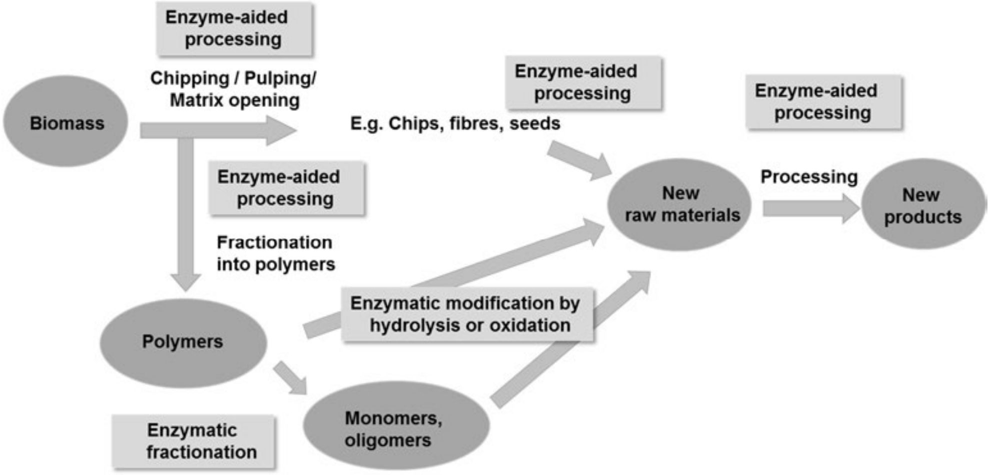

Figure 1. Enzyme-aided processing of biomass.

A wide variety of potential enzymes suitable for processing of forest and agricultural residues and food side streams are listed in Table 1. These enzymes are expected to play a key role in future biomass processing.

Table 1. Enzymatic tools for biomass upgrading.

Component	Enzyme group	Tools	Exploitation
Cellulose	Cellulases	EG	Depolymerisation, structure modification
		CBH	Structure modification
		Mix	Total hydrolysis
Hemicellulose	Hemicellulases	Xylanases, mannanases	Depolymerisation
		Accessory enzymes	Side-group cleaving, transfer reactions for depolymerisation, structure modification, functionalisation
		Mix	Total hydrolysis
Lignin	Lignin oxidizing enzymes	Laccases	Radical formation, functionalization, depolymerisation with mediator
		LiP, MnP	Oxidation, depolymerisation with mediator
Extractives	Enzymes acting on extractives	Lipases, Laccases	Degradation by hydrolysis, oxidation
Pectin	Pectinases	Pectinases	Cleavage, demethylation
Protein	Proteases	Various proteases	Depolymerisation, crosslinking
	Others	Hydrophobins Swollenins	Surface hydrophobisation Loosening of cellulose fibre structure

Enzyme technologies for the production of high-value polymers and chemicals from forest resources

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Abstract

Accessory hemicellulases and carbohydrate oxidases were produced to tailor the branching structure of hardwood xylans and for site-specific activation of selective hydroxyl groups, respectively. While the accessory hemicellulases were chosen to increase the uniformity of hemicellulose recovered from pretreated wood fibre, the carbohydrate oxidases can facilitate regioselective chemical derivatization of polysaccharides with fewer protection/deprotection steps. In particular, accessory hemicellulases selected for this study include α-arabinofuranosidases from glycoside hydrolase (GH) family 62, α-glucuronidases from GH115, and acetylxylan esterases from carbohydrate esterase (CE) family 1. Carbohydrate oxidases include oligosaccharide oxidases and galactose oxidases of fungal origin. Fitting with our aim to harness enzyme specificity to synthesize high-value biopolymers from wood polysaccharides, in all cases the enzymes were selected and further engineered for enhanced activity on polymeric substrates, including xylans, cellulose, and galactoglucomannan.

Introduction

The production of high value co-products can significantly improve the process economics of lignocellulosic biorefineries whose main product is bioenergy. This is particularly true for forest biorefineries located in northern countries that rely on slower growing trees that produce high-quality fibre.

The aim of our research is to engineer enzymes that can be used to synthesize new, high-value polymers and chemicals from renewable plant materials. Our enzyme approach harnesses 1) the regio- and stereo-specificity of enzyme catalyzed reactions that have evolved to transform lignocellulosic substrates, and 2) our ability to manipulate protein function using genetic tools, to enhance or alter protein function. Notably, the catalytic specificity of enzymes is important to reproducibly tailor the composition and performance of wood polysaccharides. Moreover, the aqueous and mild reaction requirements of enzyme catalyzed reactions can help retain the degree of polymerization of xylans and glucomannans recovered from pretreatment hydrolysates.

Experimental

Each enzyme construct was recombinantly produced in either *E. coli* or *P. pastoris* and purified to homogeneity using NiNTA affinity resin and ion chromatography. While proteins expressed in *P. pastoris* were secreted to the culture medium, proteins expressed in *E. coli* were recovered from cell lysates. Induction of recombinant protein expression in *P. pastoris* cultures at 15°C and in the presence of casamino acids and leupeptin increased the stability of chimeric enzymes produced with a bacterial CBM.

Commercial compounds used to biochemically characterize purified hemicellulases included paranitrophenyl acetate, pNP-arabinose, alduronic acids, cellulose acetate, glucuronoxylan, and arabinoxylan; acetylated xylan was also produced from glucuronoxylan. In addition to xylan, polysaccharide oxidases were tested using galactomannan, xyloglucan, carboxymethyl cellulose, and regenerated amorphous cellulose. Product formation was monitored using standard chromogenic detection or by HPLC. In addition to activity measurement, affinity gel electrophoresis was used to characterize the effect of CBM addition on enzyme binding to various polysaccharides.

Result and summary

Given our aim to develop enzymes for hemicellulose and cellulose engineering rather than conversion to sugars, the enzymes were selected based on having comparatively high activity on oligomeric or polymeric substrates (Table 1) [1, 2, 3, 4]. Moreover, to assess the potential of carbohydrate-binding modules (CBMs) to increase enzyme action on polymeric substrates, bacterial CBMs from families 3, 6, 11, 22, 29 and 44 were covalently linked to particular enzyme targets (Table 1).

Table 1. Enzymes produced and characterized in the current study.

Catalytic Domain	**Predicted Activity**	**Linked CBM family** [a]
Galactose oxidase	Oxidizes primary alcohol of galactose	29
Oligosaccharide oxidase	Oxidizes the alcohol of the anomeric carbon	3, 11, 22, or 44
CE1	Acetylxylan esterase	3 or 6
GH62	arabinofuranosidase	None added
GH115	α-glucuronidase	None added

[a] Binding affinities are reviewed in Boraston et al. [5]

While all enzymes targeted were of fungal origin, enzymes selected from GH62 and GH115 were functionally expressed to high yield in *E. coli*. Moreover, all enzyme activities were retained after covalent linkage to a bacterial CBM. Preliminary results with selected oxidases indicate that the addition of a CBM does not affect enzyme stability, but increases the specific activity of the enzyme on corresponding polysaccharides. On-going kinetic analyses and affinity gel electrophoresis will assess the contribution of binding affinity to enzyme efficiency on polymeric substrates.

References

1. van den Brink, J., de Vries, R.P. 2011. Fungal enzyme sets for plant polysaccharide degradation. Appl. Microbiol. Biotechnol. 91(6), pp. 1477–1492.

2. Chong, S.L., Battaglia, E., Coutinho, P.M., Henrissat, B., Tenkanen, M., de Vries, R.P. 2011. The α-glucuronidase Agu1 from Schizophyllum commune is a member of a novel glycoside hydrolase family (GH115). Appl. Microbiol. Biotechnol. 90(4), pp. 1323–1332.

3. Parikka, K., Leppänen, A.S., Pitkänen, L., Reunanen, M., Willför, S., Tenkanen, M. 2010. Oxidation of polysaccharides by galactose oxidase. J. Agric. Food. Chem. 58(1), pp. 262–271.

4. Lee, M.H., Lai, W.L., Lin, S.F., Hsu, C.S., Liaw, S.H., Tsai, Y.C. 2005. Structural characterization of glucooligosaccharide oxidase from Acremonium strictum. Appl. Environ. Microbiol. 71(12), pp. 8881–8887.

Boraston, A.B., Bolam, D.N., Gilbert, H.J., Davies, G.J. 2004. Carbohydrate-binding modules: fine-tuning polysaccharide recognition. Biochem. J. 382, p. 769–781.

Thermostabilizing mutations improved the stability of *Trichoderma reesei* GH11 xylanase in high pressure

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Abstract

High pressure can be utilized in biotechnological applications, e.g. in the treatment of food materials and lignocellulose. High pressure is an extreme condition that inactivates the enzymes, although in a limited range it may also increase enzyme activity. Only few earlier studies have been reported to show how mutations changing the thermostability affect the pressure stability. We studied the pressure stability of disulphide bridge mutants of *Trichoderma reesei* xylanase XYNII at pressure 500–5 000 bar. The inactivation of XYNII and its mutants was strongest above the pressure of 4 000 bar. We found that the pressure stability order correlated with the thermostability order of the XYNII mutants. In combination with high pressure, a mild heating already inactivated the wild type enzyme, whereas the thermostabilizing mutations largely counteracted this effect. Our results showed that thermostabilization mutations may increase the performance of enzymes at high pressure.

Introduction

Endoxylanases (EC 3.2.1.8) are widely used and have much potential in the food, feed, paper and biofuel industries. However, high temperature and pH limit the utilisation of xylanases in industrial applications. Therefore, the engineering of family GH11 xylanases to tolerate extreme conditions has been a goal in a large amount of site-directed and random mutagenesis studies. Only a few enzymatic biotechnological processes utilise high pressure, although there can be unutilised potential in this area. Mild pressure increases enzyme stability, which might be utilised in industrial processes (Kirsch et al., 2011). In addition, pressure pretreatment also enhanced the xylan removal from Eucalyptus Kraft pulp by xylanase enzyme (Oliveira et al., 2012). If higher pressure and other conditions together are destructive to enzymes in industrial applications, then developing enzymes to tolerate these conditions may have biotechnological relevance. In this study, we tested how our earlier mutants of *T. reesei* XYNII tolerated high pressure.

Experimental methods

U111 high pressure device (KGT Kramer, Poland) was used to generate pressure for the stability experiments at pressure range of 500–5 000 bar. *T. reesei* XYNII wild type and thermostable mutants DS2, DS5 and DB1 made by site-directed mutagenesis were from the earlier studies (Jänis et al., 2004; Xiong et al., 2004). The enzymes were incubated for 17 hours in the pressure device and the residual enzyme activity was measured by DNS (3,5-dinitrosalisylic acid)-method.

Results

Three thermostable mutants of *T. reesei* XYNII were used to test their behaviour at high pressure. The thermostability properties of XYNII and the three mutants are summarised in Table 1. The stability experiments showed that *T. reesei* XYNII is very stable at high pressure (Figure 1A); the inactivation was fast only above 4 000 bar. The mutants were only slightly more stable at 22°C. When heat was introduced into the system, the pressure and heat together, especially at 40°C, were very destabilizing for the wild type XYNII (Figure 1B). The mutations, especially the most stabilizing mutant combination (DB1), protected against the harmful effect of combined heat and pressure.

Table 1. Thermostability of XYNII and its mutants (Jänis et al., 2004; Xiong et al., 2004).

Xylanase	T_{opt} (°C)	T_{half} at 65 ^{o}C	T_{m} (°C)
XYNII	56–62	<1 min	63
DS2	52–59	10 min	65
DS5	56–62	110 min	68
DB1	63–74	>56 h	82

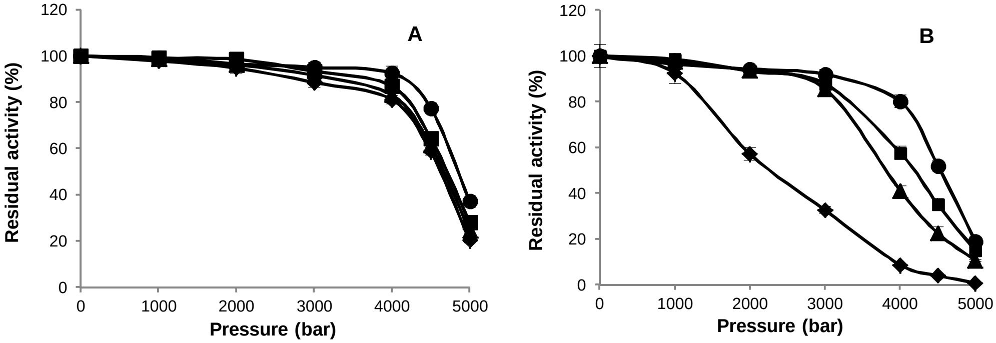

Figure 1. Inactivation of XYNII and its mutants as a function of pressure. The results are shown for experiments at 22°C (A) and 40°C (B). Symbols: XYNII (♦), DS2 (▲), DS5 (■), and DB1 (●). Figures are modified from Li et al., 2012.

Conclusions

Thermostability order of xylanase mutants correlated with pressure stability order, which was XYNII<DS<DS5<DB1. Our results indicated that at low temperatures (below 22 ^{o}C) there may be no essential difference in pressure stability between XYNII and its mutants. Thermal inactivation appeared to dominate under high pressure at elevated temperatures. In conclusion, thermostabilization of enzymes can be important for applications in high pressure.

References

1. Jänis, J., Turunen, O., Leisola, M., Derrick, P., Rouvinen, J., Vainiotalo, P. 2004. Characterization of mutant xylanases using fourier transform ion cyclotron resonance mass spectrometry: Stabilizing contributions of disulfide bridges and N-terminal extensions. Biochemistry 43, pp. 9556–9566.

2. Kirsch, C., Zetzl, C., Smirnova, I. 2011. Development of an integrated thermal and enzymatic hydrolysis for lignocellulosic biomass in fixed-bed reactors. Holzforschung 65, pp. 483–489.

3. Li, H., Murtomäki, L., Leisola, M., Turunen, O. 2012. The effect of thermostabilising mutations on the pressure stability of *Trichoderma reesei* GH11 xylanase. Prot. Eng. Des. Sel., Doi:10.1093/protein/gzs052.

4. Oliveira, S.C., Figueiredo, A.B., Evtuguin, D.V., Saraiva, J.A. 2012. High pressure treatment as a tool for engineering of enzymatic reactions in cellulosic fibres. Bioresour. Technol. 107, pp. 530–534.

5. Xiong, H., Fenel, F., Leisola, M., Turunen, O. 2004. Engineering the thermostability of Trichoderma reesei endo-1,4-β-xylanase II by combination of disulphide bridges. Extremophiles 8, pp. 393–400.

Some aspects of the changes in the birch wood morphological structure and its components' composition in the acidic hydrolysis process

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Abstract

Despite the huge scope of research, wood is still insufficiently utilised as the source for obtaining basic substances for chemical and pharmaceutical production. Pre-treatment of wood is a substantially important stage to make its components more accessible for conversion to valuable products. Our goal was to investigate the impact of the mild hydrolysis pre-treatment of birch wood for improving the cellulosic part accessible to pyrolysis for obtaining sugars and especially anhydrosugars.

Material and methods

Lignocellulose (LC) was obtained after separating hemicelluloses from birch wood chips by treating with 3% of sulphuric acid from wood o.d.m. and the following acid hydrolysis with steam in the temperature range of 100–180°C during 60 min, with subsequent aqueous washing of wood residues till pH 4.5. From LC, holocellulose was isolated and degree of polymerisation was detected, as well as α-, β- and γ-cellulose content. EPR spectroscopy parameters were determined directly from the spectrum, and the amount of paramagnetic centres (PMC) and conjugation units was calculated.

Results

Important information about the changes in LC was obtained from *electron paramagnetic resonance (EPR*), which showed changes in the organic free radicals' amount (Figure 1). The EPR spectra of lignocelluloses, obtained by hydrolysis at different temperatures (100–180°C), are characterised by the presence of stable PMC. Taking into account the hydrolysis conditions, the registered PMC are assigned to the stable free radicals of polyconjugated systems (PCS), which can be evaluated by the amount and sizes of conjugation units. With increasing hydrolysis temperature, the value of the *g*-factor gradually decreases from the values, typical for the localisation of PMC on oxygen atoms (for example, for the phenoxyl radicals of the untreated wood lignin), to the values, typical for PCS. The parameter *n* of EPR spectra, corresponding to the average number of the CH fragments included in the region of the delocalisation of the non-conjugated electron of PMC, characterises the size of the conjugation units. In the case of increasing wood hydrolysis temperature, the *n* value increases, beginning with the temperature 130°C, showing the progress of the processes of condensation and aromatisation in the lignin (lignocellulose) structure, especially markedly at 160–180°C. The amount of conjugation units, taking into account the complexity of the structure of the natural polymer with a system of polyconjugated PMC, approximately corresponds to the content of stable PMC of lignocelluloses. The developed processes of condensation in the lignocellulose structure are indicated by the increase in the content of PMC and, correspondingly, conjugation units. With increasing hydrolysis temperature above 130°C, the formed polyconjugated systems of lignocelluloses are evenly distributed throughout the volume of the organic matrix, changing the nature of the subsequent thermal degradation. With simultaneous decreasing (see Table 1) degree of polymerisation (DP) but increasing hydrolysis temperatures above 150°C, pseudolignin arose, and it is reasonable to believe that condensation reactions between lignin and cellulose occurred; hence, traditional component detection methods were not suitable.

Table 1. Changes in the free radicals' concentration and DP in LC depending on pre-treatment temperature.

Hydrolysis temperature, °C	*g*-factor	n	DP
Birch wood	2,00458	8,653560	553
100	2,00414	9,935548	436
110	2,00427	9,278498	359
120	2,00409	9,935548	342
130	2,00418	10,67404	304
140	2,00395	12,12759	260
150	2,00377	13,93515	170
160	2,00356	15,81822	-
180	2,00337	17,30583	-

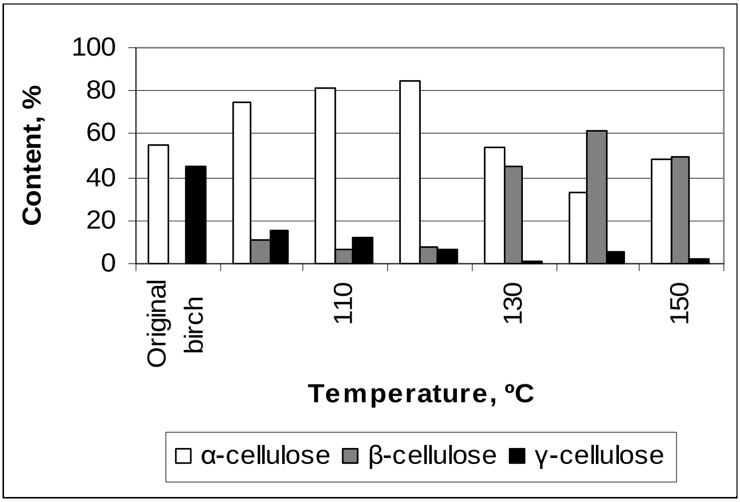

Figure 1. Content of α-, β- and γ- cellulose in the LC depending on pre-treatment temperature.

The content of α-, β- and γ- cellulose in the LC strongly depends on the pre-treatment temperature (Figure 1), and the α- cellulose content increased up to a temperature of 120°C, but after that decreased and the content of the β-cellulose increased, which testified the depolymerisation of cellulose macromolecules.

Acknowledgement

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Low temperature sulfonation of lignocellulose for effective biomass deconstruction and conversion

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Abstract

Sulfite based pretreatment of Norway spruce was studied, comparing a previously published sulfite pretreatment process (SPORL) to two modified sulfite pretreatment concepts. To investigate the effects of hemicellulose pre-extraction a combined Hot water – SPORL process was tested. Further, in a modified process, here termed “Low temperature sulfonation”, the effect of increased lignin removal by selective sulfonation at mild acidic bisulfite conditions was investigated (cf. the Borregaard BALI process). Significantly higher cellulose conversion was found using this method, than using the SPORL or the Hot water – SPORL process. Enzymatic saccharification yields increased with the degree of delignification. Rather extensive dissolution of lignosulfonates was obtained while avoiding severe hemicellulose degradation. Hence, low temperature sulfonation of spruce gave efficient fibre deconstruction, cellulose conversion and lignosulfonate formation.

Introduction

Few pretreatment technologies have achieved satisfactory enzymatic saccharification yield for softwoods due to its strong recalcitrance. However, recently sulfite processing has shown promising results. In Norway Borregaard has applied for a patent regarding sulfite based biorefining in general, termed the BALI process [1], currently operating at demo scale. Others have also demonstrated high enzymatic saccharification and low inhibitor formation upon sulfite pretreatment of softwood [2]. This latter process, termed SPORL (sulfite pretreatment to overcome recalcitrance of lignocellulose) gave moderate delignification and good hemicellulose removal. In SPORL, hemicellulose removal was considered just as critical as lignin sulfonation for cellulose conversion. The objective of the present study was to compare SPORL to two alternative sulfite based pretreatment concepts. Firstly, hot water extraction was introduced prior to SPORL treatment to investigate effects of hemicellulose pre-extraction. Secondly, a modified bisulfite process (Low temperature sulfonation) was tested to investigate effects of increased lignin removal by selective sulfonation at mild acidic bisulfite conditions.

Experimental

Norway spruce wood chips from a Norwegian paper mill were used. Hemicellulose pre-extraction was done by hot water treatment (160°C, 5 hours). SPORL pretreatments, performed as recommended [2] (3–11% bisulfite, 0.5–2.5% sulfuric acid, 180°C, 30 min), were followed by hammer milling. Low temperature sulfonation was performed at high bisulfite concentration (20%), rather low temperature (140°C), increased retention time (2–10 hours) and sulfuric acid addition for pH control. Pretreated samples were analysed for Klason lignin, carbohydrates and sulfonic acid groups. Enzymatic hydrolysis was done using cellulase (Celluclast 1.5, 10.5 FPU/g od substrate) and β-glucosidase (Novozyme 188, 37.5 CBU/g od substrate) at 50°C, pH 4.8 for 48 hours.

Results and discussion

In our trials Low temperature sulfonation gave significantly higher enzymatic saccharification than SPORL and Hot water – SPORL pretreatments (Figure 1). Cellulose conversion increased with increasing delignification, indicating that enzyme accessibility is critical. Low temperature sulfonation gave efficient lignin removal while avoiding severe hemicellulose degradation. After treatment, 35–60% of the hemicelluloses were still present. At 75% delignification, more than 70% of the cellulose was converted. For SPORL treatment, approx. 20% conversion was obtained in our trials, much lower than the reported [2]. The reason behind this is currently unknown.

Low temperature sulfonation removes lignin by dissolution of lignosulfonates, cf. the BALI process [1]. In sulfite pulping lignosulfonates become water soluble when more than approx. 3 sulfonic acid groups are introduced per 10 lignin units. After SPORL pretreatment the residual lignin contains 1.2–1.7 sulfonic acids groups per 10 lignin units, suggesting that the SPORL sulfonation is too low for dissolving lignin. Hot water pre-extraction of hemicelluloses prior to SPORL was not favourable as this made the lignin less susceptible to sulfonation. Thus, the degree of lignin sulfonation was significantly lower for hot water extracted wood than for direct SPORL treated wood.

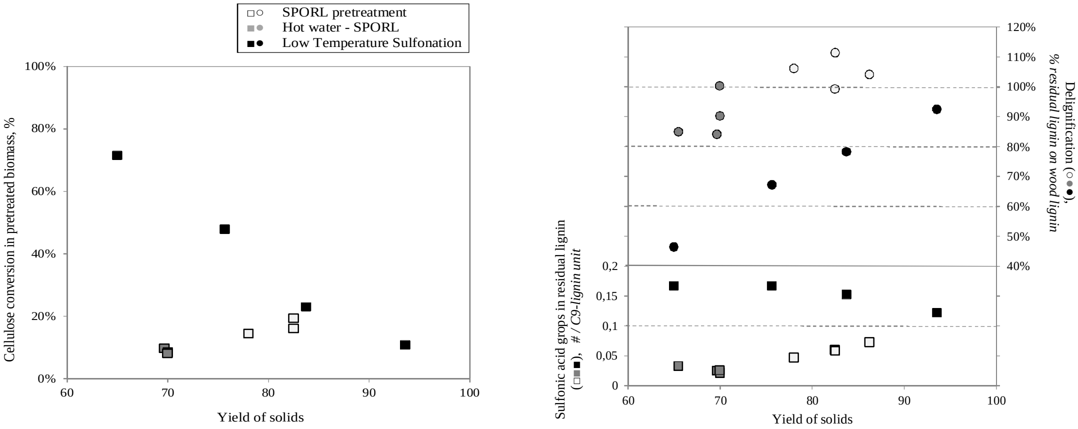

Figure 1. Sulfite based pretreatment of Norway spruce. Cellulose conversion by enzymatic saccharification (left). Sulfonation and lignin dissolution (right).

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References

1. Lersch, M., Sjöde, A., Frölander, A., Rødsrud, G. 2008. Lignocellulosic biomass conversion. Europe Patent Application WO/2010/078930 Filed December 17, 2008.

2. Zhu, J.Y., Pan, X.J., Wang, G.S., Gleisner, R. 2009. Sulfite pretreatment for robust enzymatic saccharification of spruce and red pine. Bioresource Technology 100(8), pp. 2411–2418.

Liquid phase acetoxylation of α-pinene

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Abstract

Chemical pulping and bio-refining results in many fractions such as. tall oil and turpentine that contain substantial amounts of α-pinene and other terpenes. Today these fractions are usually burned in the recovery boilers. However, the northern forest industry, primarily utilizing the boreal forests, faces serious challenges from developing markets (South America, Asia), because of lower cost of raw material resources and labor. At the same time, there is a growing concern about emissions of greenhouse gases and security of supply connected to the use of fossil oil for transportation and as a feedstock for the chemical industry. The mentioned fact renders the substitution of petrochemical-related raw materials an important field of research.

The flavor and fragrance industry is one of the main users of terpene esters. From those esters, α-terpinyl and bornyl acetates are produced from α-pinene and commonly used for bath products and perfumes. Due to the imperfection of conventional two-stage production method of the mentioned esters, which lays in the equipment corrosion, environmental pollution, large load and non-recyclability of a catalyst, the novel one-stage catalytic process is always of high priority.

The possibility of α-pinene liquid phase catalytic acetoxylation is introduced in the present study. The complex product distribution and reaction network analysis, influent reaction and catalytic factors optimization, combined with the reaction kinetic modeling were the main aims of research. The ion-exchange resin catalyst Amberlyst 70 was characterized as the catalyst used in the studied reaction and compared with the solvent-catalyzed mode. Valuable combinations of acetates were obtained for both studied modes. A wide range of process factors were studied in the batch (Parr) reactor used. The mentioned type of reactor is suitable for the consequent industrial operations scale-up calculations.

Apparatus and general reaction procedure

The α-pinene acetoxylation was carried out in a laboratory scale high-pressure reactor, equipped with a stirrer and a heating jacket. The reaction mixture, containing 0.1 g of the catalyst, 5.5 g α-pinene and 120 ml acetic acid was loaded in the reactor. The reaction temperature was adjusted by means of the heating jacket controlled by a PC. The stirring speed of 1000 min^{-1} was applied. The influence of various gas atmospheres, i.e. of N_2, O_2 and H_2, was studied. GC-GCMS combination applied for the product analysis. The SEM images were visualized with a Cambridge Stereoscan 360iXP.

Results and discussion

For the studied reaction, α-terpinyl, fenchyl, verbenyl and bornyl acetates as well as limonene, camphene and γ-terpinene were all found in the product mixture. The other products were found in amounts less than 1 wt% and were considered negligible. The formation of byproducts was not uniform in case of all prolonged reactions. A temperature range of 25 to 125°C and a pressure range from atmospheric to 20 bar were considered. The influence of the gas

atmosphere, i.e. nitrogen, oxygen or hydrogen atmosphere was also investigated. A pressurizing gas was needed to suppress the evaporation of the reactants involved. Glacial as well as aqueous acetic acid (2.5 wt% and 5 wt%, respectively) and also a blend of acetic acid and toluene or ethyl acetate (5 wt%) were tried as co-solvents. The influence of each factor was studied in catalytic (Amberlyst 70) and the solvent-catalyzed mode. Figure 1 describes the conversion of α-pinene.

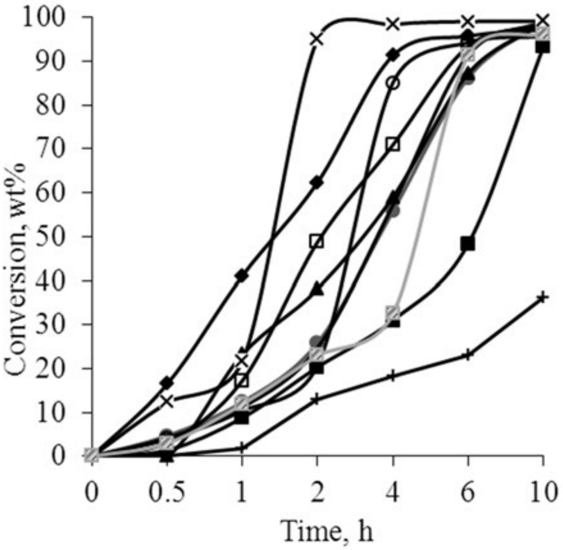

Figure 1. α-pinene conversion. Symbols: (●) 100°C, 10 bars, N_2, cat; (–) 100°C, 10 bars, N_2, no cat; (**+**) 75°C, 10 bars, N_2, cat; (♦) 125°C, 10 bars, N_2, cat; (□) 100°C, 20 bars, H_2, cat; (▲) 100°C, 20 bars, O_2, cat; (■)100°C, 20 bars, O_2, no cat; (■) 100°C, 20 bars, O_2, no cat, 5 wt % ethyl acetate/95 wt % acetic acid; (○)100°C, 20 bars, O_2, cat, 5 wt % toluene/95 wt % acetic acid; (X) 100°C, 20 bars, O_2, cat, 95% aqueous acetic acid.

According to the results, the specific surface area and pore volume were significantly reduced, thus indicating catalyst deactivation. The average pore size of the catalyst was slightly reduced under the reaction conditions. The SEM images scaled at 2.00 μm for Amberlyst 70, before and after the reaction, are presented in Figure 2. It is evident that the surface has undergone morphology changes. The fresh resin had a sphere diameter of around 350–600 μm, while the spent catalyst contained spheres of around 400–800 μm, thus demonstrating swelling of the resin particles.

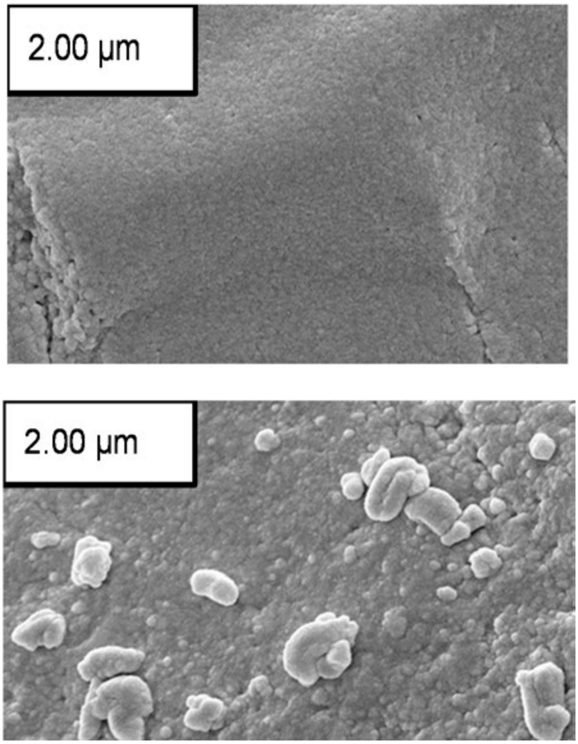

Figure 2. Amberlyst 70 SEM images – fresh and spent catalyst samples.

Conclusions

The optimal reaction conditions allowed reaching yields of 39.8% of bornyl acetate and 42.5% of limonene, in catalytic experiments. The yields in the solvent-catalyzed process were the following: 35.3% of α-terpinyl acetate, 13% of bornyl acetate, 10.6% of γ-terpinene, 9% of limonene and 14.7% of verbenyl acetate, respectively. Increased temperature or hydrogen atmosphere caused product oligomerization up to 30% in 18 h, while an oxygen atmosphere counter-effected the oligomerization.

Acknowledgements

Umeå University Business Graduate School, Processum Biorefinery Initiative AB, Aditya Birla Domsjö Fabriker, Holmen Energi AB, MoRe Research and Metsä Group Husum are gratefully acknowledged for the financial support. The Bio4Energy program is acknowledged. Rohm and Haas Nordic representative is gratefully acknowledged for providing the catalyst samples.

Biocomposites based on birch suberin

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Abstract

The suberin monomer, *cis*-9,10-epoxy-18-hydroxyoctadecanoic acid (epoxy fatty acid or EFA), was isolated from birch (*Betula verrucosa*) outer bark. The crude EFA was purified and polymerized via lipase-catalysis. The resulting polyesters were characterized by MALDI-TOF MS and SEC. Biocomposites were prepared through grafting EFA onto cellulose. The products were characterized by FTIR.

Introduction

Increasing the cellulose surface hydrophobicity is an important route targeted towards hydrostability and improved barrier properties. Natural products that are hydrophobic and biodegradable such as suberin found in birch outer bark could be suitable candidates for this purpose. Suberin has a complex structure and many sub-units. [1] EFA (Figure 1) is the most abundant sub-unit among the others, amounting to about 100 g per kg of dried bark. [2, 3] The epoxy functional group of EFA makes it possible for cellulose modification.

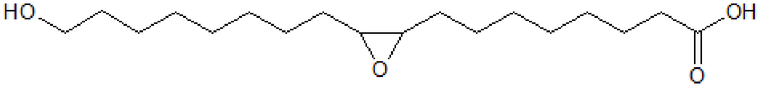

Figure 1. The structure of *cis*-9,10-epoxy-18-hydroxyoctadecanoic acid.

In this study, EFA isolated from birch outer bark was used to prepare the polyesters. The characterization was accomplished by ^{1}H NMR, MALDI-TOF MS, and SEC. Thereafter biocomposites were prepared through grafting EFA onto cellulose. The products were characterized by FTIR.

Experimental

Crude EFA was isolated by following the method of Iversen et al. [1] EFA was polymerized with the lipase (*Candida Antarctic* lipase B) as the catalyst, and fatty acid-cellulose biocomposites (FACB) were prepared through the alkali-catalyzed reaction of cellulose and EFA.

Results and discussion

Isolation of epoxy fatty acid and preparation of polyesters

The isolation of crude EFA from birch outer bark was done according to the method of Iversen et al. The obtained purity was above 95% (examined by ^{1}H NMR).

The homo-polymerization of EFA was successfully performed through the lipase-catalysis (analyzed by SEC). MALDI-TOF MS showed the polyesters consisted of linear and cyclic structures with the former dominated the composition. ^{1}H NMR showed that the epoxy groups were still intact. The co-polymers were prepared through the lipase-catalyzed polymerization of EFA and ε-caprolactone, and similar results were obtained (analyzed by MALDI-TOF MS and SEC).

Exploration and development of fatty acid-cellulose biocomposites

The grafting of EFA onto cellulose could be theoretically performed under either alkali or acid conditions, and cellulose reactivity plays an important role in this reaction. In order to activate the hydroxyl groups of cellulose as well as make them stronger nucleophiles, cellulose was transformed to alkali-cellulose.

The FTIR spectra of FACB indicated the presence of ionized carboxylic groups and long alkyl chains within the final structures. None of the spectra showed a signal of epoxy ring vibration, indicating the epoxy ring-opening was successful. These indications support the occurrence of grafting.

Conclusions

The polyesters based on EFA could be prepared through lipase-catalysis without breaking the structure of epoxide. The biocomposites should be further identified and characterized through manners such as TGA, HPLC, and CP/MAS ^{13}C NMR. The successful preparation of FACB shows the possibility of grafting EFA based polyesters onto cellulose.

Acknowledgements

We would like to express great thanks to WoodWisdom-Net Research Programme for the financial support to this project.

References

1. Iversen, T., Nilsson, H., Olsson, A. 2010. Patent WO/2010/093320.
2. Nilsson, H., Olsson, A., Lindström, M., Iversen, T. 2008. Bark suberin as a renewable source of long-chain ω-hydroxyalkanoic acids. Macromol. Symp. 272, pp. 104–106.
3. Olsson, A., Lindström, M., Iversen, T. 2007. Lipase-catalyzed synthesis of an epoxy-functionalized polyester from the suberin monomer *cis*-9,10-epoxy-18-hydroxyoctadecanoic acid. Biomacromolecules 8, pp. 757–760.

Isolation of triterpene rich extracts from outer birch bark

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Abstract

Birch wood in the Northern hemisphere is widely used in the furniture, pulp and plywood manufacture. 2% of veneer blocks' mass is made up by outer birch bark (BB) (Kislitsyn, 1994). It is readily accessible and already concentrated for further processing. In plywood plants of Latvia, for example, up to 12–14 thousand tons of outer BB can be made ready for the production of triterpene rich extractives. Pentacyclic lupane type triterpenes are promising starting materials for the synthesis of biologically active compounds with a broad spectrum of medical applications (Alakurtti et al., 2006).

Different solvents and their effect upon the composition of extracts and the contents of the main triterpenic components in extracts were studied, if the outer BB of the two most widespread birch species in Baltic Sea region states such as silver birch (*Betula pendula Roth*.) (BB-Pend) and downy birch (*Betula pubescens Ehrh*.) (BB-Pub) was used as a feedstock.

Material and methods

Milled dry BB samples were soaked by mixing from time to time in deionised water for 24 h. Outer BB floated on the top of water was collected and dried up to a moisture content of 2–4 wt.%. Extraction was carried out in Soxhlet apparatuses by the selected solvents for 11 h. Solvents were evaporated using a rotating vacuum evaporator and dried up to an oven dry state.

GC-MS analysis was performed on a 30 m × 0.25 μm × 0.25 μm film HP-5MS capillary column (GC-2010 Shimadzu) with helium as a carrier gas at a constant flow rate of 1 mL/min throughout the run. The oven temperature was maintained at 160°C for 1 min and then programmed at 10°C/min to 300°C, which was maintained for 15 min. The components were identified by comparison of the spectra with those of the standards and those in the NIST library of spectra.

Results

Table 1 shows that some difference is detected between the total yield of extractives if the specimens of outer BB are located at different levels of birch stems and also it decreases with the crop age. The betulin contents in the extractives of outer BB–Pub are even somewhat higher than that in the corresponding extracts of BB–Pend of the same crop age. However, the content of lupeol in the extractives of outer BB-Pub is almost threefold lower. Since silver birch prevails in Latvian forests, it was used for further experiments.

Different yields of lupeol and betulin in various solvents (6.0% and 8.5% extractives' mass in acetone and cyclohexane extracts, respectively) were established (Table 2). The total triterpene yield is higher if the cyclohexane as a solvent was used.

Table 1. Variability in betulin and lupeol concentrations in ethanol extracts of outer BB.

Characteristics of outer BB samples	**Solvent**	**Yield of extractives, % d.b. outer BB**	**Betulin**	**Lupeol**
			% d.b. extract mass	
BB-Pend, 60 years	95% ethanol	36.2	61.7	6.0
BB-Pend, 15 years, 0–60 cm	95% ethanol	43.0	59.6	4.4
BB-Pend, 15 years, 60–130 cm	95% ethanol	44.7	58.6	4.5
BB-Pend, 15 years, 130–210 cm	95% ethanol	43.4	62.4	4.9
BB-Pub, 60 years	95% ethanol	36.0	63.6	2.1
BB-Pub, 15 years, 0–60 cm	95% ethanol	43.1	64.2	1.5
BB-Pub, 15 years, 60–130 cm	95% ethanol	37.1	69.4	1.5
BB-Pub, 15 years, 130–210 cm	95% ethanol	36.4	64.0	1.4

Table 2. Variability in triterpene concentrations in various solvent extracts of outer BB-Pend.

Solvent	**Pre-treatment**	**Yield of extractives, % d.b. BB**	**Betulin**	**Lupeol**	**Total**
			% d.b. extract mass		
Acetone	without	33.7	73.6	6.0	79.6
Cyclohexane	without	23.1	86.3	8.5	94.8
95% ethanol	without	36.2	61.7	6.0	67.7
95% ethanol	3 h H_2O, 96°C	33.0	68.3	8.6	76.9
95% ethanol	5 h H_2O, 96°C	33.0	71.5	8.6	80.1

Certain problems in obtaining purified triterpene preparations are posed by an admixture of polyphenols in outer BB extractives. Pre-treatment of outer BB with hot water substantially improves the extracts' quality (combined betulin and lupeol yield – 67.7% and 80.1% after 5 hour treatment, respectively). The favourable effect of pre-treatment can be further improved if leaching with diluted sodium carbonate solution is realised. It is possible to improve the quality of extracts and the yield of definite components by modifying the extraction technology and the appropriate choice of solvents.

Acknowledgement

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References

1. Kislitsyn, A.N. 1994. Outer birch bark extractives: isolation, composition, properties and application. Khimiya drevesiny. Wood Chemistry 3, p. 3.

2. Alakurtti, S., Mäkelä, T., Koskimies, S., Yli-Kauhaluoma, J. 2006. Pharmacological properties of the ubiquitous natural product betulin. Eur. J. Pharm. Sci. 29, pp. 1–13.

Fractionation and structural characterisation of softwood kraft lignins

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Abstract

Lignin was isolated from black liquor (BL) by fractional precipitation triggered by step-wise addition of sulfuric acid. The chemical composition and functionality of the fractionated lignin samples was compared with regard to their potential industrial applications.

Introduction

One of the key requirements for a biorefinery concept is the efficient recovery of lignin from process liquors for subsequent utilization. Until now, only about 1.5% of the 70 million tons per year of lignin available in the pulp and paper industry are commercially utilized for other than energy purposes [1]. Knowledge of lignin main structural characteristics is required before its applications can be considered. In this work, the effect of delignification intensity and precipitation pH on lignin structure was investigated.

Results and discussion

To explore the lignin properties along the different cooking stages, BL samples derived from pine kraft cooking were taken during initial, bulk and residual delignification phases. To fractionate lignin according to the molecular weight (M_w), it was precipitated by sequential acidification to pH-levels of 10.5, 5 and 2.5 using 6M H_2SO_4. Dissolved wood lignin (DWL) was used as a reference, showing properties close to those of native lignin [2]. The Mw of the fractionated lignin decreased with decreasing the precipitation pH (Figure 1). In addition, the Mw of lignin increased with increasing pulping intensity, due to a more condensed structure of the lignin from the residual delignification stage.

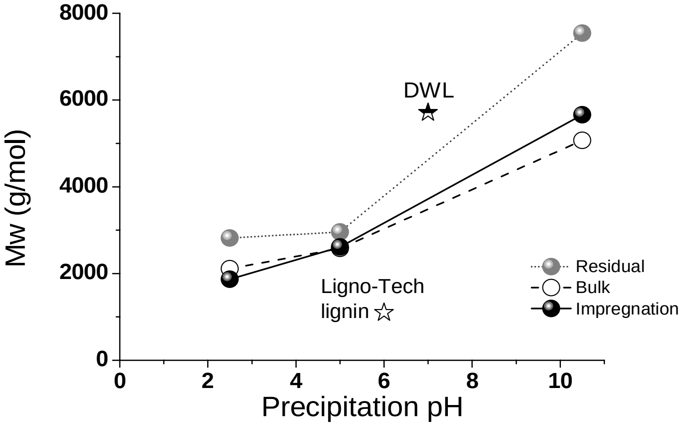

Figure 1. Precipitation pH vs. M_w of lignin fractions.

However, commercially available lignin (Lingo-Tech) [3] showed significantly lower M_w than that of fractionated lignins. The yields of lignin obtained from different fractions and precipitated at various pH values are shown in Table 1. Along with the reduction in pH of BL, the amount of total precipitated lignin increased and the BL color brightened. At any pH, the yield of precipitated lignin increased from the impregnation stage to the residual delignification stage. The increase in precipitation yield can be explained by the higher content of co-precipitated polysaccharide degradation products that are present in the liquors obtained from the later cooking stages. Nevertheless, the majority of lignin was precipitated at pH 5 for all three BLs, reaching a removal rate of about 70%. Lowering the pH value to 2.5 resulted in the precipitation of additional ca. 6% of the total lignin dissolved in the solution.

The lignin samples precipitated at pH 10.5 and 5, respectively, showed high purity (ca. 95% of lignin content). In contrast, purity of commercial available kraft lignin samples, such as Indulin AT and, especially kraft Lingo-Tech, was considerably lower. The amounts of ASL, sulphur and carbohydrates increased with decreasing pH. Sugars present in the samples were mainly attributed to glucose and especially to xylose, derived from the hemicelluloses dissolved in the BL. The presence of impurities might negatively affect the further processing of the lignin.

Table 1. Yield and chemical composition of different lignin fractions.

Sample		**Yield**		**Chemical composition, [% of o.d. sample]**				**Functional groups**	
Cooking stage	**Precipitation pH**	**[g/L BL]**	**[% on total lignin]**	**KL[1]**	**ASL[2]**	**Carb.[3]**	**Sulfur**	**OCH_3, [% of o.d. sample**	**Phen-OH, [mmol/g of o.d. sample]**
Impregnation	10.5	8.9	17.2	96.4	1.3	1.1	1.9	14.8	2.9
	5	34.0	66.2	90.4	4.6	2.6	5.8	13.3	3.9
	2.5	3.1	5.9	79.6	7.7	9.4	12.8	5.1	3.3
Bulk	10.5	13.1	20.0	94.4	2.3	2.3	2.2	14.8	3.1
	5	44.7	68.3	86.3	4.9	3.4	7.9	14.3	4.4
	2.5	4.3	6.5	70.0	10.9	15.1	8.3	6.5	3.6
Residual	10.5	14.3	19.8	94.0	2.0	2.8	2.4	15.3	2.9
	5	51.4	71.2	85.3	5.6	3.9	8.6	14.5	3.9
	2.5	4.4	6.1	46.4	9.7	39.3	14.3	17.7	3.3
Indulin AT		- -	-	88.3	-	2.2	-	14.8	3.3
Kraft L-T[4]		-	-	61.2	4.9	3.3	27.1[5]	-	-
DWL		-	-	85.4	6.2	6.0	0.2	19.1	0.9

[1] Klason lignin; [2] Acid soluble lignin; [3] Carbohydrates; [4] Kraft L-T – Ligno-Tech Iberica (Spain), values are taken from [3]; [5] Ash content

As can be seen in Table 1, lignins from all cooking stages were modified to a large extend when compare to DWL. Significant increase in phenolic hydroxyl group (Ph-OH) content is originated from both demethylation of methoxy groups and cleavage of ether linkages such as β-O-4, α-O-4 and 4-O-5 in lignin and therefore, fragmentation of the lignin. The reactivity of lignins essentially depends on the number of Ph-OH [3]. This is because the units with free Ph-OH are able to form quinonemethide intermediates, due to the activation of the aromatic ring in the O-position. The quinonemethide is then prone to nucleophilic reactions at the benzylic carbon atom. Lignins precipitated at lower pH had lower methoxyl content, which indicates that those lignins have more accessible ortho-positions in their phenyl rings, and are therefore suitable for chemical modification.

Conclusions

Lignin separation and fractionation was achieved by selective precipitation at different pH levels. Our results indicated that up to 90% of the lignin solubilized in the BL can be recovered in high purity by lowering the pH to 5. Further pH reduction leads to increased precipitation of carbohydrates, to the formation of salts and to a decrease in Mw. The lignin samples obtained from bulk delignification by precipitation at pH 5 showed high amounts of phenolic hydroxyl groups and relatively low amounts of methoxyl groups. These are clear indications of a reactive lignin structure. This fraction also exhibited high purity and relatively high Mw. It can be concluded that there are clear differences among the precipitates obtained at different pH levels with regard to the composition and the properties of lignin.

References

1. Lora, J.H., Glasser, W.G. 2002. J. Polym. Environ. 10, pp. 39–48.

2. Fasching, M., Schröder, P., Wollboldt, R.P., Weber, H.K., Sixta, H. 2008. Holzforschung 62(1), pp. 15–23.

3. Mansouri, N.-E.E., Salvadó, J. 2006. Ind. Crop. Prod 24, pp. 8–16.

Funaoka lignin facilitating sustainable and recyclable biocomposites for transportation

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Abstract

The environmental impact of transportation is almost entirely caused during the use of the vehicles. Need to improve energy efficiency and to reduce CO_2 emissions increase the importance of light weight composite materials as alternative materials for vehicles in transportation.

Use of renewable carbohydrate based load bearing fibers do offer some advantages even when compared to glass and carbon fibers: they are lighter in weight, and products produced are also softer and smoother to touch. Smoother and softer fibers reduce also the wear of the production equipment. When traditional plastics are used as matrix materials, expensive coupling agents are typically required to effectively transfer the load to the load bearing fibers.

Lignin is nature's own binder and matrix material for carbohydrate (CH) fiber based biocomposites. Funaoka lignin (FL) is isolated maintaining lignin's natural reactivity, and having its structure simplified to a controllable and processable linear form. FL combined to technologies common from plastics industry will facilitate production of novel lignin based biocomposites using naturally renewable CH's as reinforcement fibers, and often without the use of expensive coupling agents.

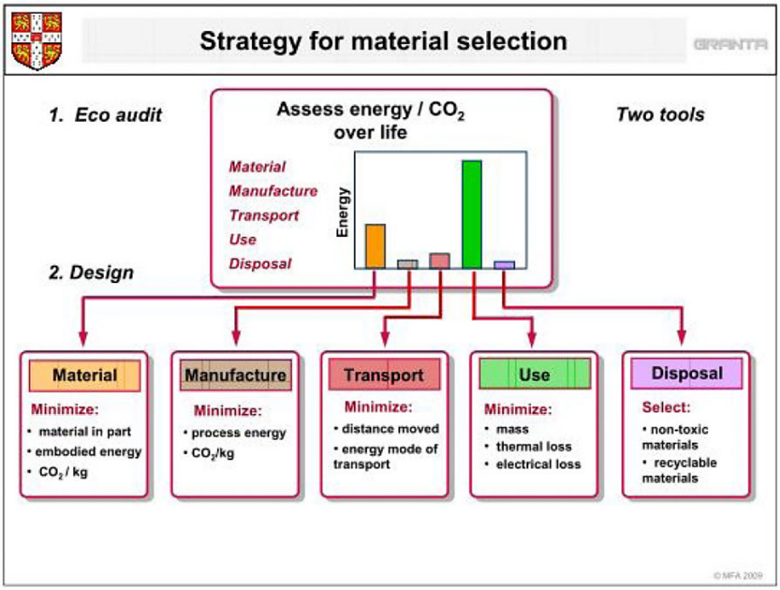
The fourth pilot scale Funaoka lignin plant just started its production and will facilitate production of testing materials for material development. Samples of commercial interest could thus be produced, which in turn will attract industrial interest in building the following FL plant to Europe.

Following presentation will describe reasons and principles behind Funaoka lignin development and use in materials for vehicles in transportation.

Keywords: Wood industry, car industry, vehicles, environment, transportation, biopolymers, compatibility, sustainability, recyclability, lignin

Use of renewable raw materials to reduce environmental effects caused by transportation

Transportation causes about 20% of CO_2 emissions in Europe. Life-cycle-analysis (LCA) and eco-audit show that most of environmental effects in the car life-cycle (use of raw materials, transport of the raw materials and parts produced, product manufacture, use of the product, product disposal) are created during the actual use of the car. In addition to political tools (costs and prices, laws and restrictions) aimed at reduction of the transportation itself) the material related production tools available could be simplified to reduction of the consumption of fossil fuels. This means reduction of the mass to be transported, and to reduction of the thermal and electrical losses of the vehicle and the engine (Figure 1).



Strategy for material selection

GRANTA

1. *Eco audit*

Assess energy / CO_2 over life

Material
Manufacture
Transport
Use
Disposal

Energy

Two tools

2. *Design*

Material
Minimize:
- material in part
- embodied energy
- CO_2 / kg

Manufacture
Minimize:
- process energy
- CO_2/kg

Transport
Minimize:
- distance moved
- energy mode of transport

Use
Minimize:
- mass
- thermal loss
- electrical loss

Disposal
Select:
- non-toxic materials
- recyclable materials

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Figure 1. Strategy for material selection for transportation (Granta). [1]

Renewable raw material based reinforcement fibers could be functional and useable in various forms in composite production. Whether stabled, used as such or even in continuous form the fiber should be carefully selected to suit the needs of the product and its production. Properly selected renewable carbohydrate based fibers do offer some advantages even compared to glass and carbon fibers: they are lighter in weight, and products produced are also softer and smoother to touch. Smoother and softer natural fibers reduce also the wear of the production equipment.

Lignin is nature's own matrix material for carbohydrate (CH) fiber based biocomposites. Compared to traditional plastics lignin might allow effective transfer of the load to the load bearing fibers even without the use of expensive coupling agents (Figure 2).

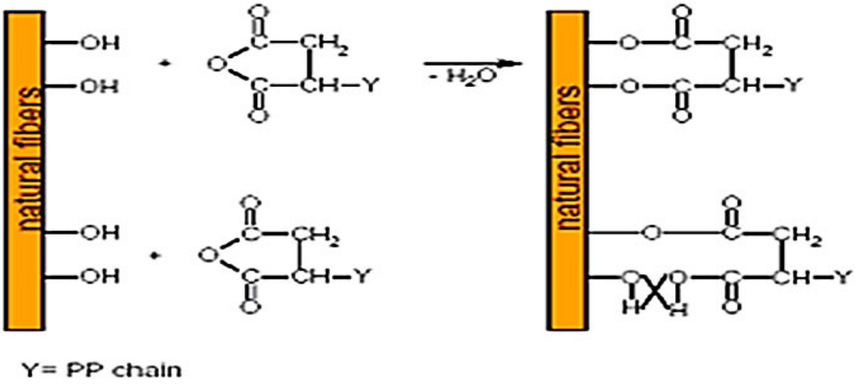

Figure 2. Lignin could simplify production of composites. [2]

Funaoka lignin (FL) is isolated having its structure simplified to a controllable and processable linear form and having its natural reactivity tailored for the chosen CH and desired product. [3] When combined to suit the chosen CH based reinforcement fiber, the composite can be tailored at molecular level to desired needs (Figure 3).

The fourth pilot scale Funaoka lignin plant just started its production in Japan and will facilitate production of testing materials for material development. [3] Samples of commercial interest will be produced, which in turn will attract industrial interest in building the following FL plant to Europe.

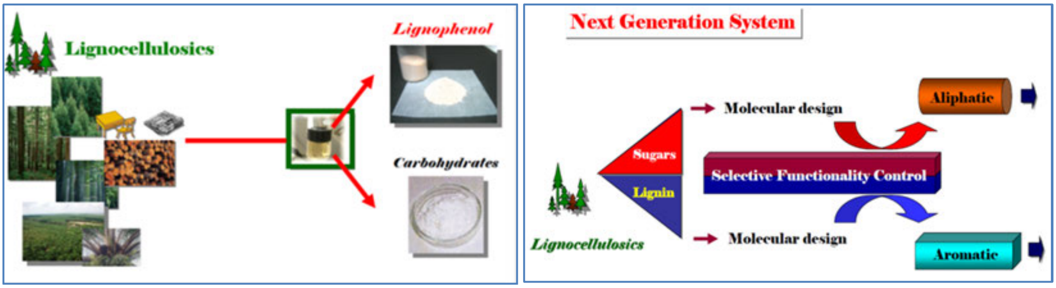

Figure 3. Design of properties at molecular level to suit the product requirements. [3]

Figure 4. Production of functional Funaoka lignin. [3]

Conclusions

Trabant was an East-German composite car produced by VEB Sachsenring Automobilwerke Zwickau. [4] It was produced from cotton-waste and phenol resin i.e. from a fiber-reinforced thermosetting plastic Duroplast. [5] Trabant has often been considered to be a historical amusement, but it has now been recognized that it also indicated the future for the car. Trabant was built using cheap and originally readily available raw materials. Now it is also important to produce cars having lower gas consumption and lower environmental emissions. Cars produced using best available technology and modern version of renewable and recyclable raw materials are surprisingly similar to Trabant (Figure 5).

European wood industry that is based on high level know-how and slowly growing forests should no longer compete with the bulk industry based on fast growing southern wood. It should instead combine the special qualities of slowly grown wood to long term industrial and scientific experience to create novel high value wood products. Tailor made Funaoka lignin combined to application specific CH material will improve competitiveness of naturally renewable resources and European wood and car industry. Car body produced by Toyota from lignin based biocomposites demonstrates the potential of Funaoka lignin, and should also function as an example for other application areas. It is time to reduce our dependency on oil and start taking full advantage of naturally renewable resources growing in our forests.

Figure 5. Composite cars from history and the future.

References

1. Vuorinen, J. 2011. Komposiitit – luonnonmateriaali? Tiedettä ja tuotteita – muoviteknologia tänään seminar. Muovi-Plastics 2011, Lahti 17.11.2011.

2. Kiesel, H., Richer, E. 2003. Licomont AR 504: Adhesion promoter and Compatibilizer. Clariant product brochure. 27 p.

3. Funaoka, M. 2012. Rapid refining of lignocellulosics to carbohydrates and lignin-based new materials (lignophenols) and design of sustainable industrial network connecting forests and chemical industries. The 4th Nordic wood biorefinery symposium, Helsinki, Finland, October 23–25.2012. To be published in Conference proceedings and in Cellulose Chemistry and Technology.

4. Wikipedia 1.9.2012. Trabant, a composite car produced by VEB Sachsenringen Automobilverke Zwickau in Sachsen. http://en.wikipedia.org/wiki/Trabant.

5. Wikipedia 1.9.2012. Duroplast, a fiber reinforced thermosetting plastic produced from waste cotton and phenolic resin. http://en.wikipedia.org/wiki/Duroplast.

Composites of kraft lignin

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Abstract

Many materials, man-made and natural, have a composite structure, i.e. they comprise two or more constituent materials with distinct differences. Concrete is a common example. It consists of sand or gravel, cement and water. Wood is also a composite. It has strong, crystalline cellulose structures glued together by hemicelluloses and lignin. The unique structure of wood can, however, not be processed as such using common industrial material processing techniques.

For decades, the market for composite materials has witnessed small steps towards increased use of bio-based constituents instead of the petroleum-based ones and especially, bio-based/natural fibers instead of man-made glass fiber. A key driver for this change is the fact that natural fibers are often cheaper and lighter. Sustainability issues also play a part in this change.

In this research, the main objective has been to develop technologies and competences enabling the production of novel composite materials, in which wood-derived, industrial kraft lignin and cellulose fiber are the main constituents. The lignin would thus replace the petroleum-based plastics as matrix constituent. The more specific objectives of the research were to determine the melt processability of kraft lignin, plasticize kraft lignin with case-suitable plasticizers to ease the processing of the material and produce kraft lignin-based composite test products reinforced with cellulose fiber.

Kraft lignin was not processable without plasticization. Suitable plasticizers were found, the plasticized kraft lignin was melt compounded with cellulose fibers, and test samples were injection molded. DSC analysis was conducted and mechanical properties were measured. The initial tensile test results of the plasticized lignin reinforced with cellulose fibers were promising. Addition of cellulose fibers into plasticized lignin matrix improved mechanical properties of the lignin significantly.

Composites of thermoplastic lignin

In literature, lignin is typically used as an adhesion promoter between aliphatic polymers and natural fibers or as a component in blends with an aliphatic polymer or modified starch. In order to improve its plasticity, lignin is often chemically modified by esterification or alkylation. Besides the internal, covalent plasticization, external plasticisers such as PVA and PEG (PEO) have been used. The purpose of plasticization is to improve the processability and performance of the material by reducing the strong intermolecular bonding and crystallinity, and sliding of the polymeric chains in the material.

In this study, the use of PEG-plasticised softwood kraft lignin as matrix material in the composites together with TMP and bleached kraft cellulose fibres was targeted. The lignin used was produced using the LignoForce process developed by FPInnovations. The concept is outlined in Figure 1.

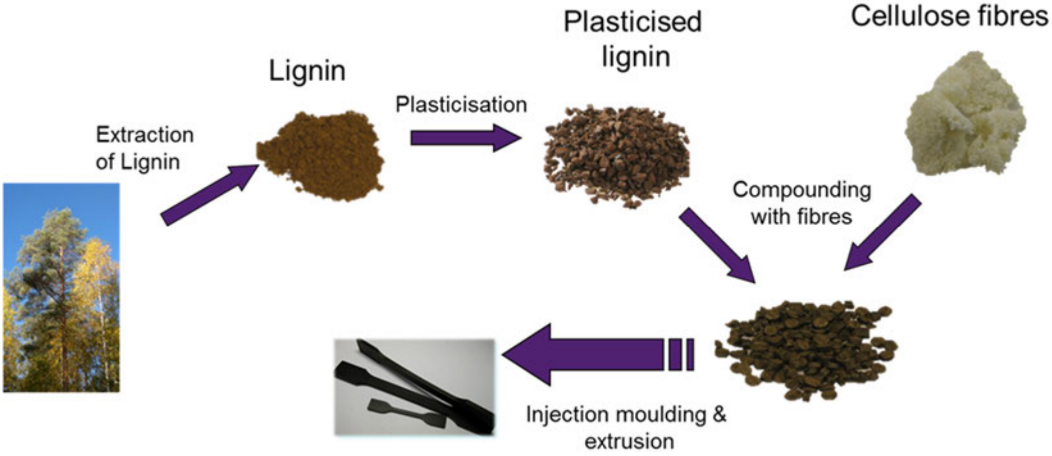

Figure 1. Process diagram for thermoplastic lignin composite production.

The degree of plasticization was evaluated by studying the shift in the Melting and Tg signals in DSC analysis of PEG and lignin, respectively. Thermal decomposition was seen to commence at above 200°C (Figure 2).

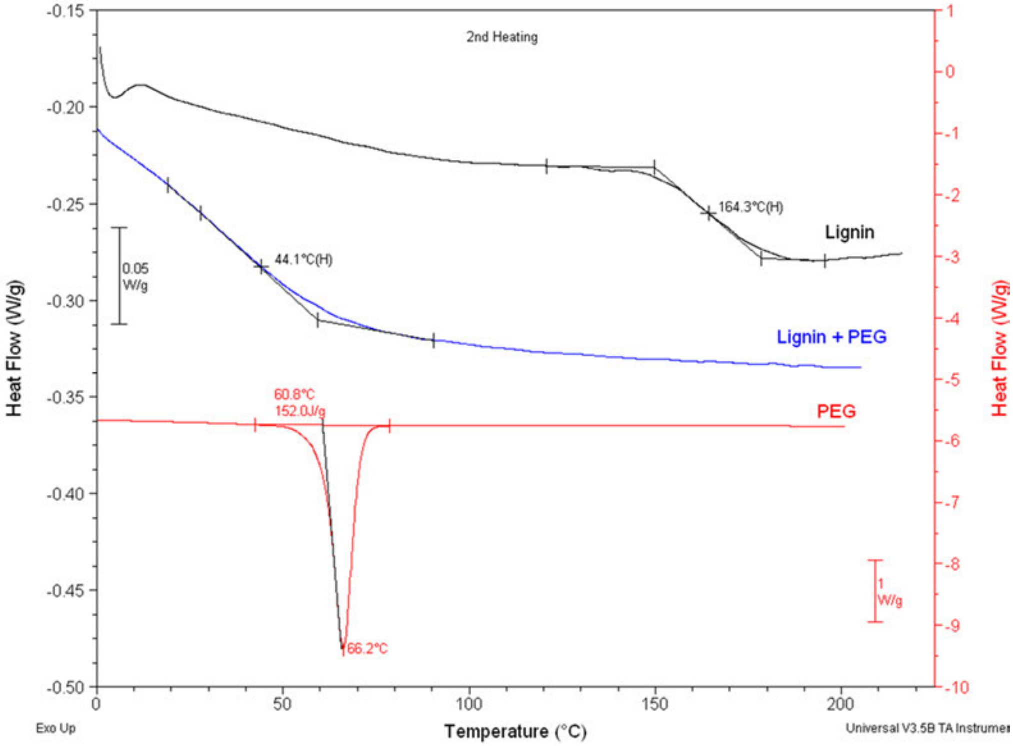

Figure 2. DSC analysis of PEG, lignin and plasticized lignin.

Initial batch processing was done to screen the component ratios and the process limits. Based on these experiments, a processing temperature range of 170 to 200°C was selected. Mini-scale specimens were moulded to characterise the material performance. To enable continuous, inline processing, a method for pelletising the fibres using an in-house designed sieve compactor was developed. At this stage of the project, the performance of the plasticized lignin composites, in terms of tensile properties, was found to be moderately good in comparison to the reference materials such as cellulose reinforced PP and PLA (Figure 3). Significant improvement is, however, needed in ductility, environmental stability (moisture, water) and release of odors.

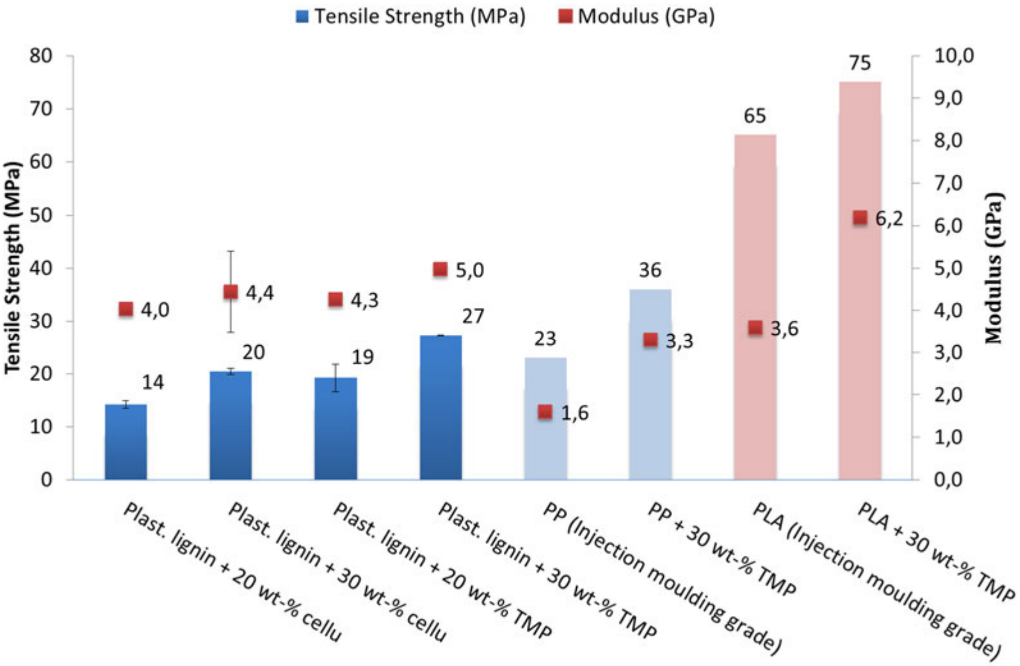

Figure 3. The performance of the plasticised lignin composites in comparison to reinforced PP and PLA reference materials.

Selective enzymatic degradation of alkali extracted lignin for the production of high-value aromatic components

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Abstract

In this study several fungal oxidoreductases were utilized with the intention to break down lignin selectively [1]. The aim was to achieve controlled partial decomposition of lignin and hydrolysis of hemicellulose. Also the use of co-oxidants was studied in terms of boosting the degradation of bulky lignin [2]. The formation of monophenolic compounds and the nature of the residual lignin were examined. A hemicellulose-rich pressurized hot water extract and lignin rich fraction pooled from an alkali extraction of native spruce wood was used in the experiments.

Fungal oxidoreductases were able to break down aromatic lignin structures and they have a potential for future utilization in lignocellulose biorefineries. However, the controlling of lignin decomposition so that it yields to small aromatic components has proved to be challenging. In addition to small molecular weight aromatic compounds, also the modified residual lignin polymer can have interesting functional properties.

Introduction

Efficient biomass fractionation is a crucial pretreatment process for most lignocellulose based biorefineries. Pressurized hot water extraction (PHWE) [4] and a succeeding alkali extraction are potential tools to fractionate softwood biomass into the three main fractions; cellulose, hemicellulose and lignin. Out of these fractions lignin is possibly the most difficult to refine due to its heterogeneous and highly complex polyaromatic structure. However, several fungal oxidoreductases are able to selectively break down lignin, which could lead to novel high-value aromatic products from wood [1]. Monomeric lignin blocks can be utilized e.g. by the cosmetic industry, the pharmaceutical industry, as aroma compounds or precursors for other chemicals.

Experimental

A lignin rich fraction pooled from an alkali extraction of native spruce wood was used in these experiments. Three oxidative enzymes were tested. These enzymes were manganese peroxidase (MnP), lignin peroxidase (LiP) and laccase. The pH of the liquid was adjusted to a suitable level for the enzymes (4.5–5). All treatments included a mixture consisting of 500 µM MnSO4, and 50mM sodium malonate. 0.5% (W/V) Tween 80, 1 mM Glutathione (GSH) and 100 µM veratryl alcohol (VA) were used as co-oxidants in some experiments. A batch-wise method for hydrogen peroxide addition was created with the addition of 10–20 mM glucose and 100–200 UL^{-1} glucose oxidase.

Samples were taken at specified time intervals for nuclear magnetic resonance spectroscopy (NMR) and liquid chromatography (HPLC) analysis of the produced lignin derived products and the structure of the residual lignin polymer.

Results and discussion

Fungal enzymes degraded aromatic structures of lignin and apparently most of the smaller oligo- and monophenols. Efficient decomposition of the bulk lignin was not achieved in this study. However, SEC-analysis (Figure 1A) showed increased amounts of soluble lignin in samples as the treatment progressed, which could result from the break-down or modification of the larger precipitated lignin. In this respect, the co-oxidants seemed to have a positive effect. 1 D NMR revealed rapid reduction in the aromatic region signals in enzyme treated samples (Figure 1B).

Decrease in the aromatic signals of PHWE samples was also observed. The yield of sugars in enzymatic hydrolysis was increased in these samples, possibly due to breakdown of lignin and lignin-carbohydrate complexes (Figure 1C).

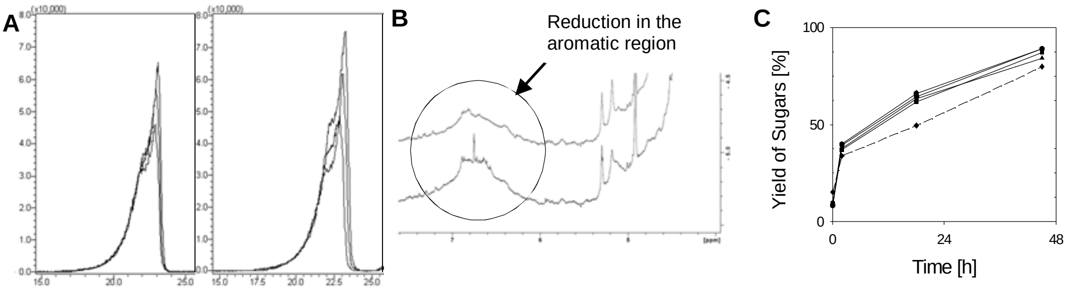

Figure 1. A: SEC-analysis of two separate enzyme treatments. MnP (60 Units) and laccase (20 Units) without added co-oxidants (left) and MnP (60 units) alone with co-oxidants Tween 80 and GSH (right). Lines from lower to upper: 0 h, 21 h and 45 h of treatment. 17.5–24 min retention is the lignin signal. **B**: 1D NMR signal from the aromatic region of the spectrum in an enzymatic treatment of alkali extract. Lines: lower (0 h), upper (2 h). **C**: Yield of PHWE hemicellulose sugars in enzymatic hydrolysis was increased by a pretreatment with fungal oxidative enzymes. Lines: dashed (control), solid (pretreated samples). Analysis was done by HPLC.

References

1. Hatakka, A. 1994. Lignin-modifying enzymes from selected white-rot fungi–production and role in lignin degradation. FEMS Microbiology Reviews 13(2–3), pp. 125–135.

2. Hammel, K.E., Cullen, D. 2008. Role of fungal peroxidases in biological ligninolysis. Current Opinion in Plant Biol. 11, pp. 349–355.

3. Hiltunen, L., Järvinen, J., Sotaniemi, V., Taskila, S., Byman, O., Leppänen, K., Ojamo, H., Ilvesniemi, H., Mattila, S. 2012. Analysis of alkali lignin degraded by oxidative fungal enzymes. XXXI Finnish NMR symposium June 2012. Poster presentation.

4. Leppänen, K., Spetz, P., Pranovich, A., Hartonen, K., Kitunen, V., Ilvesniemi, H. 2011. Pressurized hot water extraction of Norway spruce hemicelluloses using a flow-through system. Wood Science and Technology. Wood Sci. Technol. 45, pp. 223–236.

From lignins to aromatic synthons by base catalysed degradation in continuous reactors – a tentative review

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Abstract

Lignin as a renewable resource containing aromatic structures has sustainable & economical potential in bio based chemicals, materials & in the energy sector. The objective of the presented studies is the generation of oxy-aromatics from different lignins (Organosolv lignin & Sulphur-containing lignins). Both the Organosolv lignin & the sulphur containing lignin were used for based catalysed degradation (BCD) into oxy-aromatics (monomer, oligomer). Subsequently (at p: - 250 bars), the effect of parameters (catalyst, NaOH) & NaOH conc., minerals, dwell time (τ = 5–15 min), temperature (T: 250–350°C) was investigated. Liquid-liquid extraction of reactor water (pH = 3) was performed with MIBK. Oils & tars were characterized regarding the yield & their composition. Types of monomers were summarized into groups (guaiacol (G), syringol (S), catechol (C), oligomeric). Some oligomers in the oils were identified. To get an overview about main & side effects in such a complex situation, the studies on technical lignin were done using statistical Design of Experiments (DoE, Box-Behnken). A detailed evaluation regarding the main & side effects of process & substrate factors on yield of oil & tar, on the Yield of guaiacol, syringol & catechol type monomers in the oil phase and on the carbon balance/ conversion degree & on Mw & Mn of tar will be given.

Methods

The extracts (oils) & filter-cakes (tars) were characterized regarding the yield & their composition. A characterization of the monomer composition was done using GC-MSD/FID & elemental analysis (EA: CHONS-carbon balance). Types of monomers were summarized into groups (e.g. guaiacol (G), syringol (S), catechol (C), oligomeric). Oligomers in the oils were identified by Infusion & LC MSD Ion Trap & the composition of the tar by Py-GC-MSD analysis as well as the formed tar by SEC & EA.

Results and discussion

Depending on the botanical source & the generation process the used lignins differ in their structure (G-lignin, G/S-lignin, molecular weight and in mineral & sulphur content. The substrate factors effecting the degradation process during the base catalysed cleavage of aryl-aryl-ether & aryl-methyl-ether bonds. On the other hand, process factors (p, T, τ, catalyst conc. (NaOH) & type of alkaline & earth alkaline cations have a main effect on the cleavage processes, on yield & composition of the oil, on the molecular characteristic (Mw, Mn) of tar & on the carbon balance.

The following figures illustrate the options & challenges of the BCD process on lignins.

Lignin conversion into oil

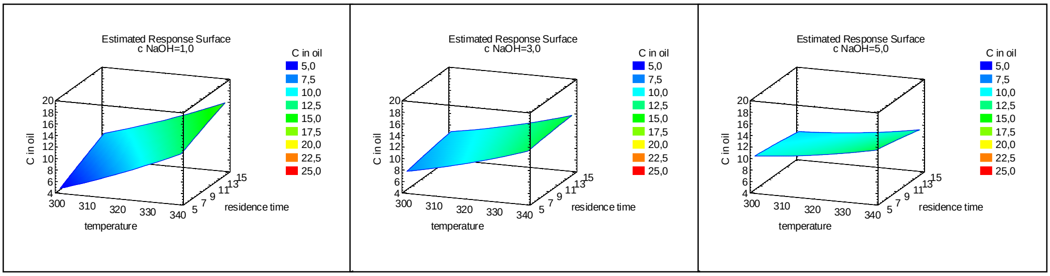

Figure 1. Effects of dwell time: 5, 10, 15 min, T: 300, 320, 340°C & NaOH conc. (1%: left, 3%: centre, 5%: right)) on the carbon amount in oil originating from sulphur containing lignin (Carbon (wt.-% of lignin) as degree of conversion.

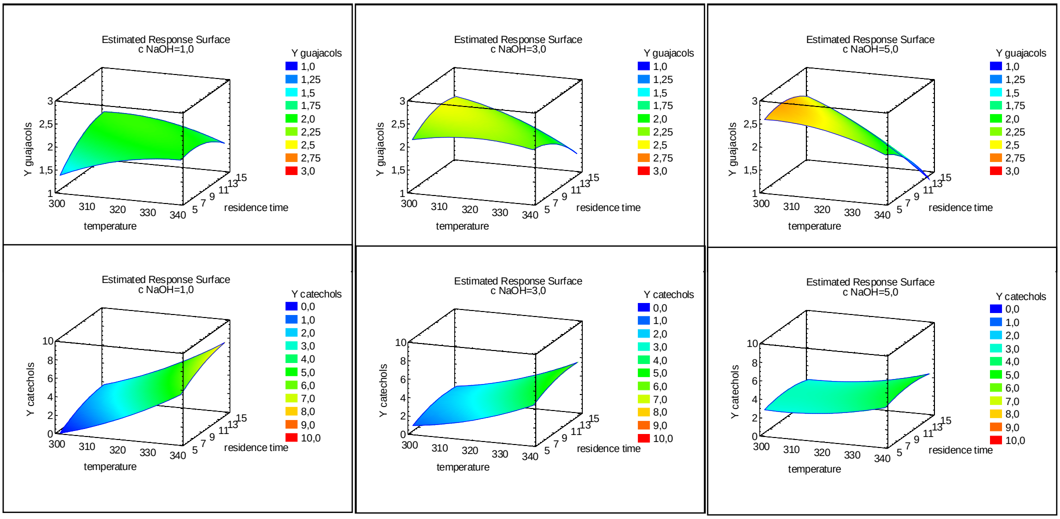

Figure 2. Effects of dwell time: 5, 10, 15 min, T: 300, 320, 340°C & NaOH conc. (1%: left, 3%: centre, 5%: right)) on the amount of guaiacols & catechols – below (wt.-% of Lignin) present in the oil after BCD of sulphur containing lignin.

Lignin conversion into tar

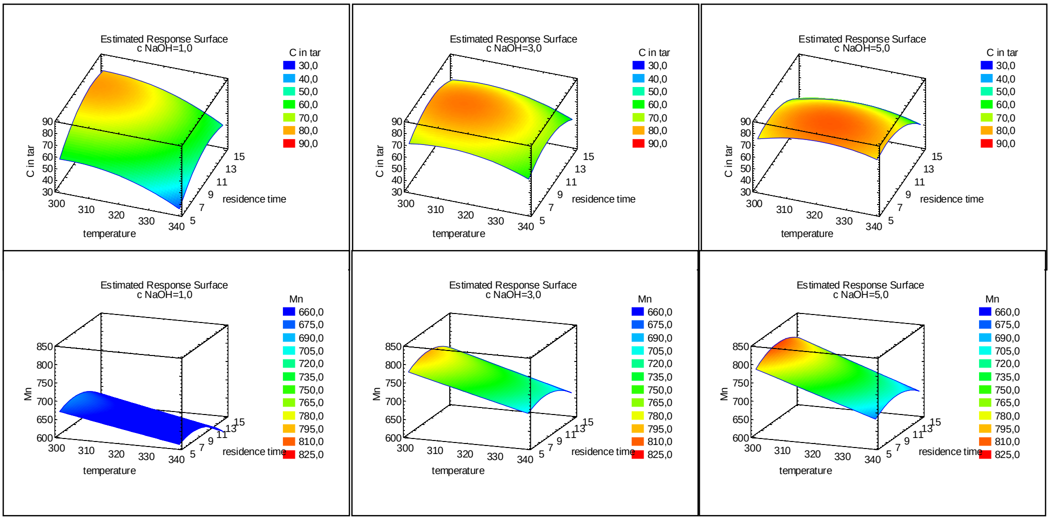

Figure 3. Effects of dwell time: 5, 10, 15 min, T: 300, 320, 340°C & NaOH conc. (1%: left, 3%: centre, 5%: right)) on the carbon amount in tar originating from sulphur containing lignin (carbon (wt.-% of lignin) upper, as degree of conversion & on molecular number Mn (g/Moles) of tar.

References

1. Miller, J.E., Evans, L.R., Mudd, J.E., Brown, K.A. 2002. Batch Microreactor studies of lignin depolymerisation by bases. 2. Aqueous solvents, 2002, SAND2002-1318, Sandia National Laboratories, Albuquerque, New Mexico, USA. Pp. 1–51.

2. Miller, J.E., Evans, L.R., Littlewolf, A.E., Trudell, D.E. 2002. Batch Microreactor studies of lignin depolymerization by bases 1. Alcohol solvents, 2002, SAND2002-1317, Sandia National Laboratories, Albuquerque, New Mexico, USA. Pp. 1–19.

3. Schmiedl, D., Unkelbach, G., Graf, J., Schweppe, R. 2009. Studies in catalyzed hydrothermal degradation processes on Sulphur-free Lignin and extractive separation of aromatic SYNTHONs. 60 Poster proceeding: 2nd NWBC, 2009, 2–4 Sep, Helsinki, Finland, 2009. Pp. 189–197.

4. Pacific Northwest National Laboratories; PNNL-16983: Top Value added chemicals from biomass. Volume II – Results of screening for potential candidates from biorefinery lignin, October 2007. Pp. 1–87.

5. Vigneault, A., Johnson, D.K., Chornet, E. 2006. Advance in the thermal depolymerisation of lignin via base-catalysis. In: Science In Thermal And Chemical Biomass Conversion, 2. A.V. Bridgwater and D.G.B. Boocock (Eds.). CPL Press, Newbury Berks, UK. Pp. 1401–1419.

Optimization of the kraft lignin copolymerization with ε-caprolactone for higher value lignin-adhesives

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Abstract

Within the pulping process 50 million tons lignin per year accrue; biorefinery concepts add another 20 million tons to this amount. There are only a few industrial applications for lignin such as dispersants or precursors for vanillin. It is also used as a replacement for phenol in phenol-formaldehyde resins in plywood. Until now the majority of the lignin is used to cover the required energy of the pulping process. Any excess energy which is produced is fed into the national energy grid. Hence a concept for the material use of kraft lignin must imply a higher value than the profit arising from energy recovery.

Introduction

In order to get a higher lignin valorisation chemical modification and synthesis into polymeric materials are the best approaches. In a first step lignin is copolymerized with ε-caprolactone to achieve solubility for polyurethane synthesis. In a second step the copolymer is reacted with 4,4`-methylene-diphenylene diisocyanate (MDI), 1,6-hexane diisocyanate (HDI) and dimethylene propionic acid (DMPA) to a water dispersible polyurethane adhesive. In order to synthesize lignin- ε -caprolactone copolymers on an industrial scale a defined specification on the lignin purity is necessary. In addition to optimize the reaction and to get a high lignin content in the end product this pre-treatment is mandatory to assure homogenous reaction conditions.

Experimental

Indulin AT was used as softwood lignin obtained by the kraft pulping process. The esterification reaction with kraft lignin and ε-caprolactone was synthesized according to de Oliveira and Glasser [1]. The kraft lignin pre-treatment was performed with a bead mill with bead sizes about 0,8–4 mm together with ε-caprolactone for 10 min. The reaction was executed with different amounts of lignin in the range of 10–40% (w/w). In addition the reaction time was reduced from 15 to 3–5 hours. Lignin-based copolymers were characterized by differential scanning calorimetry (DSC), size exclusion chromatography (SEC) in THF, ^{1}H- and ^{13}C-NMR and the lignin-ε-caprolactone-dispersants were analyzed by laser diffraction measurements.

Results and discussion

The applied milling process assures homogenous reaction conditions and a larger reactive surface. Because of the mechanical pre-treatment with the bead mill the produced copolymers show a faster reaction kinetic and different melting points compared to the untreated lignin products. Figure 1 show precipitated lignin-ε-caprolactone copolymer particles in SEM. The untreated lignin copolymers show a bigger ratio of crystalline morphology resulting in stiff and brittle products. Lignin copolymers which are prior mechanically treated getting softer with higher lignin content. During the esterification reaction some SEC samples were retrieved and measured. It is shown that after the monomer reaction is done the molecular weight still increases and the lignin copolymer reacts further. This directs to the decreasing of carboxyl groups from the lignin which undergo crosslinking reactions [2].

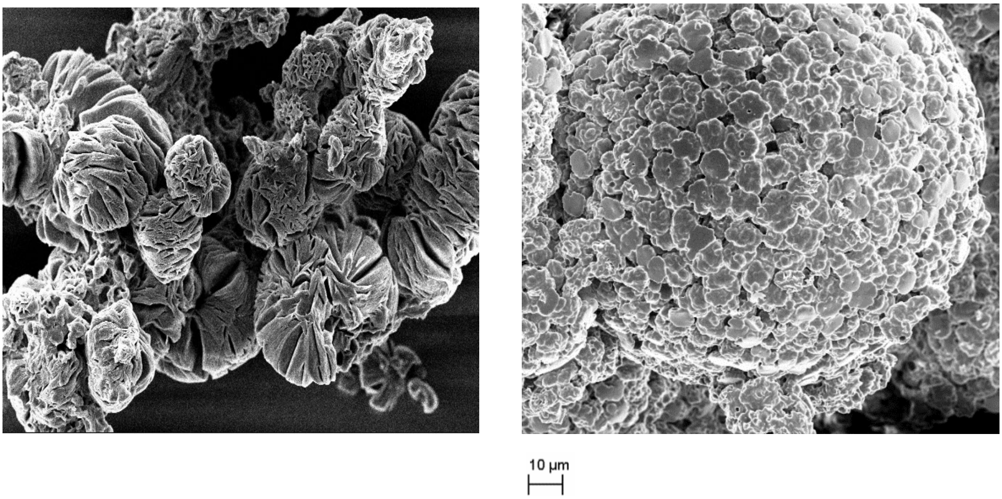

Figure 1. SEM pictures of the lignin copolymer left: untreated right: pre-treated with a bead mill.

Conclusion

The conditioning with a bead mill allows the synthesis of lignin-ε-caprolactone copolymers with higher lignin content compared to non-treated lignin. The surface morphology of the copolymer changed into a less crystalline one so copolymers with other characteristics just due to mechanical pre-treatment are synthesized. Therefore the thermomechanical behaviour also changed. Summarizing a lignin copolymer with short reaction times and controlled crosslinking is produced. A product that is excellent qualified for polyurethane reactions to synthesize adhesives was obtained.

Acknowledgement

Staerkle & Nagler for providing Indulin AT and to Christine Burmeister for doing the laser diffraction measurements.

References

1. De Oliveira, W., Glasser, W. 1994. Multiphase Materials with Lignin. 11. Starlike Copolymers with Caprolactone. Macromolecules 27, pp. 5–11.

2. Matsushita, Y., Inomata, T., Takagi, Y., Hasegawa, T., Fukushima, K. 2011. Conversion of sulphuric acid lignin generated during bioethanol production from lignocellulosic materials into polyesters with ε-caprolactone. J. Wood Sci. 57, pp. 214–218.

Fast catalytic pyrolysis of lignin

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Abstract

Lignins from different isolation methods and sources were pyrolized by micro-pyrolyser connected with gas chromatograph mass spectrometry. Thermal degradation with regard to temperature was investigated by analyzing monomeric compounds. The effect of catalysts on thermal decomposition is presented by composition difference at certain temperature, which can be interpreted as enhanced degradation or selective degradation. Phenolic compounds and phenol composition have been changed by applying catalyst at certain temperature. Moreover, long chain hydrocarbon such as hexadecanoic acid from empty fruit bunches has been detected during pyrolysis, which may come from residual palm oil or from recombination between broken hydrocarbons from phenolic compounds.

Introduction

Lignocellulosics which is the most abundant and renewable material is the most suitable resource to replace fossil fuel. Several routes can be applied to lignocellulosics to obtain appropriate fuel form that has high energy density and eco-friendly flue gas. Direct conversion from wood to bio-oil through thermal conversion is believed to be the shortest and cheapest route. However, high oxygen content which is mainly from cellulose and hemicelluloses could decrease oil stability due to the acidity of oil [1]. In this work, lignin which is residue of two-step hydrolysis of lignocelluloses in bio-ethanol production was pyrolized. The elimination of celluloses and hemicelluloses can decrease oxygen ratio in oil product. However, lignin structure originally contains oxygen which is forming as hydroxy and methoxy group; therefore, catalytic deoxygenation is necessary.

Experimental

Material and method

Lignins were prepared by two-step hydrolysis of oak wood and empty fruit bunch (EFB). First step was conducted with high concentration of sulphuric acid (70 wt%). The second step was conducted by diluted sulphuric acid concentration (30 wt%) and increased reaction temperature. Lignin was obtained after filtering the resultants, and been washed and dried before further utilization.

Pyrolysis was conduct with micro pyrolyzer CDS pyroprobe 5000 US directly connect to Gas Chromatography Agilent HP 6890 with HP DB-1701, 30m X 0.32 mm id X 1.00 μm film as a column and compound were detected by Mass Selective Detector HP 5973. Pyrolysis duration was set in 20 seconds and temperatures were varied from 400–800°C. In catalytic pyrolysis, ratio between catalyst and lignin is set to 2:1.

Result and discussion

Pyrolysis of EFB and Oak lignin produces variety of compounds which are mainly consist of phenolic compound. Compounds with guaiacyl and syringyl moieties are dominant in Oak lignin pyrolysis, while in EFB lignin compounds with hydroxyl phenyl moieties was also present in considerable ratio. Aromatic compound without oxygen was found in very small ratio in both of lignin pyrolysis especially in oak lignin. At higher pyrolysis temperature phenol and its derivatives tend to increase while guaiacol and syringol and its derivatives tend to decrease, suggesting that rate of demethoxylation increases as temperature increases.

Pyrolysis under H-ZSM-5 catalyst shows impressive performance in increasing aromatics without oxygen compound. Figure 1 shows aromatics free of oxygen for Oak and EFB lignin with and without H-ZSM-5. Interestingly, among aromatic compounds free of oxygen 1,3-dimethyl benzene is the highest ratio for Oak lignin, while 1,4-dimethyl benzene is for EFB lignin. Thus, H-ZSM-5 seems to have high selectivity in dimethyl benzene. Furthermore, several aromatic compounds with double and triple rings were found. It suggested that H-ZSM-5 has a role in oligomerization [2] and deoxygenation. Catalytic pyrolysis with various temperatures shows that H-ZSM-5 is not deactivated at temperatures above 600°C.

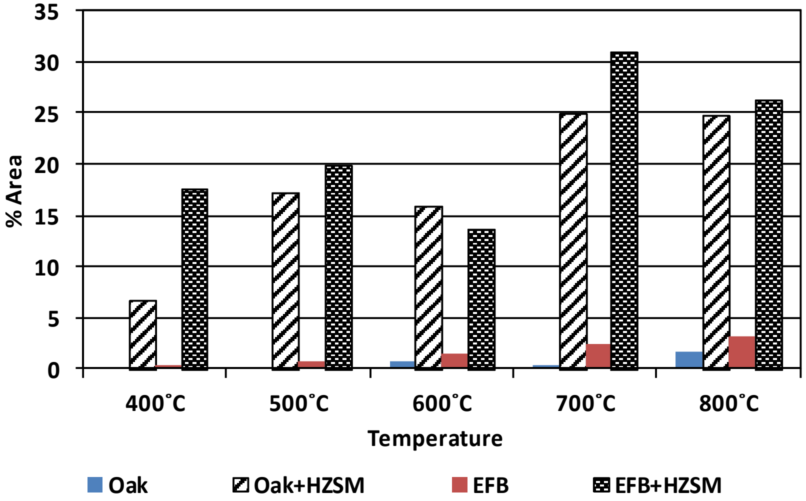

Figure 1. Aromatic free oxygen product in Oak and EFB lignin pyrolysis with and without H-ZSM-5.

Reference

1. Mohan, D., Pittman, C.U., Steele, P.H. 2006. Pyrolysis of Wood/Biomass for Bio-oil: A Critical Review. Energy & Fuels. 20(3), pp. 848–889.

2. Cheng, Y.T., Jae, J., Shi, J., Fan, W., Huber, G.W. 2012. Production of Renewable Aromatic Compounds by Catalytic Fast Pyrolysis of Lignocellulosic Biomass with Bifunctional Ga/ZSM-5 Catalysts. Angew. Chem. 124(6), pp. 1416–1419.

Analytical tools to study the chemistry of hydrothermal lignin depolymerisation

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Introduction

Lignin is a natural aromatic polymer, it is considered to be one of the main factors that limit the determination of the quality of biomass to be converted to bio-ethanol and pulp. Hydrothermal depolymerization of lignin is one of the hot topics in the liquefaction process of biomass. The ability of lignin degradation products to re-polymerize and forming char is a fact that hinders the maximization of biomass valorization [1].

Temperature, residence time, concentration, etc are factors affecting the degradation product that can affect the whole process. To enable the understanding of the chemistry of such complicated process, robust analytical tools must be developed.

Experimental

Analytical method based on HPLC-DAD has been developed and used to increase the understanding of the chemistry of lignin de-polymerization process (Figure 1). The above mentioned factors are studied to optimize a hydrothermal process of lignin in sealed transparent quartz capillaries reactors using a fluidized sand bath to set the temperature as desired.

Results

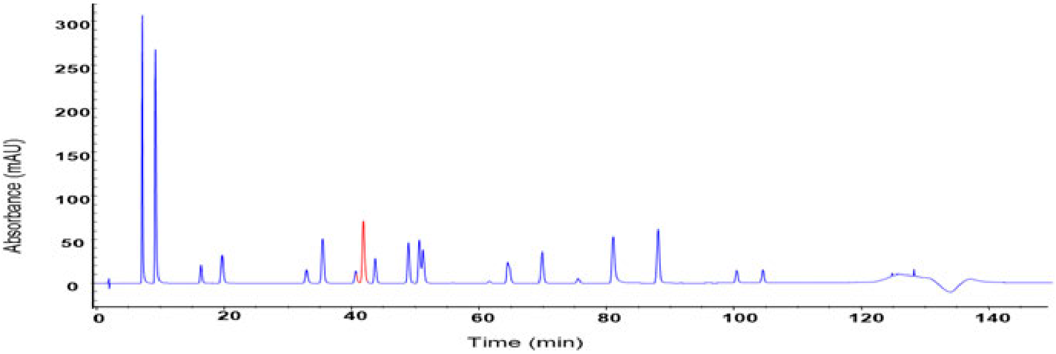

Figure 1. Represent 20 standard compounds for lignin degradation products separated by C18 column using methanol and water as mobile phase at 280 nm.

References

1. Lavoie, J. M., W. Bare, Bilodeau, M. 2011. Depolymerization of steam-treated lignin for the production of green chemicals. Bioresour Technol 102(7), pp. 4917–4920.

Pulsed corona discharge oxidation in lignin modification

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Introduction

Lignin is a potential raw material for various products including phenolic substances and aromatic aldehydes (vanillin, syringaldehyde, vanillic acid, syringic acid) (Rodrigues Pinto et al., 2011), activated carbon, carboxylic acids, and motor fuel (Radoykova et al., 2011). Traditional methods of lignin modification resulting in phenolic products include oxidation with nitrobenzene, mild wet air oxidation and catalytic oxidation. Drawbacks of these methods include severe toxicity problems with nitro compounds, strict safety requirements and thus high capital costs, and often poisoned costly catalysts. The study considers the hypothesis that modification of lignin with pulsed corona discharge (PCD) oxidation at ambient conditions may appear feasible and beneficial method of lignin modification by its economic performance and environmental safety. The method has hydroxyl-radical and ozone as the main oxidation species effective in oxidation of lignin.

Materials and methods

Commercial alkali lignin supplied by Sigma-Aldrich was used as an experimental material. Figure 1 shows the outline of the experimental set-up. Aqueous lignin solution was circulated from the reservoir tank through the reactor by a pump. Solution is spread between electrodes, where the lignin aqueous solution is treated with oxidants. The experiments were carried out at alkaline pH with different initial concentrations of lignin and the composition of the gas phase – air and nitrogen-enriched air with the volumetric oxygen concentration of 5 to 7%. The discharge pulse parameters include voltage amplitude of 20 kV, current of 400 A, and 100 ns duration giving the single pulse energy 0.3 J at pulse repetition frequency of 840 pulses per second (pps). The concentration of lignin was measured photometrically with tyrosine method. Aldehyde concentration was determined by the colorimetric method developed by Evans et al. (1973).

Results and conclusions

Lignin appeared to be easily degradable by PCD treatment. On the course of treatment aldehydes' accumulation was observed in all experiments. The experimental results are shown in Table 1. Energy efficiency of lignin oxidation in air is, as expected, higher than in low oxygen gas, showing the tendency of growth with growing lignin concentration. This is not true, however, for low oxygen oxidation. One can see no tendency in aldehyde production yield in air and the increasing aldehyde formation yield with increasing initial lignin concentration in the low oxygen atmosphere. It indicates the growing selectivity of PCD oxidation at low oxygen concentrations: aldehyde formation prevails over aldehyde oxidation.

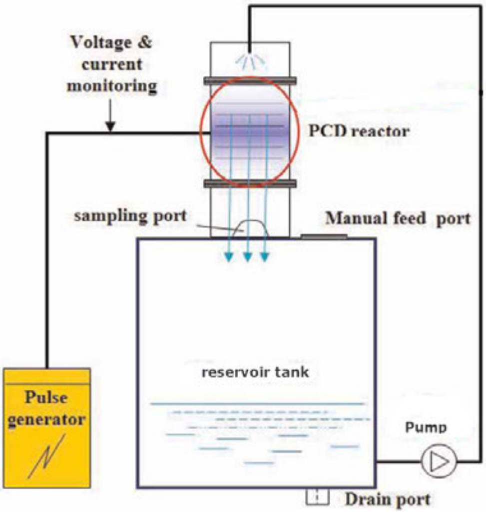

Figure 1. Experimental setup.

Lignin solution was observed to have a buffering effect: the higher the lignin concentration, the more stable pH was observed during the experiment.

Table 1. Experimental results.

Initial lignin concentration, mg/L	**Final lignin concentration, mg/L**	**Final aldehydes concentration*, mg/L**	**Aldehyde formed / lignin oxidised, %**	**Energy efficiency in lignin oxidation, g/kWh**	**Energy efficiency in aldehydes formation, g/kWh**
Gas composition: 5–7% O_2					
74	47,03	2,18	8,08	10,8	0,872
136,82	89,79	5,16	10,97	18,8	2,06
285,05	239,44	6,04	13,24	18,2	2,42
650	604,30	12,44	27,22	18,3	4,98
Gas composition: Air					
78,4	14,25	8,79	13,70	25,6	3,52
141,1	34,2	9,76	9,13	42,8	3,90
276,5	125,42	14,50	9,6	60,4	5,80
558,7	393,36	17,37	10,51	66,1	6,95

*- Aldehyde concentration was recalculated to acetaldehyde content

References

1. Radoykova, T., Stanulov, K., Nenkova, S. 2011. Lignin derived methoxyphenols as anti-oxidant additives for gasoline. Oxidation Communication 34(2), pp. 463–468.

2. Rodrigues Pinto, P.C., Borges da Silva, E.A., Rodrigues, A.E. 2011. Insights into oxidative conversion of lignin to high-added-value phenolic aldehydes. Eng. Chem. Res 50, pp. 741–748.

3. Evans, W.H., Dennis, A. 1973. Spectrophotometric determination of low levels of mono-, di- and triethylene glycols in surface waters. Analyst 98, pp. 782–791.

Synthetic humic materials from ligneous waste materials of the South-African pulping and sugar industries. Synthesis and properties

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Abstract

Over-utilisation, overgrazing and clear-felling of natural forests are current serious environmental issues. These activities lead to soil erosion and inevitably to soil degradation as the fertile top soils, which contain most of the accumulated nutrients and humic substances that control the natural cycle of organic matter in the biosphere, are lost. Rehabilitation of soils, i.e. soil improvement and re-establishment of vegetation, with nitrogen-rich modified lignin-based materials that share a number of similarities with natural humic substances, appear to provide an effective solution. Homogeneous oxidative ammonolysis of technical lignins under mild conditions using an immersion jet set-up was confirmed to be a suitable technology to simulate the natural humification process. The formation of different N-binding forms and their mineralisation in soil at different rates render the ammonoxidised lignins long-term N-fertilisers. Ammonoxidation according to the proposed procedure was shown to give an acceptable nitrogen enrichment of up to 6.25 w% for most of the studied ligneous materials i.e. calcium lignosulphonate, pine Kraft lignin (INDULIN AT™), autohydrolysis bagasse lignin (SUCROLIN™) and a lignocellulosic residue from sugar cane bagasse autohydrolysis. Pre-oxidation of the ligneous materials, e.g. using H_2O_2, was shown to further increase the nitrogen contents. Performance evaluation of the organo-mineral fertilizers on yellow mustard, Sinapis alba, revealed that ammonoxidised SUCROLIN™ and the lignocellulosic residue, despite having different nitrogen contents, resulted in (plant) dry mass yields that were similarly high as when Novihum™, a coal-based product, was applied as a reference.

Results and discussion

The characteristics of the products (table 1) reveal different responses of the raw materials towards nitrogen incorporation, which are influenced by process conditions and their mineral and lignin contents as well as the degree of lignin oxidation. Comparing the two purified lignins, it was found that the total N incorporated was clearly higher in the more oxidised SUCROLIN™ (6.25%) than the INDULIN™ (3.15%). The proportion of NH_4^+ in N-SUCROLIN™ was about 8% higher than for N-INDULIN™ due to the its distinctly higher degree of degradation of the Sucrolin as a result of the steam explosion process from which the lignin originates. From the plant nutrition perspective, too high NH_4^+-N and too low *sob*-N contents are not desirable, due to the risk of over-fertilising or nitrogen leaching and as such, the envisaged long-term unachievable. The total nitrogen and NH_4^+-N contents of the N-modified lignocellulosic residue are distinctly lower compared to N-SUCROLIN™ due to the lower lignin content. The N content in calcium lignosulphonate was in an acceptable range. However, the high proportion of sulphonic groups results in a high percentage of short-term plant available NH_4^+-N (52.7% of total N) mainly by cationic exchange. Such high NH_4^+ values are usually not desired for soil conditioner, especially when applying the products on sandy soils since the percentage of plant-available nitrogen is too high and susceptible to leaching.

The obtained C/N ratio for Sucrolin and lignosulphonate (9.8 and 12.60 respectively) were in the range that is acceptable for high grade humus fractions (9 to 13), while that of Indulin AT and the lignocellulosic residue were high at 19.8 and 19.50 respectively. When the lignocellulosic residue was pre-treated with 1% H_2O_2 prior to oxidative ammonolysis, a total nitrogen content of 3.08%, corresponding to a C/N ratio of 15.50 was obtained.

Table 1. Elemental composition of the products (values based on dry matter).

Product	**Carbon [%]**						**C/N Ratio**
	H_2O_2	Total N	NH_4^+-N	NH_2-N	Sob-N		
N-Sucrolin		***6.25***	***38.42***	***13.00***	***48.58***	***61.30***	***9.80***
Indulin AT		***3.15***	***30.5***	***11.4***	***58.1***	***62.5***	***19.8***
N-lignocellulosic residue		**2.64**	36.57	14.92	51.59	48.50	19.50
N-lignosulphonate		**3.36**	52.70	11.90	35.40	42.00	12.60
NOVIHUM™*		**3…5**	**10…41**	**14…21**	**44…73**	**60…65**	**ca.11**
Natural humus**		**1…5**	**10…25**	**21...25**	**ca.50**	**41…62**	**ca.17**
N-lignocellulosic residue	1%	**3.08**	26.95	14.61	58.44	47.80	**15.50**

Legend: AP = Ambient pressure. HP = Hip pressure (7.5bar). *NOVIHUM ™ = patented reference product. **Values obtained from [2].

Evaluation on crops

Soil treatment with N-modified SUCROLIN™ has similar effect on the growth of yellow mustard (*Sinapis alba)* as NOVIHUM™, the standard reference product (Figure 1). Dry mass yields from N-Lignocellulosic residue (N-LRC) soil treatments were considerably good considering the low N content. However, the lower nitrogen content resulted in reduced yield in the second season. In contrast, soil treatments with N-modified calcium lignosulphonate (N-CLS) resulted in very low yields even in combination with urea (NCLS-urea).

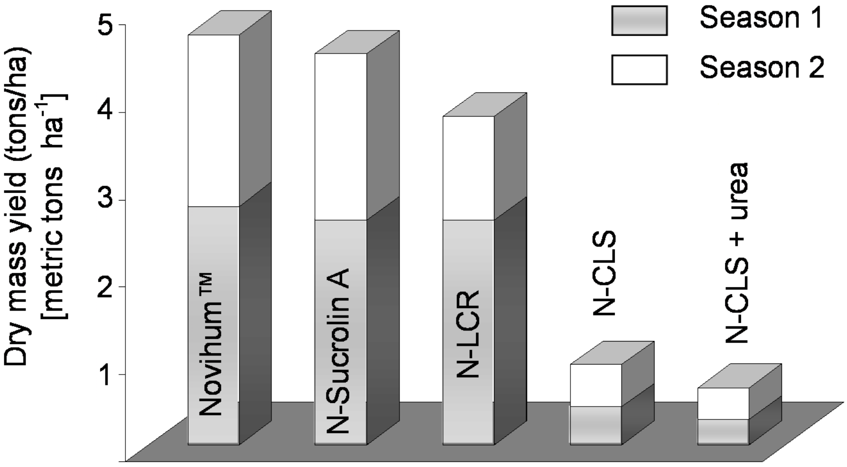

Figure 1. Dry mass yields of yellow mustard treated with N-modified products at an application rate of 1% (*w/w*).

Conclusions

The feasibility of utilizing the selected raw materials has been demonstrated. There are differences in response towards nitrogen incorporation which are related to elemental as well as functional group contents. SUCROLIN™ yielded a satisfactory distribution of the various proportions of nitrogen. The results obtained with the lignocellulosic reside are quite positive especially when the raw material is pre-treated with H_2O_2. The N-modified product prepared from calcium lignosulphonate had comparatively high NH_4^+ and low *sob*-N contents, indicating that stronger oxidative conditions should be used. This would reduce the water solubility of the products by reducing the content of sulphonic groups on the one hand, while decreasing the content of NH_4^+ groups on the other hand.

References

1. Fischer, K., Katzur, J., Chiene, R. 1994. Organische Düngenmittel und Verfarhren zu deren Herstellung. EP 0689526 B1, 18.3.1994.

2. Fischer, K., Schiene, R. 2002. Nitrogenous fertilizers from lignins – A review. In Chemical modification, properties, and usage of lignin, ed.; Hu, T.Q., Plenum Pub. Corp.

3. Liebner, F., Fischer, K., Katzur, J., Böcker, L. 2006. Novihum™ – high grade artificial humus and long lasting fertilzer for accelerated rehabilitation of degraded areas. ed.; UNESCO office: Beijing.

4. Wang, P.Y., Bolker, H.I., Purves, C.B. 1964. Canad. J. Chem. 42, p. 2434.

5. Schiene, R., Pruzina, K.-D., Wienhaus, O., Fischer, K. 1979. Über die Oxidative von Sulfitablauge (I). Zellstoff und Papier 4, pp. 163–166.

Effect of black liquor type and lignin fractionation on the polymerisation of a Kraft lignin by laccase. Optimisation of the operation conditions

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Abstract

The capability of the commercial laccase NS51003 from *Myceliophtora thermophila*, either alone or in the presence of mediators, to polymerise Kraft lignins isolated from black liquors was evaluated. A solvent fractionation process was carried out in order to obtain lignin fractions with possible remarkable polymerisation ability.

To establish the optimum polymerisation conditions, an evaluation on the effects of pH, temperature, enzyme dosage and treatment time on the molecular weight increase was made.

Polymerisation products were analysed by size exclusion chromatography and Fourier transform infrared spectroscopy. The results evidence structural oxidation and a major increase in molecular weight that, in some cases 110-fold its initial molecular weight.

Introduction

A growing awareness of ecological problems by the population and its rulers led to legislation increasingly strict that came to affect conventional manufacturing processes for all industries. The environmental friendly enzymatic processes already have application in the forest based industry while many others are being investigated. Laccase is one of the most promising enzymes to be applied in forest industry particularly in the pulp and paper industry (Widsten & Kandelbauer 2008). Laccases are phenoloxidases capable of oxidising substrates such as phenolic compounds and also non-phenolic compounds by means of a laccase mediator system (LMS). Laccases act over the phenolic structure of lignin where they can both cause delignification (by rupture of lignin bonds) or, on the contrary, may cause polymerisation (by cross-linking of lignin molecules).

In the pulp and paper industry the undesired lignin is separated from lignocellulosic materials in order to obtain an enriched cellulose pulp. In the Kraft process, dominant in the pulp industry, lignin is concentrated in so called black liquor that is afterwards incinerated for energy recovery in the process itself. The Kraft process is in surplus in terms of energy. For this reason a portion of the lignin can be isolated and removed from the black liquor and used as a raw material in various products, without any negative effect on the industrial process. Although is well recognized that lignin is a high value, non-toxic material, lignin has some characteristics such heterogeneous polymer structure, size and functional groups that hampers its immediate applicability in some specific industrial areas. Lignin structure modification could be a possible pathway for the resolution of these handicaps.

In the present work laccase capability to oxidise and polymerise Kraft lignins from distinct origins was evaluated. Furthermore, the influence of lignin fractionation according to their molar mass and the introduction of some mediators on the enzymatic polymerisation was also studied. The operational conditions, namely pH, temperature, enzyme dosage and treatment time were optimised in order to promote polymerisation. Lignins, before and after treatment were characterized by size exclusion chromatography and Fourier transform infrared spectroscopy.

Materials and methods

Black liquors from Kraft cooking of *Eucalyptus globulus* were kindly provided from the pulp and paper companies ENCE (Spain) and Portucel-Soporcel (Portugal) and while Europac (Portugal) supplied black liquor from Kraft cooking of the mixture of *Pinus pinaster/Eucalyptus globulus*

(75/25). The corresponding lignins named EK1, EK2 and EK3 respectively were obtained by acid precipitation with H_2SO_4. The black liquor from ENCE subjected to solvent fractionation as detailed in Gouveia *et al.* (2012) led to four distinct lignin fraction: F1, F2, F3 and F4.

The commercial enzyme NS51003 was clarified in a General Electric Sephadex G-25M column before application. Laccase activity was determined by the oxidation of 4-hydroxy-3,5-dimethoxybenzaldehyde azine (SGZ). The effect of pH and temperature on the laccase activity was analysed by means of Central Composite Design (CCD) and Response Surface Methodology (RSM) indicating that the optimum conditions are 70°C of temperature and pH 6. The enzymatic treatment was carried out in a reaction vessel adding 0.25 to 2 U/mL of NS51003 and 1,5g/L of lignin. The enzymatic reaction was held at 60 to 80°C for 2 to 24 h and pH values from 5.5 to 8.0. All the phenolic compounds used as mediators, namely, syringaldehyde (S), pyrocatechol (P), guaiacol (G), vanillin (V), violuric acid (AV) and polyphenon 60-Green tea (PH60) were purchased from Sigma-Aldrich.

Mid-Infrared spectra of the lignin samples were recorded in a Jasco FT/IR – 4100 by ATR technique. Two Polysec columns, GPC P4000 and P5000 coupled in series were used to analyse the lignin samples by Size Exclusion Chromatography (SEC).

Results and discussion

The initial treatments were performed in the conditions determined by the RSM method as the optimum for laccase activity in SGZ. Based on the enzyme thermostability in those conditions the reaction treatment time was established in 1 h. The presence of mediators at the tested concentration revealed no detrimental effect on the enzyme stability (data not shown). Enzymatic treatment produced an increase in KL1 molecular weight (Mw) as well as an increase in the polydispersity for all experiments. Nevertheless, when comparing the final values with untreated KL1 value, the best results were obtained in the absence of mediators (Control) where the initial Mw 10-fold.

Knowing that laccase activity may change dramatically when the substrate is modified, the optimization of operational conditions was made by evaluation of lignin Mw increase. Temperature, pH, treatment time and enzyme addition type (single or continuous) were adjust in order to produce lignin with higher Mw as possible. The experimental results determined that the best polymerisation conditions with laccase NS51003 were pH 7.3, T = 70°C, 2 Uml^{-1} in a single addition and 2 h of treatment time. A comparison between the distinct lignins is presented in Figure 1. F2 fraction was the best succeeded in multiplying its initial weight while F4 was the one that reached higher molecular weight in absolute terms (data not shown).

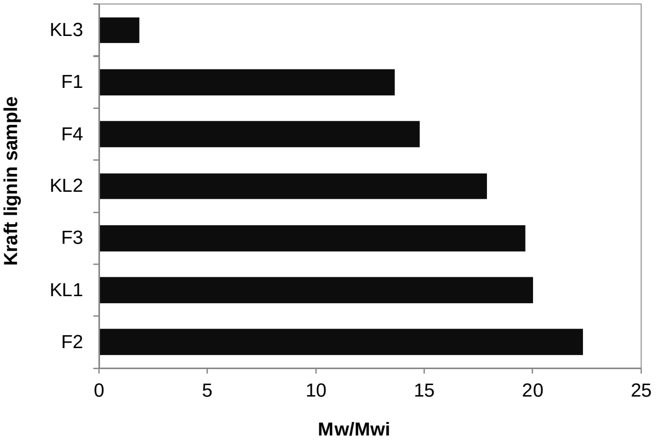

Figure 1. Molecular weight increase (average molecular weight after treatment / initial average molecular weight) in lignin samples after 2 h enzymatic treatment at pH 7.3, 70°C and 2 UmL^{-1}.

From the SEC chromatogram observation three peaks can be clearly distinguished after the enzymatic treatment. In the case of KL1 (Figure 2), peak 1 reaches Mw that 110-fold the untreated KL1 Mw.

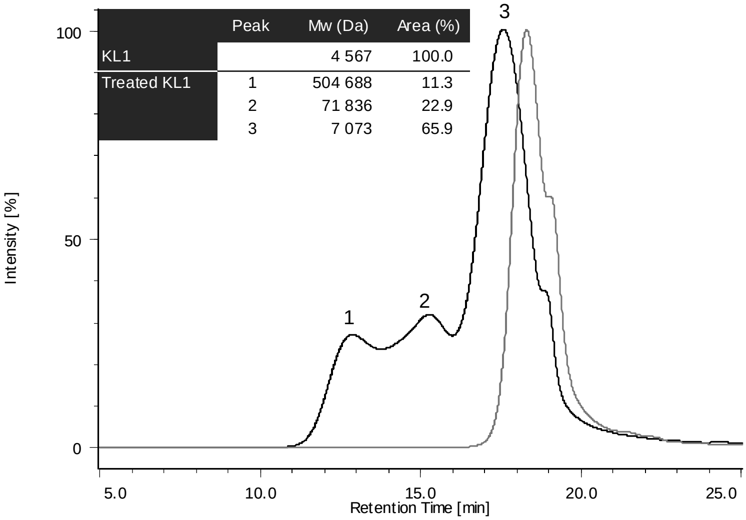

Figure 2. SEC of untreated KL1 (——) and KL1 after 2 h enzymatic treatment at pH 7.3, 70°C and 2 UmL^{-1} (——). Inset: Mw values and percentage of area for each peak.

FTIR analysis detected changes in lignin structure after polymerisation. The most relevant differences were observed at the peaks corresponding to C = O stretching and also the intensity for aromatic ring vibration plus C = O stretching increased after the treatment with NS51003 laccase. However, lignin maintained its aromatic structure, keeping the typical aromatic triplet. Previous reports (Areskogh *et al.* 2010), using laccase for lignosulphonates polymerisation, obtained similar results.

Conclusions

Structural changes detected by FTIR revealed that Kraft lignins were successfully oxidised by laccase NS51003. This oxidation led to lignin polymerisation with a factor range that varied according to the type of lignin and operational conditions.

Lignin fractions obtained by solvent fractionation showed distinct polymerisation capability. Some of the fractions led to polymers with higher average Mw than the unfractionated Kraft lignin. Also, laccase NS51003 revealed to be less efficient polymerising softwood than hardwood Kraft lignin.

The studied mediators did not improve the degree of polymerisation obtained by the laccase alone.

When operating under optimum conditions the enzymatic treatment led to three distinguishable polymers with different molecular weight distributions. The biggest one of them has increased the initial KL1 Mw by 110.

Acknowledgements

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References

1. Areskogh, D., Li, J., Gellerstedt, G., Henriksson, G. 2010. Structural modification of commercial lignosulphonates through laccase catalysis and ozonolysis. Industrial Crops and Products 32(3), pp. 458–466.

2. Gouveia, S., Fernández-Costas, C., Sanromán, M.A., Moldes, D. 2012. Enzymatic polymerisation and effect of fractionation of dissolved lignin from *Eucalyptus globulus* Kraft liquor. Bioresource Technology 121(10), pp. 131–138.

3. Widsten, P., Kandelbauer, A., 2008. Laccase applications in the forest products industry: A review. Enzyme and Microbial Technology 42(4), pp. 293–307.

Recovery strategies control the wood hydrolysate barrier performance

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Introduction

Environmental concerns together with the quest of a sustainable society have trigged considerable efforts in the development of bio-based and environmentally friendly packaging materials. Within this context, non-cellulosic polysaccharide materials from plants and wood, such as xylan and galactoglucomannan, have received much attention for potential use as barrier films and coatings because of their abundance, the renewability of their natural sources, and their excellent oxygen barrier property. [1, 2] The low oxygen permeability is a result of the hemicellulose highly packed structure arising from the cohesive energy between macromolecular chains. [3, 4] However, the use of hemicelluloses in large scale applications is still restricted by the multiple step procedure required for hemicellulose extraction and purification, which reduces the environmental and economic benefits of their application in packaging. The purpose of this work is to design oxygen barrier films and coatings based on a non-cellulosic polysaccharide-rich wood hydrolysate (WH), derived from hardwood hydrothermal treatment process water. A further aim was to improve the oxygen barrier properties in particular by controlling the recovery routes of WH through different upgrading pre-treatments.

Experimental

Materials. The hardwood hydrolysate, produced from birch mixed with a small fraction of aspen wood chips by hydrothermal treatment in a batch reactor, was kindly provided by Södra Cell AB, Sweden. The hydrothermal procedure have been described in more detail previously. [5] Highly purified xylan from birch wood and carboxymethyl cellulose (CMC) sodium salt was used as received from Sigma-Aldrich. Commercially used poly(ethylene terephthalate) (PET) films with a thickness of 38 µm were kindly supplied by Tetra Pak Packaging Solutions AB, Sweden and used as a coating substrate.

Instrumentation. High performance anion exchange chromatography (HPAEC-PAD, Dionex ICS-3000) was used for sugar composition analysis. Thermogravimetric analysis TGA Mettler Toledo TGA/STDA 851e were used to determine the water and ash content. The contained hemicelluloses molecular structures were studied by proton nuclear magnetic resonance (^{1}H NMR). Size exclusion chromatography (SEC) was used to determine molecular weights and molecular weight distributions, of the different WH fraction with respect to pullulan standards. The WH based films' and coatings' oxygen barrier and tensile performance were characterized on a Mocon Oxtran 2/20 (Modern Controls, Minneapolis, MN) and an Instron universal materials testing machine equipped with a 50 N load cell, respectively.

Upgrading pre-treatments The WH was upgraded according to one of three alternative industrially feasible routes: 1) ultrafiltration (resulting in fraction WH1), 2) ultrafiltration followed by diafiltration (WH2), and 3) ethanol precipitation (WH3). Pellicon cassette filters with a hydrophilic membrane made from regenerated cellulose (PLAC Prepscale, Millipore) with a nominal cut-off of 1000 Da and a surface of 100 cm^2, was used during the ultrafiltration and diafiltration steps. In addition, a crude WH fraction (WH0) was used where the process water did not undergo any other treatment that centrifugation.

Films and coating preparation WHs based films and coatings containing 40% w/w of CMC and 60% of any of the WH fractions were prepared. The water based CMC/WH mixtures were casted and dried at 23°C and 50% RH. For the coatings, the WH/CMC mixtures were applied onto 12 × 23 cm^2 PET films using paint brush.

Results and discussion

The chemical composition, average molecular weight and structural analysis studies showed that the upgrading pre-treatments in general resulted in WH fractions containing less amount of lignin and a larger share of higher molecular weight compounds. Furthermore, the hemicellulose in the up-graded fractions had less branched structures than the one in the crude wood hydrolysate (WH0), while the degree of acetylation did not change during the up-grading pretreatments. The most significantly changes of the wood hydrolysate structure and composition was obtained by ethanol precipitation.

The oxygen permeability results of the coatings are represented in Figure 1. WH-coated PET films, regardless of the fraction of WH used, display a significantly lower oxygen permeability compared to the uncoated films. The lowest OP value of 1.3 cm^3 µm m^{-2} day^{-1} $kPa^{-1}$was obtained for the coating made from WH0, while the highest OP value (6.1 cm^3 µm m^{-2} day^{-1} kPa^{-1}) was obtained for the ethanol precipitated WH3. Furthermore, the tensile testing showed that films made from upgraded WHs display higher Young's moduli and tensile strengths compared to those made from highly purified commercial xylan (BrX) and crude WH0.

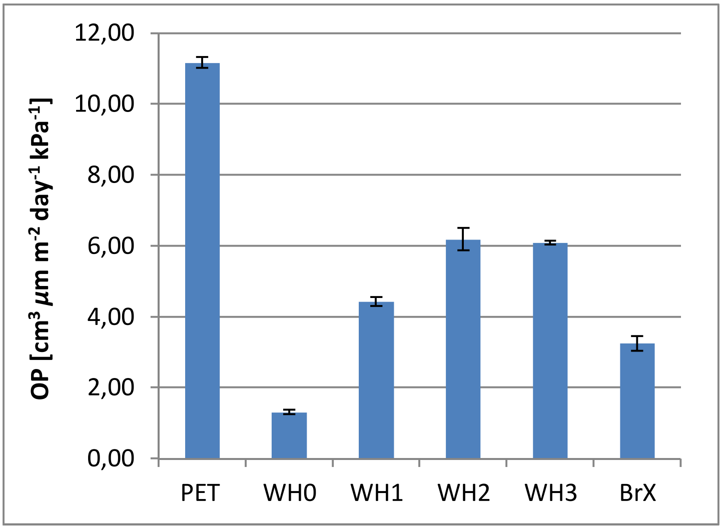

Figure 1. Oxygen permeability (OP) of the uncoated and coated PET films with coatings based on highly purified commercial birch xylan (BrX), or on the different wood hydrolysate, crude (WH0), ultrafiltrated (WH1), ultrafiltrated and diafiltrated (WH2) and ethanol precipitated (WH3).

Conclusions

Films and coatings were successfully produced from hardwood hydrolysates, rich in xylan and originating from the hydrothermal treatment of birch mixed with a small fraction of aspen. The recovery routes of the WH had a major impact on tensile and oxygen barrier performance of the respective films and coatings. The crudest WH fraction without any upgrading pretreatment produced coatings with the best performance with respect to oxygen permeability and was superior to analogous films based on highly purified xylan.

Acknowledgements

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References

1. Hartman, J., Albertsson, A.-C., Lindblad, M.S., Sjöeberg, J. 2006. J. Appl. Polym. Sci. 100, pp. 2985–2991.

2. Edlund, U., Ryberg, Y.Z., Albertsson, A.-C. 2010. Biomacromolecules 11, pp. 2532–2538.

3. Ryberg, Y.Z.Z., Edlund, U., Albertsson, A.C. 2011. Biomacromolecules 12, pp. 1355–1362.

4. Edlund, U., Yu, Y., Zhu Ryberg, Y., Krause-Rehberg, R., Albertsson, A.C. 2012. Anal. Chem. 84, pp. 3676–3681.

5. Ibn Yaich, A., Edlund, U., Albertsson, A.-C. 2012. Biomacromolecules 13, pp. 466–473.

Design of new bioresource packaging from wood hydrolysates

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Abstract

Two types of hemicellulose-based spruce wood hydrolysates were upgraded through ultrafiltration and diafiltration to separate the higher molecular weight fraction of the wood hydrolysates. Upgraded wood hydrolysates were thereafter used, together with different co-components to produce films with very good oxygen barrier properties and acceptable mechanical properties.

Introduction

Softwood hydrolysates are liquids extracted from hydrothermal treatments of wood. Such process waters and effluents typically contain non-cellulosic oligo- and polysaccharides as a main component of dry matter, a fraction which can be recovered and concentrated by different strategies. A cost-effective way of adding the value of by-products in commercial processes, such as pulping or fiberboard industries would be to utilize the wood hydrolysates, in a more or less refined state, in the manufacturing of polymer products.(Figure 1) Functionalizations and product formulations based on highly purified hemicelluloses have been reported over the years, but from an economic perspective, the hydrolysates could advantageously be separated from the product streams and used without extensive refining other than some enrichment in high-molecular weight fractions. The aim was to utilize the upgraded wood hydrolysates as a barrier material.

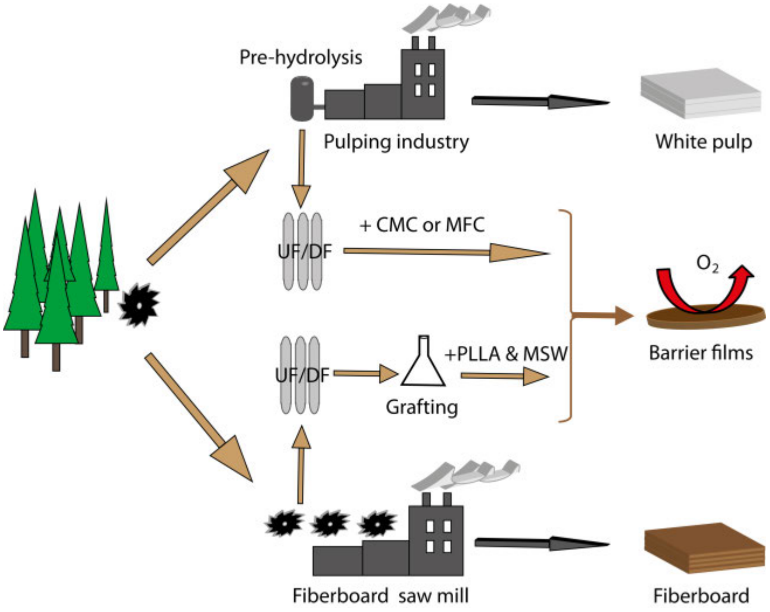

Figure 1. Process flowchart for the developed conversion of side-stream of pulping and fiberboard industries leading to fabrication of renewable barriers from wood hydrolysate.

Experimental

Two types of softwood hydrolysate were used; the first one (SWH) was from hydrothermally treated wood chips which were then upgraded through ultrafiltration and diafiltration through membranes with different cut-off ratio. The second softwood hydrolysate (MSW) was a water-based fraction which was collected directly from the fiberboard mill Masonite AB in Sweden, and upgraded through ultrafiltration and diafiltration with 1 kDa cut-off membrane. Both SWH and MSW were freeze-dried and analysed using size exclusion chromatography (SEC), ion exchange chromatography (IC), infrared (IR) spectroscopy and nuclear magnetic resonance (NMR) spectroscopy. Barrier films were solution casted from SWH together with carboxymethyl cellulose (CMC) or microfibrillated cellulose (MFC) as co-component and deionized water. The hemicellulose-rich MSW was chemically modified by grafting L-lactide branches on the hemicellulose backbone, through ring opening polymerization (ROP) of L-lactide and the copolymer was used later as a compatibilizer in poly L-lactide (PLLA)/MSW blend films. Afterwards mechanical and oxygen barrier properties of the films were characterized.

Results and discussion

It was shown that the upgrading conditions and membrane cut-off affects the oxygen permeability of the blend films with CMC and MFC as co-component. Higher cut-off ratio membranes could separate higher molecular weight wood hydrolysates and the films made of higher molecular weight wood hydrolysates possess better oxygen barrier properties. On the other hand, addition of chemically modified MSW enhanced the miscibility of the hydrophilic wood hydrolysate within the hydrophobic PLLA matrix which as a result improved the flexibility of the blend films significantly.

Conclusion

Films with oxygen permeability (OP) values as low as 0.35 cm^3 µm day^{-1} m^{-2} kPa^{-1} at 50% relative humidity, were produced from aqueous solutions from SWH and CMC. With only 1% (w/w) of compatibilizer the homogeneity of the PLLA/MSW films increased substantially that led to a significant increase of strain-at-break which corresponds to a more flexible film.

Acknowledgments

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References

1. Saadatmand, S., Edlund, U., Albertsson, A.-C. 2011. Compatibilizers of a purposely designed graft copolymer for hydrolysate/PLLA blends, Polymer 52, p. 4648.

2. Saadatmand, S., Edlund, U., Albertsson, A.-C., Danielsson, S., Dahlman, O. 2012. Prehydrolysis in Softwood Pulping Produces a Valuable Biorefinery Fraction for Material Utilization. Environ. Sci. Technol. 46, p. 8389.

Spray application of biopolymers and tailored refining as tools in the production of formable paper material for novel applications

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Abstract

Novel types of fibre-based packaging materials are the promising direction in the product portfolio of modern biorefineries. Despite of the advantageous features of fibre-based packaging material such as: biodegradability, recyclability and renewability, it is lacking the level of formability that plastic packaging materials do have.

The formability of material determines how advanced shapes can be formed for the end product. In respect to the paper-based packaging, high formability would allow to produce containers, trays, shells etc. with an advanced design, using deep-drawing or corresponding type of forming process.

The influence of high-consistency refining, and combination of high and low consistency refining as well as the spraying of different biopolymers on the formability, strength properties and drying shrinkage of the samples has been evaluated in this work. By combining of the above-mentioned treatments it was possible to improve formability strain of the samples from 6.5% to 13.5%.

Experimental

The pulp used in this study was market sulphate pulp from first thinning pine (Pinus sylvestris) produced at UPM Kymmene Pietarsaari mill. The applied xyloglucan (XG) was purified tamarind kernel powder XG; the rest of biopolymers were isolated and prepared at VTT Rajamäki.

High-consistency refining (25% d.s.) was performed at an elevated temperature (110°C) using wing defibrator device (Sundström et al. 1993). Low consistency refining (LCR) was performed in Valley Beater according to SCAN-C 25:76. A4-sized handsheets (grammage 170 g/m^2), were prepared using automatic sheet former “Juupeli” in VTT Jyväskylä. Biopolymers as 2% water solution were sprayed onto wet sheets using a high pressure spray nozzle. After spraying sheets were allowed to dry freely. Formability strain was measured using 2D-formability tester developed at VTT Jyväskylä.

Results

High consistency refining (HCR) has a positive effect on the elongation of paper by curling and axially compressing fibres. LCR straightens fibres, increasing amount of fibre contacts and thus improves bonding within the sheet (Seth 2005). By varying the HCR refining conditions it is possible to create deformations in fibres which would exist in fibres after LCR. The microscopic image of the axial compressions in fibres after combined HCR and LCR treatment is shown in the Figure 1. Figure 2 shows the formability strain of the paper sprayed with different biopolymers, the formability strain was measured at 72°C.

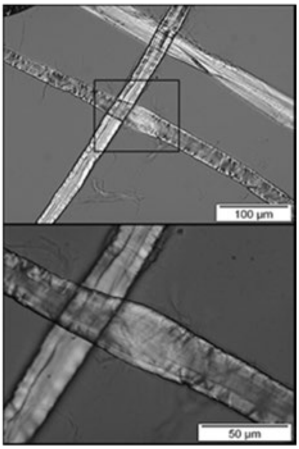

Figure 1. Microscopic Images of the fibres after combined HCR and LCR treatment.

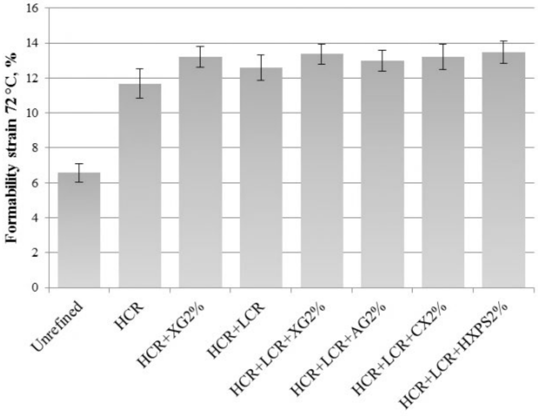

Figure 2. The influence of various chemical and mechanical treatments on the formability strain (72°C) of freely dried paper; (HCR-high consistency refining, LCR-low consistency refining, XG-xyloglucan, AG-arabinogalactan, CX-cationic xylan, HXPS-hydroxypropylated starch).

Combined HCR and LCR treatment has improved elongation of the paper on the almost 7%-points. Spraying of the of the carbohydrate polymers has improved elongation of the paper on somewhat 0.5–1.5%.

It can be suggested that the addition of carbohydrate biopolymers is improving bonding within the sheet by adsorbing on the fibres and creating gel-like layer (Ahrenstedt *et al.* 2008).

Summary

Induction of the certain types of fibre deformations and spraying of biopolymers is the one strategy for the improvement of the strength of fibre joints and bonding in general. Strong bonding within the sheet and high elongation potential of fibres yields in the paper with high formability.

Acknowledgements

Future biorefinery programme of Forestcluster Ltd. and VTT Graduate School are gratefully acknowledged for providing financial support for this work.

References

1. Seth, R.S. 2005. Understanding sheet extensibility. Pulp and Paper Canada 106(2), pp. 33–40.

2. Ahrenstedt, I. et al. 2008. Paper dry strength improvement by xyloglucan addition: Wet-end application, spray coating and synergism with borate. Holzforschung 62(1), pp. 8–14.

Renewable barrier films from wood hydrolysates

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Abstract

To study, develop and enable industrially feasible utilization of wood hydrolysates (WHs), a Hansen's Solubility Parameter (HSP) model was developed. The model aims to design formulations based on WH for efficient oxygen barrier films and coatings. Analyses such as Position Annihilation Lifetime Spectroscopy (PALS) and oxygen permeability (OP) tests strongly supported the model.

Introduction

WHs are hemicellulose-rich biomass derived from liquid side streams of wood processing industries. Our HSP model aims to design and predict formulations of WHs for barrier films and coatings [1–4] for food packaging. The model calculated solubility parameters to relate the chemical composition of WH to oxygen barrier performances.

Experimental

Both softwood and hardwood hydrolysates were collected from hydrothermal treatment of wood chips. Ion exchange chromatography (IC) was used to determine sugar compositions of WH. Films and coatings were produced by casting blends of WHs and other polysaccharides such as carboxymethyl cellulose (CMC) or chitosan. Our HSP model determined the interactions between components in the WH-based films/coatings and further predicted OP. PALS and OP tests were conducted to characterize the films/coatings to support the model (Figure 1).

Results and discussion

Hansen's solubility parameter

The developed HSP model quantified the correlations between chemical structures and molecular interaction of WH-based film and coatings. The results showed that there were strong interactions between lignin and hemicellulose in WH as well as between WH and other co-components such as CMC and chitosan. Stronger interactions lead to a densely packed system and may thus lead to a good barrier performance.

Characterization

PALS detected size and distributions of free volumes in WH-based films and results showed that the predicted more densely packed films had accordingly smaller size for free volumes holes. OP tests also confirmed that films/coatings with a stronger interaction possessed a lower OP.

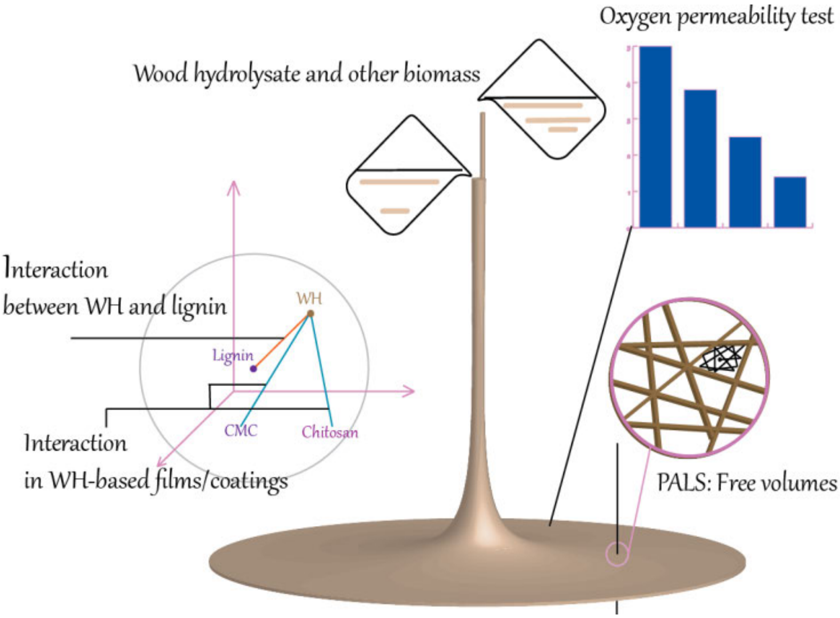

Figure 1. HSP model quantified interactions in WH-based films/coatings relating them to oxygen barrier performance.

Conclusions

We have developed a model based on HSP which has shown a great potential to introduce WH to food packaging industry. The developed model successfully quantified the chemical structure as well as interactions in WH-based films/coatings. Stronger interactions result in a densely packed matrix and thus tend to have a better oxygen barrier performance. Results from PALS and OP analyses strongly supported the model.

Acknowledgements

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References

1. Edlund, U., Ryberg, Y.Z., Albertsson, A.-C. 2010. Barrier films from Renewable Forestry Waste. Biomacromolecules 11(9), pp. 2532–2538.

2. Ryberg, Y.Z., Edlund, U., Albertsson, A.-C. 2011. Conceptual Approach to Renewable Barrier Film Design Based on Wood hydrolysate. Biomacromolecules 12(4), pp. 1355–1362.

3. Yu, Z., Edlund, U., Ryberg, Y.Z., Krause-Rehberg, R., Albertsson, A.-C. 2012. Position Lifetime Reveals the Nano Level Packing in Complex Polysaccharide-Rich Hydrolysate Matrix. Anal. Chem. 84, pp. 3676–3681.

4. Ryberg, Y.Z., Edlund, U., Albertsson, A.-C. 2012. Retrostructural Model to predict biomass formulations for barrier properties. Biomacromolecules 13(8), pp. 2570–2577.

Functionalizing of cellulosic fibres through patented modification reactions to increase hydrophobicity

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Abstract

Cellulose is modified with a patented method from OrganoClick to produce a highly hydrophobic fibre.

Introduction

Alkoxysilanes present highly reactive species which have attained considerable interest by the scientific community and the industry, as they allow for industrial relevant times. Today, OrganoClick AB is in possession of a technology which employs silanes for functionalization of cellulose-based materials. This process is tested on cellulosic fibres from Domsjö Fabriker in order to modify the polarity of the fiber.

Experimental

Specialty pulp with 100 and 50% dry content were used throughout the project. The pulp was disintegrated and thereafter stirred (soaked) in OC-aquasil™, (ethanol (95% purity) solution containing 10% active agents) for 15 minutes. Excess formulation was thereafter filtered of and pressed out and the modified fibres were dried at 150ºC for 5 minutes. The fibres were subsequently washed (to remove the catalyst) by stirring them in water for 20 minutes, filtered and placed in the oven until they were completely dry.

Results

A highly hydrophobic fiber was synthesized trough the patented process. The hydrophobicity has been evaluated by a series of analytical tests.

Contact angle measurements of sheets produced with the hydrophobic fibers were performed with contact angles of up to 150°, see Figure 1.

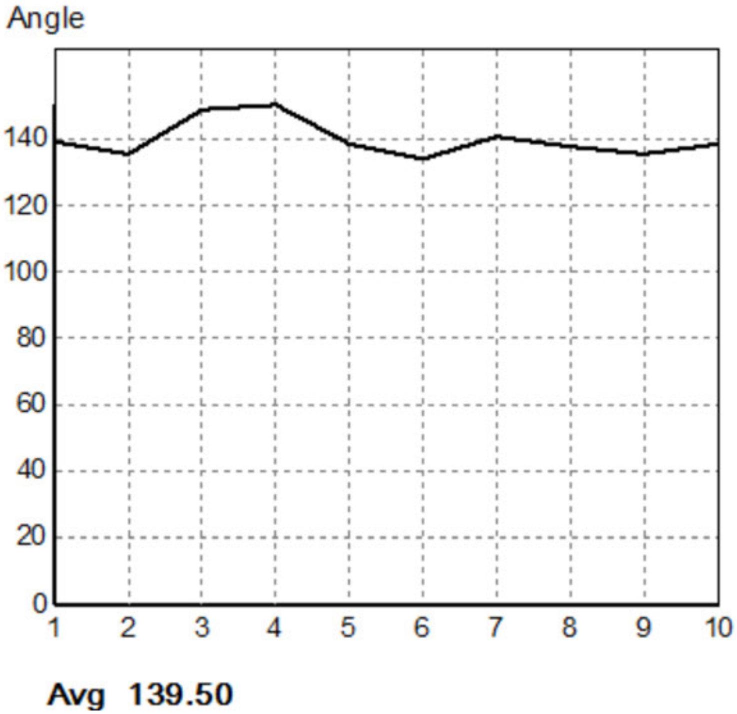

Figure 1. Contact angle measurement.

The fibres preference for various solvents were tested with a clear result that they always preferred the most hydrophobic solvent (see Figure 1 and 2).

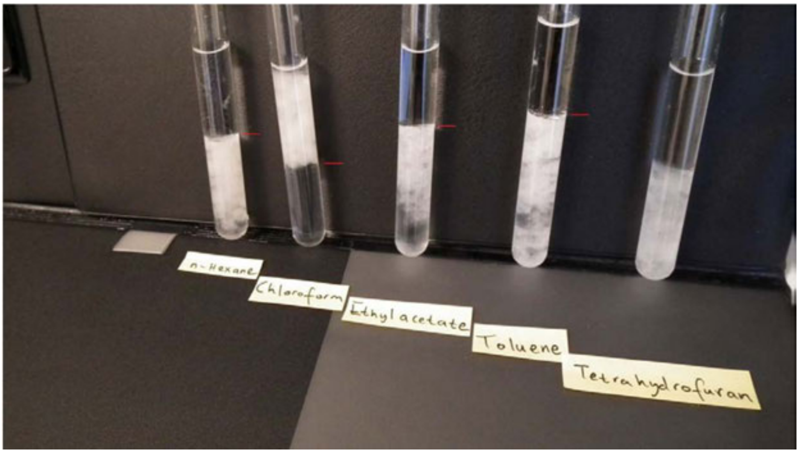

Figure 2. Non-modified cellulose in organic solvent/water system.

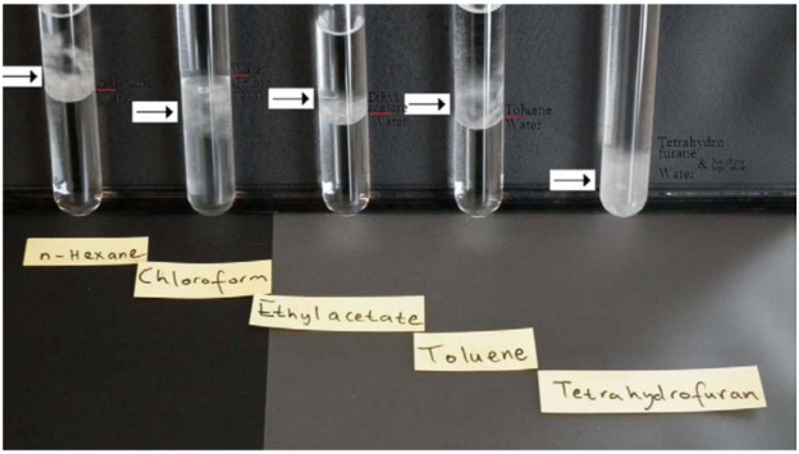

Figure 3. Hydrophobized cellulose in the same system.

Furthermore, analysis of silicon content, as well as WRV and Soxhlet extraction with 1-propanol were performed, all indicating that the fibre had became more hydrophobic and that the hydrophobicity remained also after extensive washing.

Conclusion

The possibility of using the OrganoClick®-technology to functionalize the specialty cellulose of Domsjö Fabriker AB was investigated by using the OC-aquasil™ product to hydrophobize the fibres. It was shown that the mentioned technology can be successfully used to render the fibres hydrophobic, demonstrated by the large contact angle (average 139,5 o using water droplets), by the silicon content, by the WRV and by the fact that the samples stayed hydrophobic even after a prolonged Soxhlet extraction using 2-propanol. It was also clearly shown that the modified fibres prefer organic solvents to water in contrast to untreated fibres.

The potential future applications for the hydrophobic fibres developed in this project can possible be in areas such as bio composites (e.g. plastic components), and in the construction industry, e.g. gypsum where a hydrophobic fibre could be of interest to make the gypsum core less sensible to mold.

Nanocellulose as a toughening agent

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Abstract

Bleached birch Kraft pulp was oxidized using 2,2,6,6-tetramethylpiperidine-1-oxyl radical (TEMPO) mediated oxidation to obtain TEMPO-oxidized fibrillated cellulose (TOFC). It was acetylated and added to PLA suspension in chloroform to prepare composites to weight fractions of 1, 2 and 5%. It was observed that the mechanical behaviour of the composite films was significantly altered upon the addition of TOFC. It was affected by both the weight fraction of TOFC and a DS. Toughness of PLA increased by an order of magnitude at a load of 1 wt% of TOFC with a DS of 0.6. Although the Young's modulus and tensile strength decreased at low fractions of TOFC an increase in both was achieved at 5 wt% load of TOFC having a DS of 0.6.

Introduction

Bio-composites have received a lot of attention during the last couple decades or so. Many research groups aimed to use nanocellulose, due to its high stiffness, as reinforcing agent of polymer matrices. Although many promising results were achieved the deformation mechanisms in this type of composite materials have not been explained yet. Continuum mechanics, which is widely applied, has its limitations due to the assumption of homogeneity. Most of the materials are heterogeneous at micro and nano scales thus new methods have to be applied. Contradictory reports can be found in the literature regarding the effects of nanocellulose on polymer matrices thus there is a need of in depth study of the micromechanics of nanocellulose reinforced composites.

Herein a study on TEMPO-oxidized nanocellulose reinforced composites is presented. In particular, the toughening effect of nanocellulose is addressed. The effect of chemical modification of nanocellulose on the mechanical behaviour of composites is discussed.

Experimental

Bleached birch Kraft pulp was oxidized according to the method introduced by Saito et al. [1] under alkaline conditions. It was mechanically disintegrated until a transparent gel was obtained which, hereafter, is termed TEMPO-oxidized fibrillated cellulose (TOFC). TOFC was acetylated in DMF with acetic acid at 125 ± 5°C for 45 min. A detailed description of the acetylation reaction can be found elsewhere [2].

The degree of substitution of hydroxyl groups was evaluated using a standard Eberstadt method [3]. Commercially available PLA – poly(lactic) acid (NatureWorks 2002D, NatureWorks, Minnetonka, MN, USA) was used as the matrix. PLA was dissolved in chloroform to obtain a suspension having a concentration of 2 wt%. Then it was mixed with the acetylated TOFC dispersed in chloroform to prepare composites to weight fractions of 1, 2 and 5 wt% by solvent casting.

Results and discussion

Toughness increased by an order of magnitude at a load of 1wt% TOFC with a DS of 0.6 and ~ 7 times in the case of TOFC having a DS of 0.4 (Figure 1). The Young's modulus of the composites with 1 wt % load of TOFC decreased at both DS levels. An increase in both the Young's modulus and tensile strength by 10 and 15% respectively was observed at 5 wt% load of TOFC at a DS of 0.6. Addition of 1 wt% of TOFC changes deformation mechanisms at both levels of DS. Strain-to-failure increases two-fold upon the addition of TOFC having a higher DS (Figure 1). Strain-to-failure is ~ 30 and ~ 15 times higher compared to pure PLA at 1 wt% load of TOFC having a DS of 0.6 and 0.4 respectively (Figure 1).

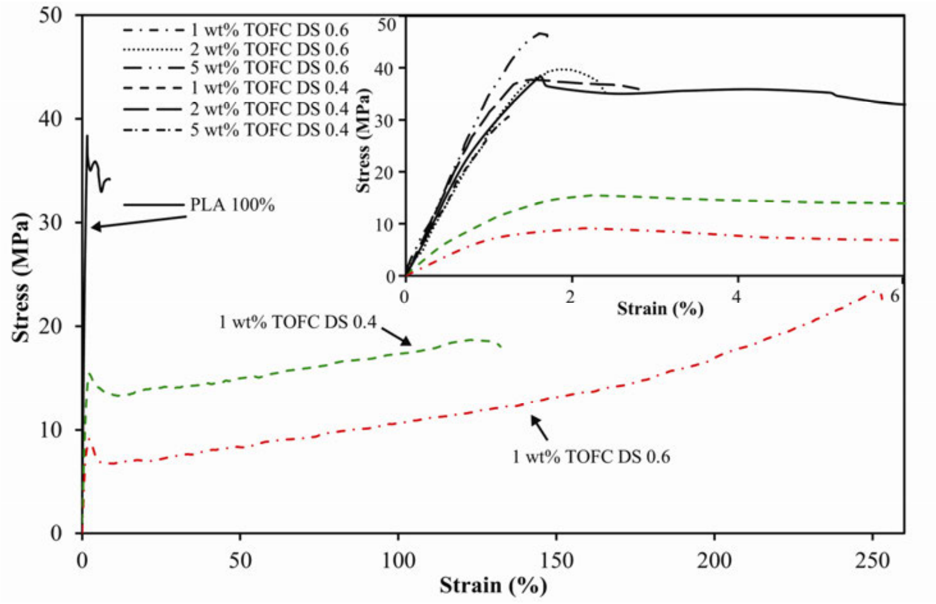

Figure 1. Representative stress-strain curves for filled PLA and pure PLA film. The inset depicts the curves up to a strain of 6% [4].

Conclusions

The addition of TOFC as well as its chemical modification has a significant influence on the behaviour of composite films. The addition of 1 wt% of nanocellulose has resulted in improved toughness of the composites.

References

1. Saito, T., Nishiyama, Y., Putaux, J., Vignon, M., Isogai, A. 2006. Homogeneous Suspensions of Individualized Microfibrils from TEMPO-Catalyzed Oxidation of Native Cellulose. Biomacromolecules 7(6), pp. 1687–1691.

2. Bulota, M., Tanpichai, S., Hughes, M., Eichhorn, S.J. 2011. Micromechanics of TEMPO-oxidized fibrillated cellulose composites. ACS Applied Materials & Interfaces 4(1), pp. 331–337.

3. Tanghe, L.J., Genung, L.B., Mench, W.J. 1963. In Methods in Carbohydrate Chemistry, Whistler, R.L., Green, J.W., BeMiller, J.N., Wolfrom, M.L. (Eds.). Academic Press Inc., London. P. 201.

4. Bulota, M., Hughes, M. 2012. Toughening mechanisms in poly(lactic) acid reinforced with TEMPO-oxidized cellulose. J. Mater. Sci. 47(14), p. 5517–5523.

Cellulose regeneration from solutions of eucalyptus wood in 1-allyl-3-methylimidazolium chloride

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Abstract

In this work, *Eucalyptus globulus* wood has been dissolved in the 1-allyl-3-methylimidazolium chloride (AmimCl) ionic liquid employing microwave radiation as heating source. The wood dissolution process was performed in the microwave oven at 140°C for 20 and 40 min. Then, cellulose was regenerated from the wood liquors using methanol as antisolvent. Fourier transform infrared spectroscopy (FTIR) was employed to characterize the recovered product and compare it to the reference material, microcrystalline cellulose (MCC).

Introduction

Cellulose is the principal component of the wood cell wall and the most abundant polymer on Earth. In the context of the biorefinery and the efficient employment of lignocellulosic materials, the development of green processes for dissolving wood and separating cellulose would be really interesting [1]. Ionic liquids are an attractive alternative in this regard. Recently, ILs have been employed as wood and cellulose solvents [2–4]. Thus, the most promising ILs for biomass dissolution seem to be those with acetate and chloride anions, and imidazolium cations [4]. The aim of this work is to regenerate cellulose from eucalyptus wood dissolved in 1-allyl-3-methylimidazolium chloride, to analyze it by FTIR and compared it to microcrystalline cellulose.

Experimental

4% samples of *Eucalyptus globulus* wood (provided by Torras Papel) were dissolved in the 1-allyl-3-methylimidazolium chloride ionic liquid (AmimCl, Iolitec) with a microwave oven (Berghof SpeedWave Four) at 140°C and two different dissolution times (20 or 40 min). Cellulose was regenerated from the wood solutions using dry methanol (Panreac) as antisolvent in a 10/1 methanol/wood solution ratio. Regenerated cellulose was collected by filtration, dried overnight, and analyzed by FTIR (Mattson Satellite 5000); the spectra of regenerated celluloses were compared to that of microcrystalline cellulose (Sigma Aldrich), employed as reference material.

Results and discussion

The FTIR spectra of MCC and the regenerated celluloses from solutions of eucalyptus wood in AmimCl at 140°C and the studied dissolution times (20 and 40 min) are displayed in Figure 1. According to the results of the FTIR spectra, regenerated cellulose was very similar to MCC, and showed the characteristic vibration bands of the glucose rings at 1160, 1111 and 897 cm^{-1} [4]. In addition, the characteristic aromatic skeletal vibration of the lignin rings, located at 1510 cm^{-1}, is not observed in the spectra of regenerated celluloses, so cellulose is not recovered together with lignin [3]. Therefore, cellulose has been successfully regenerated under the studied conditions.

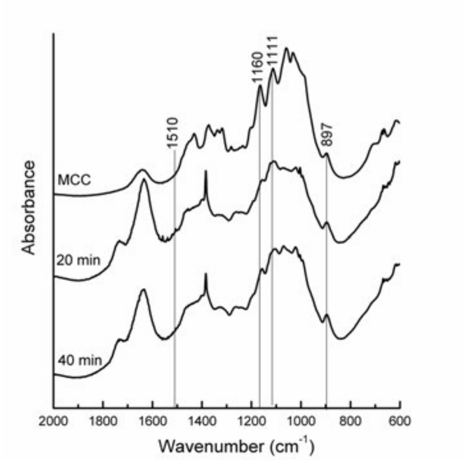

Figure 1. FTIR analysis of MCC and regenerated celluloses (140°C; 20 or 40 min).

Conclusions

The current study shows that cellulose can be regenerated from solutions of *Eucalyptus globulus* wood in 1-allyl-3-methylimidazolium chloride using methanol as antisolvent.

Acknowledgment

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References

1. Xie, H., Kilpeläinen, I., King, A., Leskinen, T, Järvi, P., Argyropoulos, D.S. 2010. Opportunities with wood dissolved in ionic liquids. ACS Symposium Series, 1033, p. 343.
2. Fort, D.A., Remsing, R.C., Swatloski, R.P., Moyna, G., Rogers, R.D. 2007. Can ionic liquids dissolve wood? Processing and analysis of lignocellulosic materials with 1-n-butyl-3-methylimidazolium chloride. Green Chem. 9, p. 63.
3. Casas, A., Alonso, M.V., Oliet, M., Rojo, E., Rodriguez, F. 2012. FTIR analysis of lignin regenerated from Pinus radiata and Eucalyptus globulus woods dissolved in imidazolium-based ionic liquids. J. Chem. Technol. Biotechnol. 87, p. 472.
4. Casas, A., Palomar, J., Alonso, M.V., Oliet, M., Omar, S., Rodriguez, F. 2012. Comparison of lignin and cellulose solubilities in ionic liquids by COSMO-RS analysis and experimental validation. Ind. Crop. Prod. 37, p. 155.

Production and separation of water soluble cello-oligomers by supercritical water treatment and membrane filtration

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Abstract

Microcrystalline cellulose was dissolved using rapid supercritical water treatment. Formed cello-oligomers of DP3-9 were separated and concentrated by membrane filtration (500 Da cut-off).

Introduction

Supercritical water treatment dissolves cellulose as a low molar mass polymer in a very rapid reaction. [1] Cellulose undergoes fragmentation reactions under supercritical water conditions resulting in water soluble mono- and oligosaccharides and acids from retroaldol reactions. Depending on the conditions, a certain cellulose fraction is solvated as polymer that regenerates as cellulose II substrate upon cooling. [2]

Experimental

A plug-flow reactor was used to treat microcrystalline cellulose in supercritical water at 385°C for 0.15 s at 25 MPa. After the removal of precipitated cellulose, membrane diafiltration was performed by an Alfa Laval TestUnit M20 with a LabStack M20 filtration module. Used membrane was a Nadir NP030 P of 500 Da cut-off. The operated filtration surface area was 0.144 m^2. 5 liters of the solution from the supercritical water treatment was applied in the filtration unit. The volume was kept constant by adding ion exchanged water during the process. In total 25 liters of permeate was removed. In order to determine the effectiveness of the purification, the development of flux, absorbance, and TOC were followed. Oligomer concentrations were analysed by HPAEC-PAD with a PA-100 column.

Results and discussion

Supercritical water treatment at 385°C resulted in practically complete dissolution of microcrystalline cellulose. In the following 24 hours, 26 wt% of dissolved cellulose precipitated at room temperature and was removed by a 5–10 µm filter. In subsequent membrane filtration, low molar mass compounds permeated through the membrane and were removed with permeate whereas the compounds of higher molar mass were retained in the system. HPAEC-chromatograms (Figure 1) confirm that a majority of the monosaccharides and degradation products were removed. A significant amount of the DP3-9 oligomers remained in the retentate resulting in purification of the cello-oligomers. The polymeric cellulose fragments of higher molar mass were already largely removed by precipitation and filtration prior to the membrane filtration.

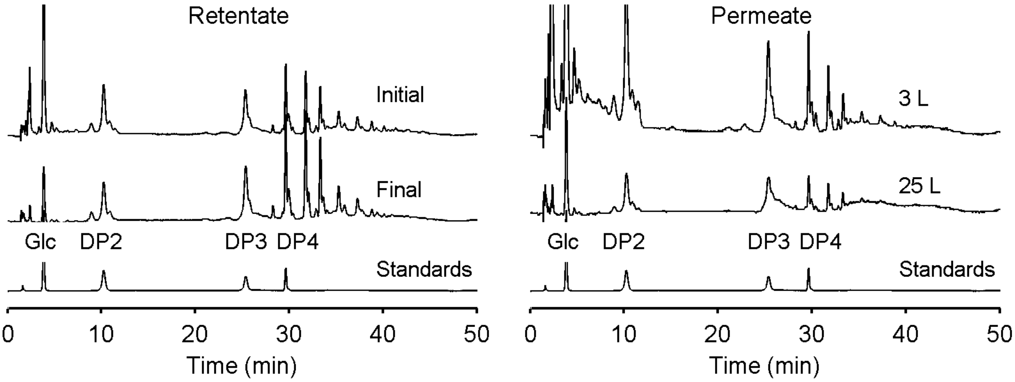

Figure 1. Concentrations of glucose and cello-oligomers in retentate in the beginning and at the end of the experiment (left), and in permeate after 3 and 25 liters were removed (right).

During the filtration, the total organic carbon content of the solution was reduced from 340 mg/L to 150 mg/L. The development of the absorbance was in accordance with the TOC-results. During the filtration, the flux decreased from 60 to 32 L / (m^2 h) due to concentration polarization. Figure 1 shows that although the 500 Da cut-off membrane is capable to retain a majority of the cello-oligomers in the retentate, a part of the oligomers permeate through the membrane. Therefore, it seems possible to enhance the separation efficiency by using a membrane with a lower cut-off.

Conclusions

We successfully demonstrated how cello-oligomers are purified by a membrane filtration with a 500 Da cut-off membrane. Therefore, it is a feasible downstream process in the production of water soluble oligosaccharides from cellulose by supercritical water treatment. We estimate that the performance of the filtration can be improved by optimizing filtration time and by selecting a membrane of lower cut-off.

Acknowledgements

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References

1. Sasaki, M., Adschiri, T., Kunio, A. 2004. Kinetics of Cellulose Conversion at 25 MPa in Sub- and Supercritical Water. AIChE J. 50, pp. 192–202.

2. Yu, Y., Wu, H. 2009. Characteristics and Precipitation of Glucose Oligomers in the Fresh Liquid Products Obtained from the Hydrolysis of Cellulose in Hot-Compressed Water. Ind. Eng. Chem. Res. 48(23), pp. 10682–10690.

Comparison of oxygen delignification of high-kappa pine Kraft pulp in throughflow and batch mode

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Abstract

A high delignification-cellulose degradation selectivity is needed for oxygen delignification of high-kappa softwood pulps in order to produce a bleachable-grade pulp of good viscosity. This may be achieved by keeping the NaOH concentration at a relatively low but constant value throughout the delignification process [1]. To evaluate this concept, a 65 kappa pine Kraft pulp with viscosity of 1295 ml/g was oxygen delignified in a throughflow type Berty reactor where the pulp is kept in a basket at medium consistency. A relatively high feed flow rate of the oxygenated caustic solution results in essentially constant NaOH and dissolved oxygen concentrations during the delignification process. These experiments show that it is possible to obtain a significantly higher degree of delignification in the Berty reactor than in a batch reactor at similar viscosities and lignin-free yields of the pulps.

Introduction

A promising method for increasing the efficiency of softwood delignification to reach a bleachable grade pulp is cooking to a high kappa number pulp (60–90) followed by oxygen delignification to a given kappa number [2]. Until now, the oxygen delignification kinetics of high- kappa number pine Kraft pulp has been examined only in batch reactors. Since the caustic concentration decreases in batch reactors over time due to acid formation in the reaction process, the efficiency of the process decreases and requires multiple stages with fresh alkali introduction to reach a bleachable grade pulp. An alternative approach is to use a through flow reactor with sufficient supply of an oxygenated caustic solution. This approach also may potentially increase the pulp yield and viscosity of the final Kraft pulp [3].

Results and discussion

An industrially produced high-yield pine kraft pulp (kappa number 65, intrinsic viscosity of 1295 mg/l and pulp yield 51%) was used. Table 1 shows the conditions for the batch reactor multistage oxygen delignification at 10% consistency and 3, 2 and 1% NaOH (o.d pulp) corresponding to an initial alkali concentration of 3.3, 2.2 and 1.1 g/l NaOH. The alkali concentrations in three separate flow-through experiments are 1.1, 1.8 and 2.2 g/l NaOH, all at 90 min, 95°C, 7 bar O_2. The results of these four experiments are compared in Figure 1 and 2.

Table 1. Conditions of different oxygen delignification experiments

Batch reactor (Airbath digester)		
OOO (pulp kappa 65)	3% NaOH	30 min, 85°C, 7 bar O_2
	2% NaOH	60 min, 95°C, 7 bar O_2
	1% NaOH	60 min, 95°C, 7bar O_2
Berty reactor (Continuous stirred tank reactor)		
O (pulp kappa 65)	1.1, 1.8 and 2.2 g/l NaOH	90 min, 95°C, 7 bar O_2

The results in Figure 1 show that the high kappa softwood Kraft pulp can be delignified to the same level (kappa 20) in both approaches with a slightly higher viscosity (30 ml/g) in flow-through experiments performed using 1.8–2.2 g/l NaOH. More importantly, the improvement in lignin-free pulp yield obtained with the throughflow approach in Figure 2 is almost 1.5% based on the original wood weight.

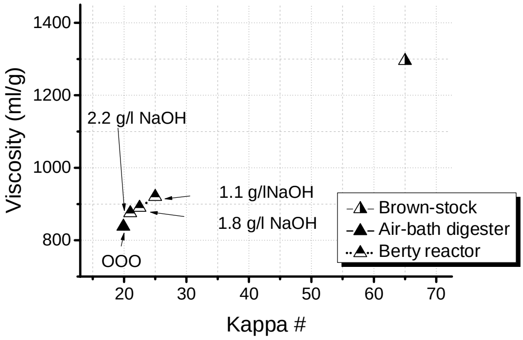

Figure 1. Effect of alkali charge on viscosity and kappa in flow through and batch reactor.

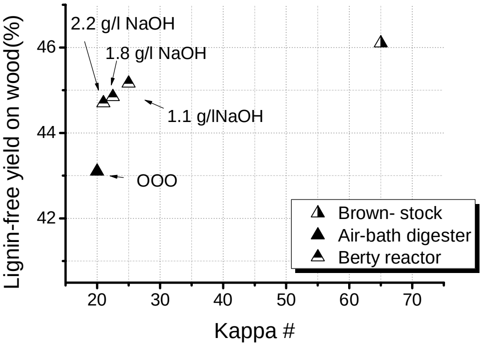

Figure 2. Comparison of Lignin-free yield on wood (%) versus kappa number for pulps used in flow through and batch reactor.

Acknowledgement

The authors like to acknowledge the Forestcluster LTD for financial care.

References

1. van Heiningen, A., Ji, Y. 2012. Southern pine oxygen delignified pulps produced in a Berty throughflow reactor: How to obtain the highest degree of delignification while maintaining pulp yield and quality. Tappi Journal 11(3), pp. 9–18.

2. Agarwal, et al. 1999. Kinetics of Oxygen Delignification. JPPS 25(10), pp. 361–366.

3. Ji, Y., Van Heiningen, A. 2007. A new CSTR for oxygen delignification mechanism and kinetics study. Pulp & Paper-Canada 108(5), pp. 38–42.

Hemicellulose precipitation in methanol-water solutions and its effect with solubility parameters

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Introduction

The interest in the use of the wood hemicelluloses has increased in the last years, specifically as a raw material for materials production because their film forming properties. This research contributes to the understanding of the phenomenon by studying the solubility of the hemicellulose. Regarding this, evaluation of Hansen solubility parameters (HSP) will allow a first step towards the prediction of hemicellulose solubility in different organic solvents. The following questions are expected to be responded regarding precipitation of hemicelluloses:

- What is the effect of the methanol concentration in precipitation yield?
- Which is the effect of hemicellulose structure and purity on its precipitation?
- Are HSP a tool to predict precipitation behavior of hemicellulose?

Methodology

Background

The HSP concept (Hansen 2000) regards the total cohesion energy for a molecule as a sum of three individual intermolecular interactions; the nonpolar forces (D), the dipole dipole interactions (P), and the hydrogen bonding (H) so that the solubility parameter, δ, may be expressed in accordance with eq. (1):

$$\delta^2 = \delta_d^2 + \delta_p^2 + \delta_h^2 \tag{1}$$

The difference "R_a" between the two molecules to be mixed, denoted P and S respectively, is quantified by eq. 2 and it represents a measure of the interaction between two molecules:

$$(R_a)^2 = 4(\delta_{Dp} - \delta_{Ds})^2 + (\delta_{Pp} - \delta_{Ps})^2 + (\delta_{Hp} - \delta_{Hs})^2 \tag{2}$$

Experimental

Precipitation with methanol were carried out at concentrations of 4:1, 3:1 2:1 and 1:1 (v/v) from liquors formed with hemicelluloses obtained from *Eucalyptus globulus* holocellulose (H_1) and wood (H_2) extractions with 5% KOH solution at 20°C. Precipitation yield was determinate, HPLC analysis were performed to determine sugar concentration, whereas molecular weight where obtained by HPLC-SEC. Hansen solubility parameters (HSP) for water and methanol were based on literature (Hansen 1976) while solubility parameters of hemicellulose fragments were estimated from the group contribution method based on the estimation of molecular structure. Films were made by casting with de H_1 and H_2 fractions.

Results

For H_1 and H_2 there was an increasing trend in precipitation yield with methanol addition for both hemicellulose fractions (Table 1) and they are in agreement with the HSP difference with the solvent, nevertheless small differences implies significant changes in precipitation. From carbohydrate analysis (data not shown), xylose was the predominant monomer, indicating a low quantity of ramifications if we consider the model presented by Evtuguin et al. (2003). Considering this model for H_1, a xylose linear chain was proposed for carry out the calculations with the group contribution model to obtain the HSP of the H_1 fraction. Lignin content in H_2 was 12% and this content was included in the calculations of HSP.

Table 1. Solubility parameters of the different hemicellulose fractions.

				R_a (methanol concentration)			
Component	δ_d	δ_p	δ_h	(1:1)	(2:1)	(3:1)	(4:1)
H_1	27,79	16,24	32,19	25,06	25,46	25,82	26,09
Precipitacion yield				**48,10%**	**76,26%**	**81,22%**	**84,28%**
H_2	27,08	15,98	30,35	23,71	23,86	24,11	24,32
Precipitacion yield				**40,71%**	**77,01%**	**78,26%**	**80,02%**

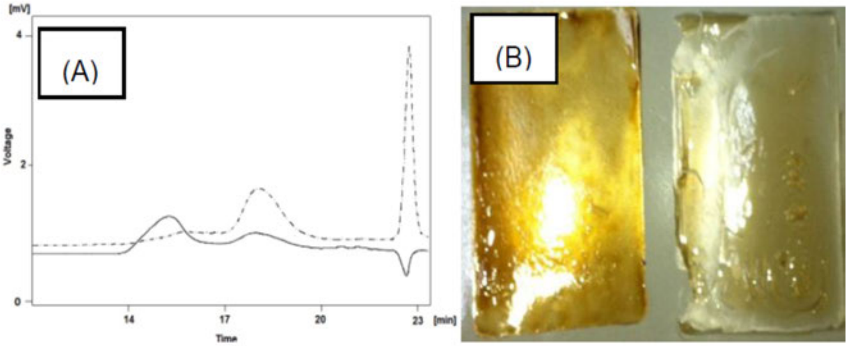

Figure 1. (A) SEC analysis of hemicellulose fraction H_2. Dotted line: IR signal. Solid line: UV signal. **(B)** hemicellulose films, H_2 (left) and H_1 (right).

SEC analysis presented a bimodal behavior (Figure 1A), showing at least two different populations of precipitates at approximately 8 kDa (23 minutes) and 100 kDa (17 minutes approx.) in hemicellulose H_1, in hemicellulose H_2 8kDa and 120kDa. The simultaneous signal at IR and UV detector show evidence of lignin associated to hemicellulose, and that is the reason of the difference between both fractions. Films with the H_1 and H_2 fractions were produced by casting (Figure 1B), and the H_2 films higher stability and elasticity, perhaps because the presence of lignin which can act as a plasticizer, this topic requires further investigation.

Conclusion

There was an increasing trend in precipitation yield with methanol addition for both hemicellulose fractions (H_1 and H_2). HSP represents the phenomenon of precipitation evaluating the interactions between molecules, nevertheless small differences implies significant changes in precipitation. SEC analysis presented a bimodal behavior, showing at least two different populations of precipitates at approximately 8 kDa and 100 KDa (H_1), and 120 kDa (H_2). This increment of 20 kDa could be explained because of the associated lignin with the hemicellulose. Lignin present in hemicellulose fractions could act as a plasticizer in films produced.

Acknowledgements

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References

1. Evtuguin, D.V., Tomas, J. L. et al. 2003. Characterization of an acetylated heteroxylan from Eucalyptus globulus Labill. Carbohydrate Research 338(7), pp. 597–604.

2. Hansen, C.M. 2000. Hansen solubility parameters : a user's handbook. Boca Raton, Fla., CRC Press.

Recovery of high molar mass hemicelluloses from birch saw dust

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Introduction

One group of the interesting raw materials possible to harvest from biorefinery process streams is the hemicelluloses having a molar mass higher than 15 kDa. They can be used, for instance, in manufacturing of packaging films. The fraction used in the film manufacturing should contain only small amount of impurities such as lignin derivatives. Moreover, the hemicellulose content of the fraction should be high. This study aims to developing of a process, in which the high molar mass hemicellulose fraction is produced from birch saw dust.

Materials and methods

The hemicelluloses were extracted from birch saw dust with pressurized hot water in a flow-through system with a 300 liter extraction chamber. The extraction temperature was below 175°C and flowrate approximately 20 L/min in all the extractions. The wood extract was treated with the RC70PP ultrafiltration (UF) membrane (10 kDa, regenerated cellulose, Alfa Laval) to produce the fraction containing the high molar mass hemicelluloses. The fractionations were performed with the CR-filters at 60°C at 2 bar. Fouling of the membrane was evaluated by measuring pure water flux before and after the fractionation. Membranes were cleaned with alkaline cleaning agent.

Results and conclusions

This study has shown that producing of a high molar mass hemicellulose rich fraction from birch saw dust is possible by combining pressurized hot water extraction process with UF. The best produced fractions fulfilled the requirement for molar mass (Table 1). However, after the UF the lignin derivative content of the fractions was too high, about 20% of TDS (Table 1). Diafiltration after the UF step was not efficient enough for lignin removal. This means that for producing the high molar mass hemicellulose fractions, which contain only small amount of lignin, a hybrid process, in which lignin derivatives are removed either before or after the UF step, is needed. The lignin removal step before the UF might also improve the filtration capacity, which decreases significantly due to the increasing TDS of the feed when the fractionation was proceeding.

Table 1. Information on fractionation results achieved during this study.

The birch extract used as the feed		**The produced high molar mass fraction**		
TDS, %	**Hemicelluloses, %**	**Average Molar mass, kDa**	**Hemicelluloses, g/L**	**Lignin from the TDS, %**
4.7	3.3	**31**	124	18
2.3	1.7	**27**	93	21

This study proved that the hydrophilic RC70PP membrane is a feasible membrane for concentration of the high molar mass hemicelluloses. Although the fouling potential of the wood extracts is high, the RC70PP membrane is not significantly fouled when wood extracts are treated and its filtration capacity can be fully restored by alkaline cleaning (Figure 1).

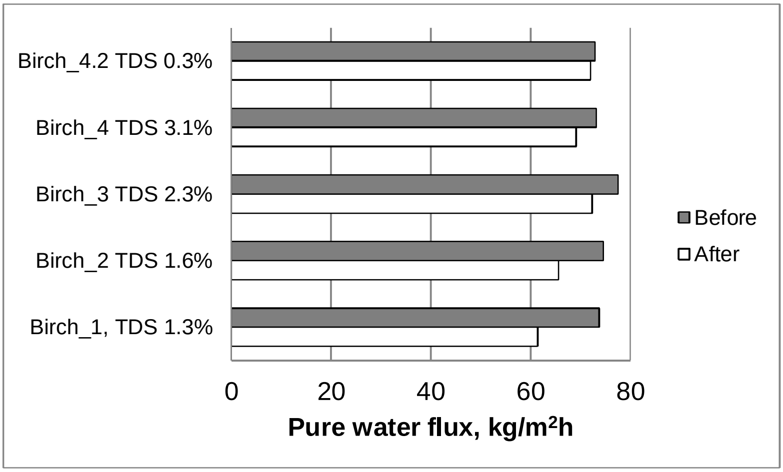

Figure 1. Pure water fluxes of the RC70PP membrane measured before and after the fractionation of wood extracts with the CR-350 filter at 50°C and at 1 bar. The rotor speed was 9.5 m/s. The membrane was cleaned with alkaline cleaning agent after the experiments.

Acknowledgements

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Scale-up of pressurised hot flow-through extraction system

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Introduction

Oligomeric and polymeric hemicelluloses are a renewable raw material source, which is not fully utilized in industry. Wood hemicellulose can be utilised industrially e.g. for films and barriers in packaging. Xylo-oligosaccharides from lignocellulosic biomass have also been used to produce food additives and nutraceuticals [1]. Pressurised hot water extraction (PHWE) using a flow through technique has been proven to be an effective way to extract hemicelluloses from wood [2, 3].

Experimental

Pressurised hot water extraction was performed at two different scales: laboratory scale (50 mL extraction vessel) and pilot scale (300 L extraction vessel). Laboratory-scale extractions were carried out in order to determine the optimal extraction conditions (temperature, time, and flow rate) for extracting oligomeric and polymeric hemicellulose from birch and spruce sawdust. The small scale experiments are rapid, allowing relatively quick screening of the extraction parameters. The best extraction conditions obtained in the laboratory scale experiments were selected and tested in the pilot scale extraction system (Table 1). Extraction vessel was pre-filled with water using higher flow rate and the actual extraction started when air was released from the extraction vessel and the slower constant flow through vessel was adjusted.

Table 1. Extraction parameters.

	Spruce	**Birch**	**Spruce**	**Birch**
Volume of the extraction vessel	300 L		50 mL	
Sawdust	117 kg	137 kg	19.4 g	22.8 g
Extraction temperature, °C	180	165	180	165
Extraction time, min	60	60	60	60
Flow, L/min	20	20	-	-
Flow, mL/min	-	-	3.3	3.3
Pre-filling stage	5min 40 L/min	5min 40 L/min	5 min 6.7 mL/min	5 min 6.7 mL/min

Results and discussion

The most of carbohydrates were extracted from spruce sawdust at 20 minutes (Figure 1). For birch sawdust the most of carbohydrates were extracted after 25–30 minutes.

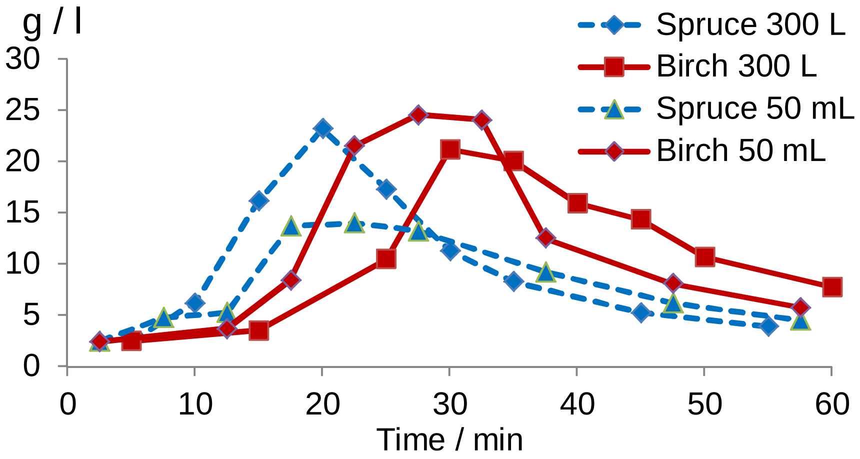

Figure 1. Extracted carbohydrates obtained with small and large scale extraction vessels.

Yield of the extracted carbohydrates was higher with spruce sawdust compared to birch sawdust due to higher extraction temperature. Birch sawdust was extracted using lower temperature to decrease the formation of lignin precipitates, which otherwise contaminate the product. Also larger 300 L extraction vessel gave higher extraction yield for spruce at the 20 minutes than 50 mL vessel, probably due to technical differences between large scale and small scale systems, especially the temperature control. Xylans from birch sawdust were released earlier after 20 minutes with 50 mL vessel than with 300 L vessel.

Conclusions

Based on these results, laboratory scale and scaled-up small pilot scale system gave relatively similar results. Carrying out laboratory scale experiments is a rapid way to screen extraction parameters which can be applied to larger scale extractions. There are still differences between extraction yield and extraction time but small scale extractions give predictions for further experiments at large scale.

References

1. Moure, A., Gullón, P., Domínquez., Parajó, J. 2006. Advances in the manufacture, purification and applications of xylo-oligosaccharides as food additives and nutraceuticals. Process Biochem. 41, pp. 1913–1923.

2. Kilpeläinen, P., Leppänen, K., Spetz, P., Kitunen, V., Ilvesniemi, H., Pranovich, A., Willför, S., Pressurised hot water extraction of acetylated xylan from birch sawdust, Nord. Pulp Pap. Res. J. (Submitted.)

3. Leppänen, K., Spetz, P., Pranovich, A., Hartonen, K., Kitunen, V., Ilvesniemi., H. 2011. Pressurized hot water extraction of Norway spruce hemicelluloses using a flow-through system. Wood. Sci. Technol. 45, pp. 223–236.

Fractionation of PHW extracts in a pulp mill biorefinery. Part I: a process concept

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Introduction

Pulp mill biorefinery schemes have been investigated from several points of view. These include the influence of hemicelluloses extraction on the quality of pulp and the overall energy balance, energy efficiency of thermal separations, investment and operation costs as well as the role of subsidies for process economy. Obviously, separation technologies play a key role in production of bio-based chemicals in forest biorefineries. Here we focus on production of monosaccharides and other chemicals from hemicelluloses extracted from pine with pressurized hot water prior to pulping. The proposed process scheme (Figure 1) involves fractionation of the hot water extract with membrane filtration, hydrolysis of hemicelluloses with sulfuric acid, and recovery of monosaccharides and other products by chromatography [1]. Each process step was investigated experimentally by using an authentic pine extract (P-factor 200).

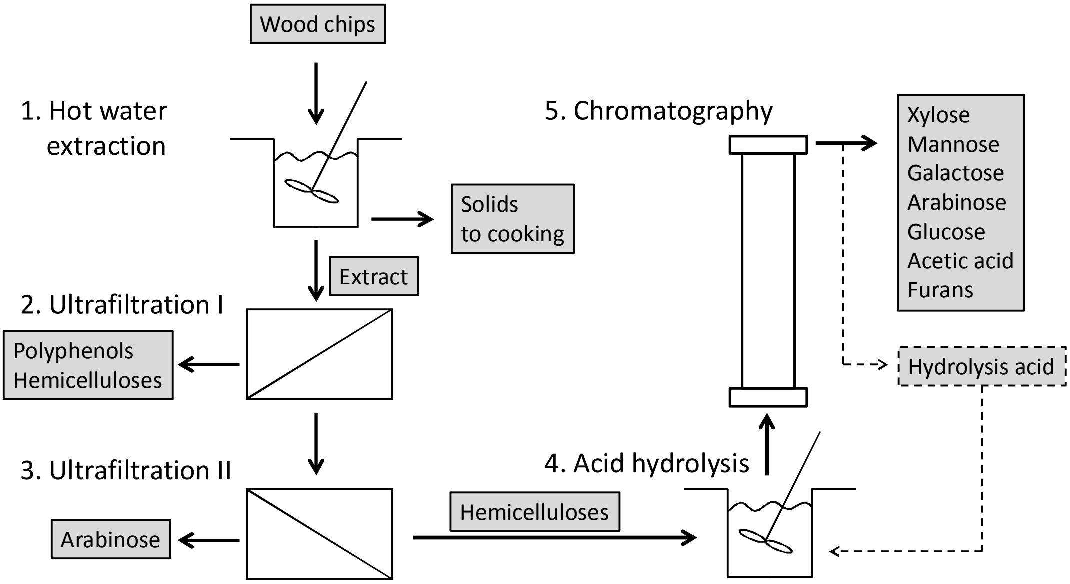

Figure 1. Scheme for processing pressurized hot water extracts in a pulp mill biorefinery.

Results

The first treatment step for hot the water extract is purification and concentration of the hemicelluloses by membrane filtration. Several membranes were tested (UC030, UFX10, UFX5, GR95PP). It was found that the extract could not be concentrated with UFX5 in a single step (Figure 2, left) but two filtration steps are necessary. In the first step, a 30 kDa UF membrane (UC030) was used to remove polyphenols. The yield of hemicelluloses was reasonably good since approximately 75% of carbohydrates passed the UC030 when VRF was 11. The first UF stage both purified the hemicellulose solution and improved the filtration capacity in the second stage where a tighter UF membrane (UFX5, 5 kDa) was used to concentrate the solution (Figure 2, left). The total carbohydrate concentration in UFX5 concentrate was 29 g/L. It was not limited by membrane performance but the amount of available extract. The monosaccharaide content of the permeate of the UFX5 membrane was interesting: it was found to contain mostly arabinose, which could thus be recovered as a separate product fraction.

Hemicelluloses recovered and purified with ultrafiltration were hydrolyzed to monosaccharides at 80°C by using sulphuric acid (5 wt-% to 21 wt-%) as a catalyst. The reaction was complete in less than two hours at the highest acid concentration. Formation of furans (furfural or hydroxymethyl furfural) from monosaccharides was found to be slow but acetic acid was formed rapidly within the first 10 minutes.

Chromatographic separation with strong acid ion exchange resin (H$^+$ form) as the stationary phase was used to fractionate the acidic hydrolysate into a number of fractions. CS16GC (Finex Oy, Finland) was selected out of several resins tested. Monosaccharides were recovered at high purity (Figure 2, right). The acid fraction contained some monosaccharides, but this does not lead to a loss of monosaccharide yield because the acid fraction can be recycled back to the hydrolysis reactor (Figure 1). The monosaccharide fraction contained all the different monosaccharides because they are not separated from each other with a SAC resin in H+ form. The third product fraction was nearly pure acetic acid. Also the fermentation inhibitors were effectively separated from other products during the chromatographic fractionation.

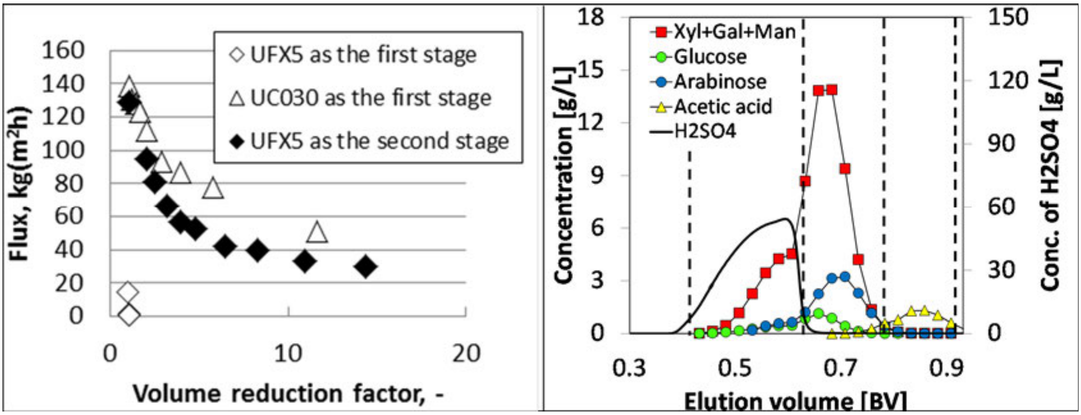

Figure 2. Left: Ultrafiltration of PHWE. Right: chromatographic fractionation of acid hydrolysed hemicellulose concentrate.

These experimental results demonstrate that membrane filtration and chromatographic separation can be combined to produce and recover several chemicals from pressurized hot water extracts in a pulp mill biorefinery.

References

1. Sainio, T., Kallioinen, M., Nakari, O., Mänttäri, M. 2012. Production and recovery of monosaccharides from lignocellulose hot water extracts in a pulp mill biorefinery, Bioresource Technology, in press.

Fractionation of PHW extracts in a pulp mill biorefinery. Part II: enhanced performance of ultrafiltration

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Introduction

Ultrafiltration (UF) in two steps (the 30 kDa UC030 followed by the 5 kDa UFX5) has been proposed for fractionation of hemicelluloses from pressurized hot water extract (PHWE) of pine [1]. Generally, it is expected that high temperature improves the filtration capacity and increases the energy efficiency of the fractionation process. However, it has been shown that the second fractionation step is almost impossible to perform due to severe filtration capacity decline and fouling if the first step is conducted at 70°C [2]. The goal of this study was to find out if the proposed fractionation process could be enhanced by adsorption pretreatment.

Experimental

Nonionic hydrophobic polymer Amberlite XAD–16 (Rohm and Haas) was chosen as the adsorbent. The pretreatment was done in two ways: by using the adsorbent in the feed tank during the filtration or by performing the pretreatment as a separate step before the UF fractionation.

Results and discussion

Adsorption pretreatment decreased the amount of lignin and wood extractives in the extract significantly (Table 1).

Table 1. Influence of the adsorbent pretreatment performed as a separate step on the content of the pine extract.

	Original pine extract	Pretreated pine extract
UV-abs. 280 nm	70	24
TOC, mg/L	8 790	5 360
Turbidity, NTU*	3 660	40
Fatty acids, mg/L	16	7
Resin acids, mg/L	18	>5
Lignans, mg/L	43	>5

*sample was not prefiltered

The pretreatment resulted in improved filtration capacity at the second fractionation step (UFX5) and enabled the operation of both fractionation steps at 70°C. However, it was also observed that the first fractionation step with the 30 kDa membrane is necessary to achieve a stable filtration capacity at the second fractionation step even in the case of adsorption pretreatment (Figure 1). The best filtration capacity of the second step (UFX5) was achieved, when the adsorbent pretreatment was performed in a separate vessel before the first fractionation step. This option was thus adopted for subsequent fractionation experiments performed in semi-pilot scale. In the semi-pilot scale the pretreatment enabled a successful operation at 70°C at the both fractionation steps. The filtration capacity at the second step (UFX5) decreased only from about 100 only to 80 kg/(m^2 h bar) although the volume reduction factor value was as high as 28 at the end of the filtration. The UFX5 membrane was not fouled during the experiment.

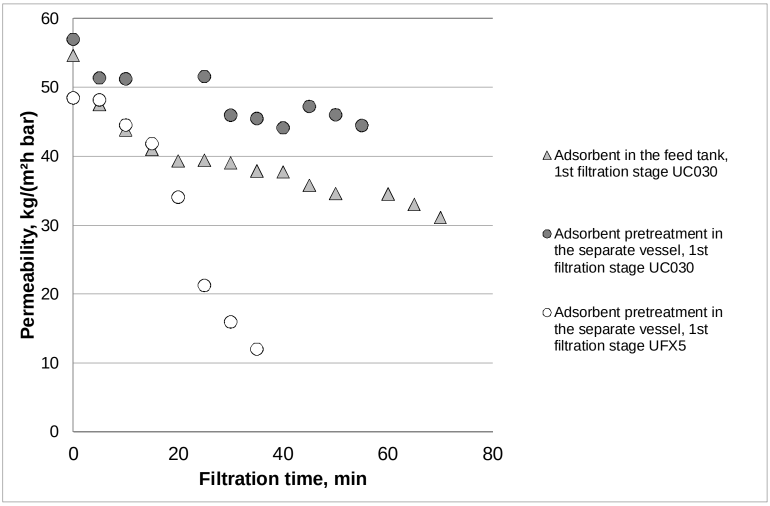

Figure 1. Filtration capacities (permeabilities) of the UFX5 membrane at the second fractionation step after the different adsorbent pretreatment options.

Conclusions

This study demonstrates that UF fractionation of wood extracts can be significantly enhanced with the adsorption pretreatment with XAD16. Optimisation of pretreatment conditions and dosing is needed to minimise possible hemicellulose losses due to the adsorption treatment.

References

1. Sainio, T., Kallioinen, M., Nakari, O., Mänttäri, M. 2012. Production and recovery of monosaccharides from lignocellulose hot water extracts in a pulp mill biorefinery, Bioresource Technology. (In press.)

2. Kallioinen, M., Koivula, E., Puro, L., Mänttäri, M. 2011. Influence of operating temperature on fractionation in ultrafiltration of wood-based hydrolysate, NWBC 2011, Stockholm, March 22–24.

Extraction of hemicellulose and condensed tannin from spruce bark

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Introduction

Tannin industry is looking for new industrial sources for condensed tannins due to the limited availability of the current raw materials such as *Acacia* bark and quebracho wood. Spruce bark is a promising source of polyphenolic compounds including condensed tannins, which can be extracted in an unpressurized hot water treatment. In addition to phenolic compounds, hot water extraction dissolves a large amount of hemicellulose and monosaccharides from spruce bark. To be able to fractionate these two groups of compounds and to find uses for the extractable bark sugars, it is important to understand the effect of extraction parameters to the extract composition and its sugar profile. The research leading to these results has received funding from the WoodWisdom-Net Research Programme which is a transnational R&D programme jointly funded by national funding organisations within the framework of the ERA-NET WoodWisdom-Net 2.

Materials and methods

Industrial shredded spruce bark was collected from FinnForest Lohja sawmill. The bark was extracted unpressurized for 120 min in a 15 L pressure cooker that rotated 2.3 rpm. The amount of bark during extraction was 5, 10 or 15% of total mass and temperature was kept at 60, 75 or 90°C. Two extractions were carried out with sodium bisulphite and sodium carbonate dosed as 2% and 0.5% of bark dry weight.

Chemical composition of the bark was analysed including lipophilic extractives (hexane extraction), Klason lignin, acid soluble lignin, ash and carbohydrates. Neutral carbohydrates were analysed by HPLC after acid hydrolysis and acidic carbohydrates by GC after methanolysis due to their degradation in acid hydrolysis. Neutral and acidic monosaccharides in the extracts were analysed by HPLC. Total neutral sugars were analysed by HPLC after mild acid hydrolysis. Methanolysis and GC analysis was performed to analyse solubilized acidic poly- and oligosaccharides in the extract. Condensed tannin was analysed with acid butanol method (Gessner and Steiner, 2005) using commercial solvent purified quebracho tannin by Silvateam, Italy, as standard.

Results and discussion

Carbohydrate content of the industrial saw mill spruce bark was 59–63% depending on the analysis method (acid hydrolysis and HPLC or methanolysis and GC). The most abundant sugars were cellulosic glucose (22.1% of bark dry matter), non-cellulosic glucose (12.8%) and galacturonic acid (8.1%) followed by small amounts of arabinose, mannose, xylose, fructose and galactose (2–4% each). The bark contained 31.1% Klason lignin, 2.7% acid soluble lignin, 2.9% lipophilic extractives and 3.1% ash. However, it must be noted that some phenolic non-lignin compounds in bark such as high molecular weight tannins precipitate in acidic conditions and show up as Klason lignin.

Up to 20.9% of bark dry matter could be solubilized in the treatment. The extract consisted mostly of tannin, free monosaccharides and bound sugars. Bound sugars can be hemicellulosic or pectic sugars, glycosidic sugars or sugars bound in some other way and released in mild acid hydrolysis or methanolysis. Monosaccharides in the extract accounted for up to 4.4% and total sugars accounted for up to 10.7% of bark dry matter. Maximum obtained tannin yield was 9.6% of bark dry matter which shows the potential of spruce bark as a raw material for industrial tannin.

Higher extraction temperature increased total extraction yield and especially the yield of condensed tannins but did not affect the extraction yield of monosaccharides. Increasing solids content during extraction decreased total extraction yield slightly. Extraction aids sodium bisulphite and sodium carbonate improved the solubilisation of tannin and decreased the extraction of bound sugars. Out of the major sugars, non-cellulosic glucose and galactose were extracted most efficiently. The monosaccharide and bound sugar profile was similar in all the obtained extracts. On average 48% of the extract monosaccharides was fructose and 47% was glucose whereas 67% of the bound sugars was glucose, 11% galactose and 9% galacturonic acid. The high amount of solubilised free and bound glucose suggests the solubilisation and partial cleavage of glycosidic compounds during the extraction.

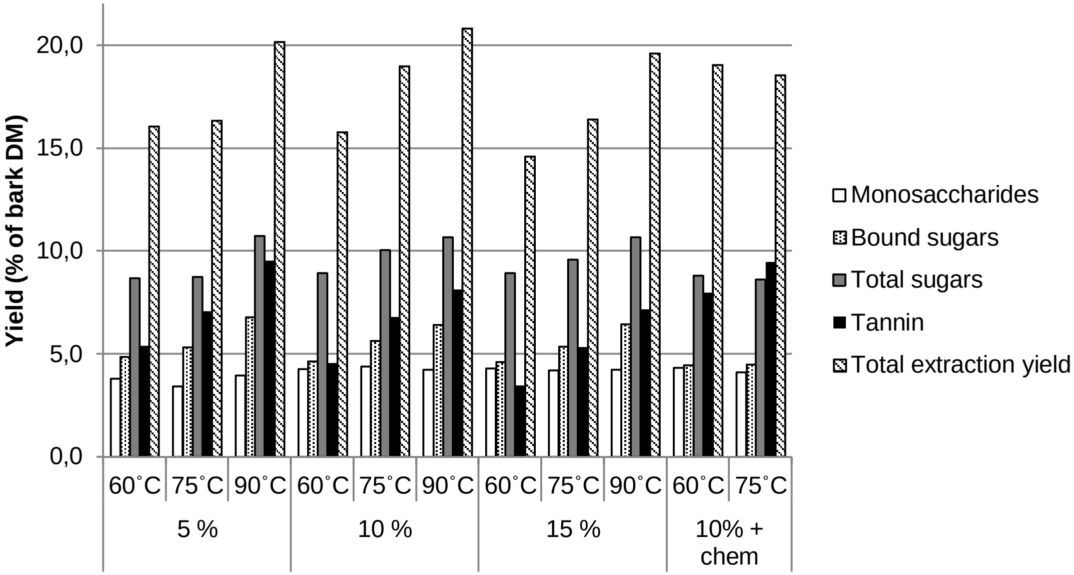

Figure 1. Total and component extraction yields during extraction of spruce bark at 5–15% bark content at 60–90°C with or without chemicals (2% sodium bisulphite and 0.5% sodium carbonate).

References

1. Gessner, M.O., Steiner, D. 2005. Acid butanol assay for proanthocyanidins (condensed tannins). In: Methods to study litter decomposition. Graça, M.A.S., Bärlocher, F., Gessner, M.O. (Eds.). Springer, Netherlands, pp. 107–114.

Methods to remove foulants from wood extracts prior to ultrafiltration

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Introduction

Wood extracts contain hemicelluloses, lignin-derived material, wood extractives and smaller amounts of other compounds. Hemicelluloses can be used in production of different commodities if they can be recovered and purified from the extract. Ultrafiltration is a potential separation process for this purpose. However, lignin and wood extractives cause fouling of the membranes [1, 2], which decreases the filtration capacity.

Adsorption with polymeric adsorbents has proven to be effective in lignin removal, but it has resulted in hemicellulose losses. Reason for that might be a linkage between some of the hemicelluloses and lignin. Thus, pretreatment method should break the linkage between hemicelluloses and lignin, and at least partly remove lignin but not hemicelluloses.

Experimental

In this study different treatments aiming to reduce the amount of lignin in birch extract were tested and their efficiency was evaluated. The efficiency of the treatment was pointed out by ultrafiltration experiments and by chemical analysis of the solutions. Permeate flux and fouling were used to evaluate the changes in the filtration capacity.

Pretreatment

Tested pretreatment methods were enzymatic (laccase) degradation (60°C, 180 min, phase ratio 0.01), flocculation (p-DADMAC, room temperature, phase ratio 0.1, mixing time 30 min, settling time 60 min), and adsorption on chitosan (60°C, 60 min, phase ratio 0.2).

Filtration

The extract was filtrated with a lab-scale stirred Amicon 8400 filter cell (membrane surface area 0.0040 m^2, 5.5 bar, 60 ^oC, volume reduction factor (VRF) value 2) and UFX5 membrane (5 kDa, PSu). Pure water fluxes (PWF) were measured before and after the filtration of the extract, and permeate flux was measured during the filtration of the extract.

Analysis

UV absorbance (at 205 nm) and hemicellulose content (monomers) were determined from the extract. UV absorbance refers to the presence of lignin-derived material, and it was measured with UV/VIS spectrophotometer. Hemicelluloses after hydrolysis were analysed with gas chromatograph.

Results and discussion

According to PWF measurements (Table I), any of tested pretreatments did not affect the fouling of the membranes, however, when comparing the permeate fluxes, improvement can be seen with enzyme treatment and chitosan adsorption. Flocculation decreased the permeate flux. In addition, enzyme and chitosan treatments decreased the UV absorbance most, while flocculant seemed to decrease it less. It was also noticed, that during enzyme treatment the UV absorbance was first decreased more, and after one hour treatment, it started to rise again towards the original value, however without reaching it in three hours.

Table 1. Tested pretreatment methods and their effect on filtration and UV absorbance of the extract.

Pretreatment	PWF decline %	Flux (kg/m^{2}h)	UV (205 nm) -	Lignin g/l
None	83	15	479	4.4
Enzyme	83	36	373	3.4
Flocculant	92	12	448	4.1
Chitosan	94	20	259	2.4

Conclusions

Enzyme treatment and adsorption on chitosan improved the permeate flux when they were used prior to ultrafiltration of birch extract. These two methods also decreased the UV absorbance of the extract. Enzyme treatment was most effective in increasing the flux, it was increased 140%, and chitosan adsorption decreased the UV absorbance most. Flocculation had negative effect on permeate flux. In future experiments, enzyme treatment might be reasonable to be stopped with inhibitor at the point where UV absorbance is lowest. In addition, it could be combined with adsorption on chitosan, or some other adsorbent.

Acknowledgements

The authors wish to thank Mr Yegor Chechurin for his valuable work with laboratory experiments. The authors are also grateful to the Future Biorefinery Research Program FuBio for financial support.

References

1. Puro, L., Tanninen, J., Nyström, M. 2002. Analyses of organic foulants in membranes fouled by pulp and paper mill effluent using solid-liquid extraction. Desalination 143, pp. 1–9.

2. Maartens, A., Jacobs, E.P., Swart, P. 2002. UF of pulp and paper effluent: Membrane fouling prevention and cleaning. J. Membr. Sci. 209, pp. 81–92.

Purification of hardwood-derived autohydrolysates

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Abstract

Birch (*Betula pendula*) chips were pre-treated (autohydrolysed) at two temperatures (130°C and 150°C) and varying pre-treatment times (30–120 minutes). Produced autohydrolysates were purified with respect to non-carbohydrate components, without carbohydrate losses, either by ethyl acetate extraction or XAD-4 resin treatment. Autohydrolysates were analyzed in terms of carbohydrates (mono-, oligo-, and polysaccharides), aliphatic carboxylic acids (formic and acetic acids), lignin, and other organics (mainly extractives and furans) before and after purification experiments.

Introduction

During the past decades, the conversion of biomass into “green chemicals” has received a growing global attention [1]. One of the most promising options is to introduce a pressurized hot-water treatment (PHWT) stage into the existing kraft pulping process mainly serving the purpose of recovering soluble hemicelluloses and other organic components from wood chips prior to delignification [2].

However, autohydrolysis is not a selective extraction process [3]. For this reason, autohydrolysates are chemically rather complex, containing a mixture of various carbohydrates and minor amounts of other organics such as aliphatic carboxylic acids, furanoic compounds, and lignin- and extractives-derived components. As many of these non-carbohydrate compounds can be detrimental, especially when considering the subsequent utilization of the carbohydrate fraction, the removal of these inhibitors is necessary.

Experimental

Autohydrolyses

Screened chips were pre-treated in an oil-heated batch digester, at two temperatures (130°C and 150°C) and with four treatment times (30, 60, 90, and 120 minutes). Pre-treatments covered the P-factor range from 10 to 238. Liquor-to-wood ratio was 5 L/kg and ultra high quality (UHQ) water was used as solvent.

Purification of the autohydrolysates

Produced autohydrolysates were purified by ethyl acetate extraction and XAD-4 resin treatment.

Analytical determinations

The content of soluble lignin was determined with a Beckmann DU 640 UV/Vis-spectrophotometer at 205 nm. Carbohydrates (monomeric and total carbohydrates) were analyzed with a Dionex high performance liquid chromatography (HPLC) equipped with a CarboPac PA-1 column. Volatile acids (formic and acetic acids) were determined by HPLC (a Dionex chromatography system and an IonPac AS 11-HC analytical column). Furanoic compounds (furfural and 5-(hydroxymethyl)furfural) were determined with a Waters HPLC system and a Phenomenex Gemini C18 column.

Results

Ethyl acetate extraction

With ethyl acetate extraction, it was noticed that in each case, roughly half of the dissolved lignin was removed by this simple extraction procedure. In addition, the furanoic compounds were effectively removed, and no detectable amounts of them were found after extractions. On the other hand, the results indicated that the ethyl acetate extraction had no significant effect on the concentration of free monosaccharides, or the total carbohydrate content. In addition, no degradation of oligo- or polysaccharides could be observed, since, in each case, the monosaccharide-to-polysaccharide ratio remained rather constant.

Treatment with XAD-4 resin

With XAD-4 treatment, roughly one-third of the dissolved lignin, and nearly 90% of the furanoic compounds could be removed from the hydrolysates. In general, XAD-4 treatments did not have any significant effect on the concentration of soluble carbohydrates, or on the monosaccharide-to-polysaccharide ratio. Volatile acids could not be removed from the hydrolysates with resin treatments.

Conclusions

Autohydrolysis is an efficient and environmentally friendly method for producing carbohydrate-containing hydrolysates, which can be further processed to various chemicals and biofuels. Due to their complex chemical nature, additional purification step is required.

Significant amounts of lignin and furanoic compounds were removed from hydrolysates containing carbohydrates (obtained from the autohydrolysis of hardwood chips prior to delignification), either by relatively simple methods such as solvent extraction (with ethyl acetate) or resin treatment (with XAD-4 resin). In addition, purification experiments caused no carbohydrate losses or degradation of oligo- or polysaccharides.

References

1. Alén, R. 2011. Biorefining of Forest Resources, Vol. 20, Alén, R. (ed.). Paper Engineers' Association/Paperi ja Puu Oy, Helsinki.

2. Amidon, T.E., Liu, S. 2009. Water-based woody biorefinery. Biotechn. Adv. 27(5), pp. 542–550.

3. Palmqvist, E., Hahn-Hägerdahl, B. 2000. Fermentation of lignocellulosic hydrolysates. I:Inhibition and detoxification. Biores. Techn. 74(1), pp. 17–24.

Hot water extraction of hemicellulose from softwood and sugarcane bagasse using microwave heating technology

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Abstract

Hemicellulose extraction from softwood and sugarcane bagasse was studied using mild extraction conditions (hot water, microwave (MW) heating) in order to avoid extensive hemicellulose degradation. For both raw materials, yields increased up to 10 minutes extraction time. At longer times, the carbohydrates began to decompose. The increase in yield was most pronounced from 175°C to 180–185°C. Optimization analyses of percentual yield and degree of polymerisation (DP) indicated that the best trade-off between the two parameters in the given temperature-time region was 183°C and 12 minutes extraction for bagasse and 183°C and 5 minutes for softwood. At these conditions, the optimization model predicted a yield of 62% and a DP of 100 for bagasse and a yield of 50% and a DP of 31 for softwood.

Introduction

Pretreatment of lignocelluloses is a crucial step in the production of fuels and chemicals, significantly affecting the composition and structure of cellulose, lignin and hemicelluloses. A strategy for avoiding hemicellulose degradation (retain high DP) during pretreatment could be to extract the hemicelluloses from the raw material prior to further pretreatment. In this way the hemicelluloses can be used for other value-added products or hydrolysed and fermented to alcohols. 4-*O*-Acetylgalactoglucomannan (AcGGM) is the predominant hemicellulose in softwoods whereas arabinoglucuronoxylan is the dominant hemicellulose in sugarcane bagasse.

Studies by others [1] on hemicellulose extraction from spruce by microwave (MW) treatment, have reported a maximum yield of 70%wt (referred to mannan) by using MW-heating at 200°C for 5 minutes. This equals 0.125 g of extracted oligosaccharides per gram dry wood. Decomposition of the polymers was most prevalent above 200°C at 2 min extraction time. Further, a study of molar mass distribution of spruce hemicelluloses after SEC-fractionation [2] found that the low molecular mass fraction contained mainly low weight arabinoglucuronoxylan oligosaccharides (DP values from 4 to 20), while for the fraction eluted lastly, *O*-acetylgalactoglucomannan was dominant, with a peak-average DP value of 14. The amount of acetyl side groups decreased as the DP decreased.

Experimental

Two raw materials were used – softwood sawmill shavings (90% Norway spruce and 10% Scots pine) and sugarcane bagasse (Brazil). A 4x4 factorial setup (Temp = 175-180-185-190°C, time = 2-6-10-20 min) was applied. Distilled water was added to give a solid:liquid ratio of 1:10. This mixture was left overnight for soaking prior to extraction. Trials were performed using a heating ramp of 1.5 min. After extraction, the vessels were cooled (ice bath, 5 min). The extraction liquid was filtered (GF/A, Whatman, 1.6 µm) and stored (-18°C) for analysis. The filtrates were analysed with respect to carbohydrate composition (HPAEC) and sugar molecular size distribution (using SEC-MALS).

Results and discussion

Extraction time and temperature significantly affected yield, DP and acidity of the hemicellulose extracts. For both sugarcane bagasse and sawmill shavings, yields increased up to 10 minutes extraction time. At longer times, the carbohydrates began to decompose. The yield increase was most pronounced from 175°C to 180–185°C, for both materials. The effect of time and temperature on DP differed markedly for the two raw materials. Whereas the bagasse hemicelluloses showed the highest DP-value around 5 min extraction time the softwood hemicelluloses started depolymerizing already after a few minutes. This may be related to deacetylation of the AcGGM in softwood, causing a lower apparent DP due to invisibility of deacetylated compounds in the analysis. Furthermore, the final pH in the extraction liquid was consistently lower for softwood than for bagasse at equal yields. This is possibly due to a higher initial acetyl content in softwood, but could also be an indication of more pronounced deacetylation in softwood than in bagasse.

Optimization analyses of the responses on percentual hemicellulose yield and DP indicated that the best trade-off between the two parameters in the given temperature-time region is found at 183°C and 12 minutes extraction for bagasse and 183°C and 5 minutes for softwood. At these conditions, the optimization model predicted a yield of 62% and a DP of 100 for bagasse and a yield of 50% and a DP of 31 for softwood. Analyses from the closest corresponding experimental conditions (185°C, 10 min and 185°C, 6 min, respectively) gave hemicellulose yield of 60% and DP = 111 (M_w = 38 400 g/mol) for bagasse and 55% yield and DP = 23 (M_w = 5 700 g/mol) for softwood.

Acknowledgement

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References

1. Palm, M., Zacchi, G. 2003. Extraction of hemicellulosic oligosaccharides from spruce using microwave oven or steam treatment. Biomacromolecules 4(3), pp. 617–623.

2. Jacobs, A., Lundqvist, J., Stalbrand, H., Tjerneld, F., Dahlman, O. 2002. Characterization of water-soluble hemicelluloses from spruce and aspen employing SEC/MALDI mass spectroscopy. Carbohydrate Research 337(8), pp. 711–717.

Modelling of hot water extraction of sawdust

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Abstract

In this paper physico-chemical model for hot water extraction of sawdust is presented. The model takes into account relevant physico-chemical phenomena: reaction kinetics, acid-base equilibrium, mass transfer, and the ion exchange property of wood, i.e. the Donnan effect. Furthermore, the changes in molecular weight distribution (MWD) of hemicelluloses during the processing are modelled. The model can be used for a priori predictions on the hot water extraction process behaviour with different raw materials and processing conditions.

Introduction

In modelling reaction kinetics of hot water extraction (HWE) of wood, accurate estimation of hydrogen ion concentration is important because hydrogen ions catalyze many reactions [1]. It has been shown that Donnan theory can be applied for modelling ion exchange, caused by dissociating acids and phenols covalently bound to fibre wall, in water – wood fibre suspension. Due to the fibres' cation exchange property, hydrogen ion concentration is higher in liquid bound to fibre wall. The acidic reactions products formed during HWE also influence on the behaviour of the pH and need to be considered in the model especially at low L:W ratios.

In this paper, the two recently conducted modelling works [1, 2] are combined for the comprehensive reaction kinetic modelling of HWE of wood meal in batch reactor setup.

Simulation model and setup

Species influencing pH in addition to GGM are considered in the model. Lignin, cellulose, and rest of the wood species are considered to be inert material. GGM's molecular weight distribution (MWD) is modelled using population balance approach [1].

In the model following phenomena are considered:

1. H^+ catalyzed degradation of GGM [1].
2. H^+ catalyzed deacetylation [2].
3. Dissolution of GGM, acetyl groups [2], and methylglucuronic acids [2] from fibre wall into fibre wall liquid.
4. Mass transfer of all soluble species between fibre wall liquid and liquid external to fibre wall [3].

Degradation reactions (phenomena 1. and 2.) for GGM and acetyl groups still attached to fibre, dissolved into fibre wall liquid, and in external liquid are included into the model and assumed to follow same kinetics.

Experimental conditions and data points used for estimation of dissolution kinetics of GGM polymers were taken from [3]. Metal ion content (having influence on the behaviour of pH) [4], initial GGM content of wood [4], and average DP of GGM [5] in wood were taken from the literature.

Simulation results

Some simulation results together with the measurement data is shown in Figure 1. With the model it is possible to obtain knowledge on the yield and MWD of the dissolved GGM. Model also gives profiles for several other chemical species, and pH.

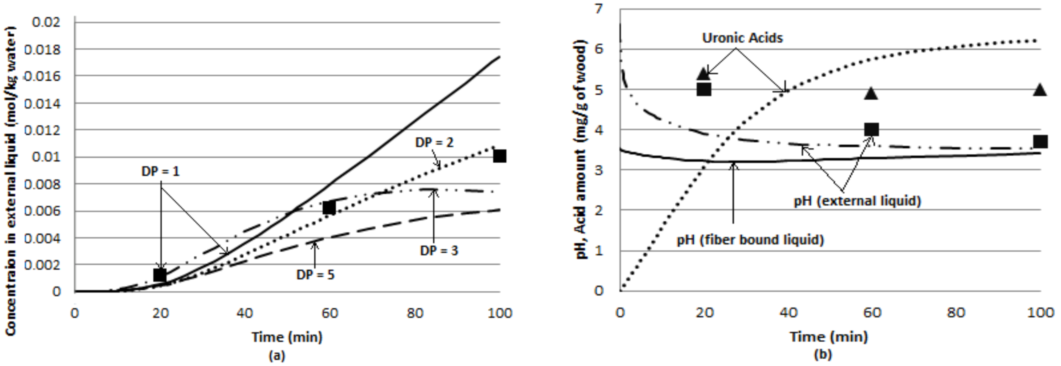

Figure 1. Simulated (lines) and measured values (tick marks) at 170°C. (a) Concentrations of GGM polymers w.r.t. time. (b) Concentrations of Uronic acid and pH w.r.t. time.

Conclusions

Comprehensive reaction kinetic model for simulation of batch HWE of wood meal was developed. Simulations give pH in both liquid phases, concentrations of reaction products (acetic acid, …), concentrations of material dissolved from fibre wall (uronic acids, …), and MWD of GGM still attached to wood and dissolved into liquid phases. In the future, model will be developed so that it will also predict degradation of cellulose, xylan, and lignin.

References

1. Visuri, J.A., Song, T., Kuitunen, S., Alopaeus, V. 2012. Model for degradation of galactoglucomannan in hot water extraction conditions. Ind. Eng. Chem. Res. 51(31), pp. 10338–10344.

2. Kuitunen, S., Alopaeus, V. 2012. The role of Donnan effect in kraft liquor impregnation and hot water extraction, 12th European Workshop on Lignocellulosics and Pulp, Espoo, Finland. Proceedings. Pp. 92–95.

3. Song, T., Pranovich, A., Sumerskiy, I., Holmbom, B. 2008. Extraction of galactoglucomannan from spruce wood with pressurized hot water. Holzforschung 62, pp. 659–666.

4. Koch, G. 2006. Raw material for Pulp in “Handbook of Pulp” edited by Sixta, H. Wiley-VCH Verlag GmbH. Pp. 21–68.

5. Sjöström, E. 1993. Wood Polysaccharides in “Wood Chemistry Fundamentals and Applications”, Academic press, 2nd edition. Pp. 51–70.

The kinetics of simultaneous aqueous extraction and hydrolysis of spruce hemicelluloses

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Abstract

The aqueous extraction of hemicelluloses has gained an increasing interest with new emerging applications for hemicelluloses in the modern forest-based biorefinery concept. The extraction kinetics play a key role in their industrial utilisation. Pressurised hot water extraction of spruce sap wood was investigated in the temperature range 120–170°C using a large liquid-to-solid ratio in an intensified cascade reactor system. The results show significant temperature dependence of the extraction rate, albeit low influence of pH. Moreover, a clear dependence of the hydrolysis rate on the temperature and pH was observed. The molecular mass of the extracted hemicelluloses was influenced by the chip size. A kinetic model was developed for describing the extraction kinetics.

Introduction

Acetylgalactoglucomannan (AcGGM) is the main hemicellulose present in softwoods and it can be utilised for varying applications in industry, due to it’s biological and physico-chemical properties. This, however, requires deep going quantitative knowledge of the kinetics and the solid-liquid reactions involved [1]. The best solvent for extracting unmodified AcGGM, according to current knowledge is neutral or slightly acidic water. Quantitative studies on the pressurised hot water extraction (PHWE) of hemicelluloses found in literature have mainly focused on hardwoods, due to their current use in industry and the information related to softwoods is rather limited [1]. The main challenges related to the effective industrial use of AcGGM are the controlled extraction and the ability to control the hydrolysis of the oligomers. Quantitative kinetic studies of both factors combined with mathematical modelling are a necessity for industrial applications.

Experimental

The kinetic PHWE experiments were performed with a novel cascade reactor system, in the current study (Figure 1). The main advantage, compared to traditional digesters, is the possibility to control the reaction conditions very precisely and rapidly, which is the basis for reliable kinetic experiments. Moreover, the system allows the sampling of both the solid and liquid phase during the reaction. The system includes online monitoring and recording of the pressure and temperatures inside each reactor chamber, which enables a detailed interpretation of the data as well as reliable modelling. More than 60 selected samples of both the solid and liquid phases were analysed for sugar composition, molar mass, and pH. The analysis of both phases contributes to the understanding the overall mass balance of the different reactions including the possible degradation of the monomers. A solid-to-liquid ratio of ~180 was used, in order to avoid the interference of thermodynamic limitations. The temperature in the experiments was between 120–170°C, which has been shown to be the most relevant range for PHWE.

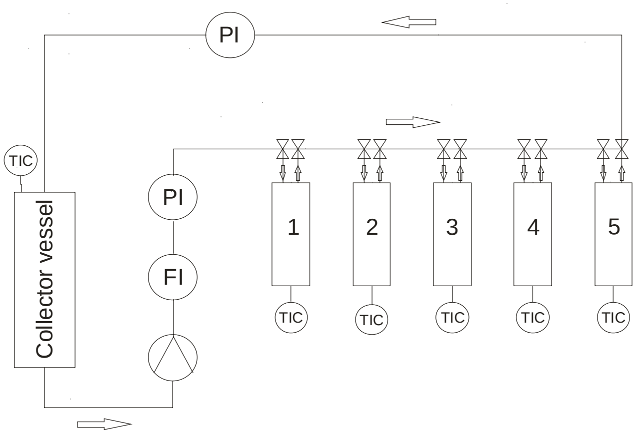

Figure 1. A simplified scheme of the reactor setup. The reactors are numbered from 1 to 5.

Results and discussion

The new cascade reactor system performed well, enabling an accurate control of the reaction conditions and sampling. The reaction was initiated and stopped rapidly; the desired reaction temperature was reached in about 3–4 min and the quenching took 1 min. The overall dissolution rate of the hemicelluloses was highly temperature dependent with an activation energy of about 120 kJ/mol. However, variations in the reaction rates of different hemicellulos fractions was noticed. This could be utilised in practice for influencing the selectivity of extraction by applying temperature profiling. Also significant temperature and pH dependence was shown for the degradation of the oligomers, which can be considered as a possibility for optimising this phenomena depending on the desired product. The pH changed throughout the reaction and a systematic correlation with the conversion was observed. Moreover, the chip size was observed to influence the molar mass of the extracted hemicelluloses. A good fit of the kinetic model to experimental data was obtained.

Conclusions

The aqueous extraction of spruce hemicelluloses is a complicated issue as the temperature, pH, as well as external and internal mass transfer phenomena influence both the overall rate and the obtained hemicellulose properties. The decoupling and quantitative assessment of the parameters is a key issue for being able to model the phenomena and being able to implement it into industrial production in order to obtain the desired products for further processing in an effective way.

Acknowledgements

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References

1. Grénman, H., Eränen, K., Krogell, J., Willför, S., Salmi, T., Murzin, D. Yu. 2011. Kinetics of Aqueous Extraction of Hemicelluloses from Spruce in an Intensified Reactor System. Ind. Eng. Chem. Res. 50, pp. 3818–3828.

Acid functionalized carbon as heterogeneous catalysts for dehydration of xylose to furfural

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Abstract

Hemicellulosic sugars offer biobased source for the production of fuel and chemical intermediates by dehydration. Dehydration of xylose was studied using acid functionalized active carbon as heterogeneous acid catalyst. Active carbon exhibited good activity and selectivity in the dehydration reaction of xylose to furfural, being also stable in the reaction conditions, at 200°C in water solution.

Introduction

Decreasing reserves of fossil raw materials and attempts to reduce CO_2 emissions inspire to utilize bio-based alternatives, where non-food biomass, especially lignocellulose, plays the key role. Significant amount of lignocellulose consists of different sugars which can be utilized after hydrolyzation. Nowadays the main reaction pathway from sugars to biofuels is fermentation to alcohols. However, the dehydration of sugars to furfurals is an optional route for the production of bio-based transportation fuels and chemicals. [1, 2].

The dehydration of sugars is catalyzed by acids and currently the commercial furfural production utilizes homogeneous acids, typically sulphuric acid. Heterogeneous acid catalysts are more sustainable by producing less waste and working without corrosion problems. However, heterogeneous acid catalysts suffer low selectivity for dehydration reaction, catalysing the formation of side products and ending up in low yields. This is due to different type of active sites on the surface (basic, weak acid and strong acid). In addition many heterogeneous acid catalysts have low stability in aqueous phase at high temperatures (150–350°C) used in dehydration reaction. [3]

This study concentrates on the use of new type of heterogeneous acids, acid functionalized active carbons, in dehydration reactions. Acidic surface groups acting as active sites in xylose dehydration can be created on the carbon surface by liquid phase oxidation, nitric acid and sulfuric acid being the most commonly used [4]. Oxygen-containing surface groups are typically carboxyl, phenol, and lactone groups. Carbons are interesting materials as catalyst in aqueous phase sugar dehydration reaction also because of their good water tolerance. [4]

Experimental

Acid functionalized activated carbon was prepared by refluxing in boiling 3M HNO_3 or 3M H_2SO_4 or mixture of them. Functionalization time was 2 hours. After refluxing, mixture was cooled down, washed with distilled water until the pH of the washing water was neutral and dried at 80°C overnight. Dehydration experiments were done in batch reactor at 160–200°C and 5 MPa nitrogen pressure in water solution. Reaction products were analyzed by Agilent 1100 liquid chromatograph, with a refractive index detector using Phenomenex Rezex Monosaccharide RHM H+ column.

Results and discussion

Functionalized activated carbon catalysts were active in xylose dehydration and they also exhibited higher selectivity towards furfural than traditional solid acid catalysts such as zeolites and TiO_2. Selectivity to furfural as a function of conversion with different catalysts is shown in Figure 1.

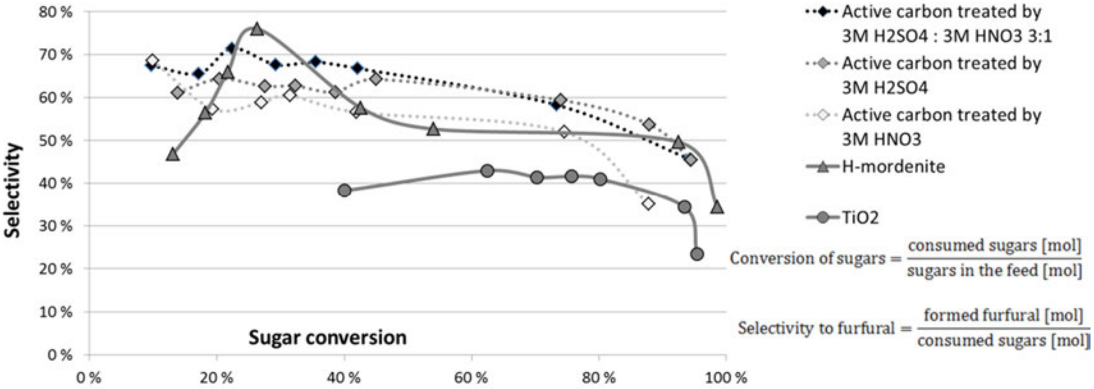

Figure 1. Furfural selectivity as a function of xylose conversion in dehydration on different catalysts.

At high conversion values the main side reaction was the formation of solids via both polymerization of furfural and condensation reaction between sugars and furfural, observed as a formation of black precipitate after longer reaction times. Also some organic acids were formed via decomposition. In addition to good selectivity, acid functionalized carbon catalyst maintained its activity in consecutive experiments, indicating that acidic surface sites were insoluble in water used as a solvent in batch experiment at 200°C.

The acids used in carbon functionalization have an effect on the carbon catalyst activity: oxygen-containing acid sites formed mainly in HNO_3 treatment and sulphur-containing surface groups formed in H_2SO_4 treatment are both active in xylose dehydration. Consequently, the carbon catalyst treated with mixture of these acids possessed the highest furfural selectivity of this study.

References

1. Lin, Y.-C., Huber, G.W. 2009. The Critical Role of Heterogeneous Catalysis in Lignocellulosic Biomass Conversion. Energy Environ. Sci. 2, pp. 68–80.

2. Stöcker, M. 2008. Biofuels and biomass-to-liquid fuels in the biorefinery: Catalytic conversion of lignocellulosic biomass using porous materials. Angew. Chem. Int. Ed. 47, pp. 9200–9211.

3. Karinen, R., Vilonen, K., Niemelä, M. 2011. Heterogeneously Catalyzed Reactions of Carbohydrates for the Production of Furfural and Hydroxymethylfurfural. ChemSusChem 4, pp. 1002–1016.

4. Toebes, M.L., van Heeswijk, J.M.P., Bitter, J.H., van Dillen, A.J., de Jong, K.P. 2004. The influence of oxidation on the texture and the number of oxygen-containing surface groups of carbon nanofibers. Carbon 42, pp. 307–315.

Kinetic study on the formation of furfural from pentoses in complex sugar solutions

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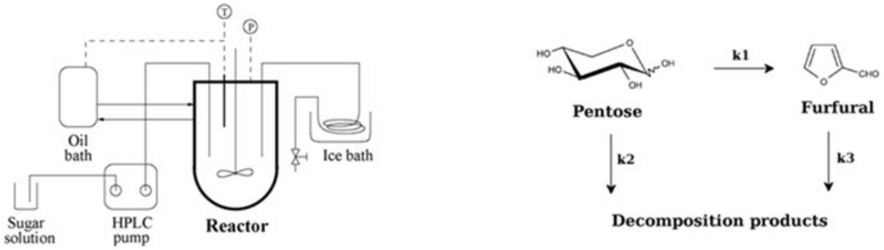
Abstract

In this study the influence of complex sugar solutions (e.g. molasses) on the kinetics of the conversion of pentoses to the platform chemical furfural is investigated. Results of two series of kinetic experiments are compared, on the one hand with molasse (a pentose-rich side stream of the Inbicon biorefinery) as the feedstock and on the other hand with pure xylose. Kinetic parameters of a first-order reaction mechanism for the xylose dehydration towards furfural are fitted on the obtained experimental results. The comparison of these kinetic parameters of the two experimental series show that pure xylose both reacts faster towards furfural and results in higher furfural yields. Presently, the mechanistic causes of these differences are investigated in a more fundamental study.

Introduction

One of the (side) products of the Inbicon biorefinery process for converting lignocellulosic (waste) biomass to bioethanol is the molasses [1]. These molasses contain mainly xylan and xylose, but also arabinose, glucose and small amounts of various other organic compounds. Previously, extensive research has been performed at Delft University of Technology on the kinetics of the formation of furfural from pure xylose, via acid-catalyzed dehydration [2]. Currently, the acquired knowledge is extended for the dehydration of pentoses in more complex solutions, such as the previously mentioned molasses.



(a) **(b)**

Figure 1. (a) Experimental setup, (b) first-order reaction mechanism.

Experimental setup

The experiments are performed in a one-liter mechanically stirred stainless steel autoclave reactor, see also Figure 1(a). The reaction temperature (180°C and 200°C) was regulated by pumping heated oil through the jacket of the reactor. The operating pressure in the reactor was the saturation pressure of the mixture. Besides hydrochloric acid (HCl), also sodium chloride (NaCl) has been added as a catalyst. The samples were analyzed using an HPLC apparatus equipped with a Rezex RHM-Monosaccharide column, 8% cross linked H^+, 300 x 7.80 mm, (Phenomenex Inc., Torrance, CA, USA). The saccharides were quantified by means of an RI detector (Varian Model 350), whereas for furfural both an RI and UV detector (Varian Model 310 Pro Star) were used.

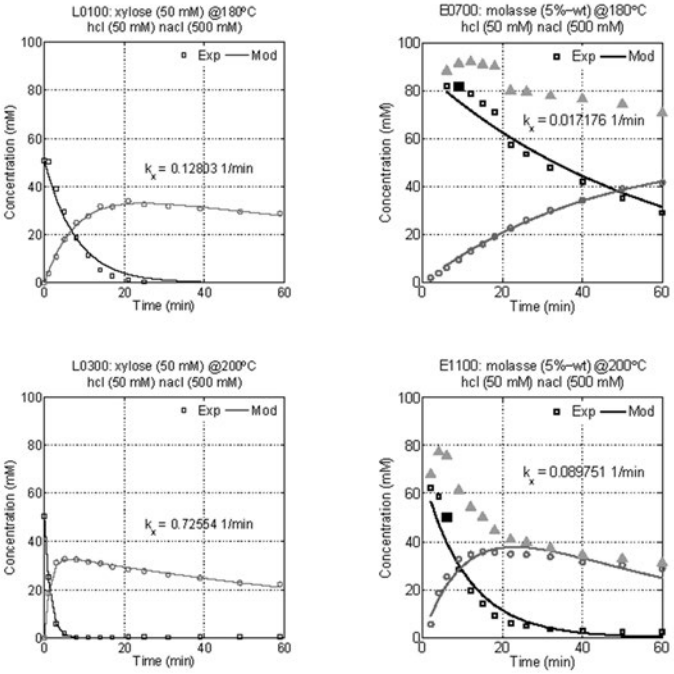
Results and discussion

In Figure 2(a) and (b) the results of the kinetic experiments with xylose and the molasses are presented, respectively. It is noted that the squares in (a) represent xylose, whereas in (b) they denote the total pentose concentration. The printed value of the reaction rate constant k_x is the sum of k_1 and k_2, see also Figure 1(b).

In the first place, the degradation of the sugars in both series show an exponential decay, which confirms the assumption of a first-order reaction mechanism. Secondly, in both cases the values of k_x are higher at higher temperature, as expected. Finally, comparing the results of the experiments with pure xylose and the molasses, two important observations can be made.

Firstly, the degradation rates of the pentoses (the value of k_x) are lower for the molasses. This is partly due to the fact that there are some polysaccharides (xylans) present in the molasses. The large filled squares in Figure 2(b) indicate the last sample where polysaccharides were observed in the chromatograms, which coincides with the peak of the total matter, i.e. the sum of pentose and furfural, indicated by the grey triangles. Another contribution to the lower dehydration rate is the fact that a part of the pentoses consists of arabinose. Arabinose is known to be dehydrated slower than xylose [3].

Secondly, it is observed that the molar furfural yield is also lower in the experiments with molasse. Whereas in the pure xylose experiments the molar yield is around 65%, in the molasses experiments this yield drops to around 50%. The cause for this difference is probably due to the rates of the loss reactions of xylose and furfural. Previously, an adapted version of the first-order reaction mechanism, where the decomposition reaction of xylose is a second-order reaction with both a xylose as a furfural molecule, has been proposed [4].



(a) **(b)**

Figure 2. Comparison of kinetics of pure xylose (a) and pentoses from the molasse (b) at two different temperatures (squares = xylose/pentoses, circles = furfural and triangles = cumulative).

Conclusion and outlook

It is concluded that the dehydration of pentoses in a complex sugar solution is both slower and yield less furfural than in the case of pure xylose. In many studies however the kinetic parameters of pure xylose are used when for example the acidic hydrolysis of biomass is investigated. Therefore, the influence of the presence of other sugars (mainly the hexoses) on the kinetics of the dehydration of xylose will be studied on a systematic basis.

References

1. Larsen, J., Petersen, M.O., Thirup, L., Li, H.W., Iversen, F.K. 2008. The IBUS process – lignocellulosic bioethanol close to a commercial reality. Chem. Eng. Technol. 31, pp. 765–772.

2. Marcotullio, G., de Jong, W. 2010. Chloride ions enhance furfural formation from D-xylose in dilute aqueous acidic solutions. Green Chemistry 12, pp. 1739–1746.

3. Kootstra, A.M.J., Mosier, N.S., Scott, E.L., Beeftink, H.H., Sanders, J.P.M. 2009. Differential effects of mineral and organic acids on the kinetics of arabinose degradation under lignocellulose pretreatment conditions. Biochemical Engineering Journal 43, pp. 92–97.

4. Weingarten, R., Cho, J., Curtis Conner, Wm. Jr., Huber, G.W. 2010. Kinetics of furfural production by dehydration of xylose in a biphasic reactor with microwave heating. Green Chemistry 12(8), pp. 1423–1429. Results and discussion.

D-Xylonate and xylitol as biorefinery products from hemicellulose

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Abstract

The European project BIO-COmmodity REfining – BIOCORE is developing and analysing the industrial feasibility of a biorefinery for conversion of a variety of non-food biomass, including cereal by-products (straws etc.), forestry residues and short rotation woody crops, into 2nd generation biofuel, chemicals and polymers.

The key technology in BIOCORE is the organosolv pretreatment with acetic and formic acids, developed by CIMV, which allows extraction of the three major components of biomass; cellulose, hemicelluloses and lignins. In the BIOCORE project, D-xylose in the hemicellulose fraction is converted to xylitol or D-xylonate biotechnically. The production is evaluated through the whole value chain from straw harvesting to the final product.

The need for robust, efficient and safe biocatalysts was addressed by engineering an industrial *Saccharomyces cerevisiae* strain, isolated from spent sulfite liquor and a similarly robust *Candida* species for xylitol and/or D-xylonate production.

D-Xylonate production at low pH

Low pH production of organic acid is considered advantageous for down stream purification. A non-conventional yeast of *Candida* sp. expressing a D-xylose dehydrogenase encoding gene produced up to 171 g l^{-1} D-xylonate from 171 g l^{-1} D-xylose at a rate of 1.4 g $l^{-1}h^{-1}$ and yield of 1.0 g [g substrate consumed]$^{-1}$. Remarkably, the productivity was almost unaffected when the pH was reduced to 3.0 (Figure 1a). High levels of D-xylonate production at low pH has not previously been reported (Figure 1 b). From the CIMV hemicellulose hydrolysate, 40 g xylonate l^{-1} was produced from 48 g xylose l^{-1} in fed-batch culture.

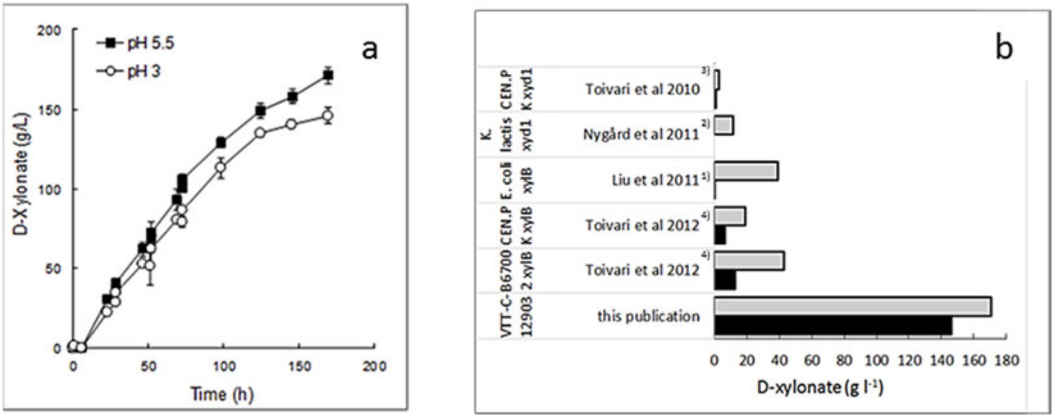

Figure 1. a) Production of xylonate at pH 5.5 and at pH 3.0 with *Candida* sp. b) Production of D-xylonate at high pH (> 5.5) (grey) and low (pH < 4.0) (black) using modified yeast or *E. coli*.

Xylitol production with *Saccharomyces cerevisiae* and *Candida* sp. from pure substrate or from D-xylose in hemicellulose fractions

On pure substrate the engineered *Candida* sp. strain had higher production rate than the engineered industrial *S. cerevisiae* strain, but the yield was lower. Xylitol titers up to 160 g l^{-1} and yields of 70–90% (g product/ g xylose used) were obtained on pure substrate.

The CIMV hemicellulose fraction is rich in formic and acetic acids and contains various phenolic compounds. In addition to the CIMV hemicellulose fraction also other pretreated biomass hydrolysates, originating from wood and wheat straw and containing less formate, were tested for xylitol production. The engineered strains performed well producing up to 88 g l^{-1} xylitol (depending on the hydrolysate, strain and conditions). Continuing metabolic engineering efforts on improving the tolerance of the engineered yeast towards formic acid together with process technical developments are likely to increase the xylitol productivity even further. The results are highly encouraging for future pilot scale trials.

Acknowledgements

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References

1. Liu, H., Valdehuesa, K.N., Nisola, G.M., Ramos, K.R., Chung, W.J. 2012. High yield production of D-xylonic acid from D-xylose using engineered Escherichia coli, Bioresour. Technol. 115, pp. 244–248.

2. Nygård, Y., Toivari, M.H., Penttilä, M., Ruohonen, L., Wiebe, M.G. 2011. Bioconversion of D-xylose to D-xylonate with Kluyveromyces lactis. Metab. Eng. 13, pp. 383–391.

3. Toivari, M.H., Ruohonen, L., Richard, P., Penttilä, M., Wiebe, M.G. 2010. Saccharomyces cerevisiae engineered to produce D-xylonate. Appl. Microbiol. Biotechnol. 88, pp. 751–760.

4. Toivari, M., Nygård, Y., Kumpula, E.P., Vehkomäki, M.L., Bencina, M., Valkonen, M., Maaheimo, H., Andberg, M., Koivula, A., Ruohonen, L., Penttilä, M., Wiebe, M.G. 2012. Metabolic engineering of Saccharomyces cerevisiae for bioconversion of D-xylose to D-xylonate. Metab. Eng. 14, pp. 427–436.

Selective oxidation of uronic acids into aldaric acids over gold catalysts

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Abstract

Aldaric acids were produced by selective aerobic oxidation of uronic acids using gold nanoparticle catalysts. Nearly quantitative conversions and selectivities were achieved in alkaline aqueous medium in mild conditions. Aldaric acids represent interesting building block chemicals for polymer, food and pharmaceutical industries and with the new oxidation method they can be produced from uronic acids found in hemicelluloses.

Introduction

Aldaric acids, or diacids of sugars, have potentially numerous applications in polymer, food and pharmaceutical industries. [1] However, current methods for their production by oxidation of monosaccharides suffer from low selectivities or the use of strong oxidizing agents such as nitric acid or bleach. [2] The potential of diacids as building block chemicals can only fully be utilized if they can be efficiently produced from carbohydrates.

Supported gold nanoparticles have shown superior selectivity and stability in the aerobic oxidation of alcohols and carbohydrates under mild conditions. [3] In case of monosaccharides the aldehyde group is selectively oxidized and the corresponding aldonic acid is produced. Oxidizing the primary hydroxyl group to obtain the aldaric acid, *e.g.* glucaric acid, requires more severe conditions and results in loss of selectivity. [4]

In case of uronic acids the oxidation of the primary hydroxyl is performed already by nature. Uronic acids are found in hemicelluloses in both hardwood and softwood and can amount up to 2% of wood dry weight. [5] At the moment, hemicelluloses are the largest polysaccharide fraction wasted in biorefineries. Here, we present an efficient new method for converting uronic acids into aldaric acids under mild conditions using a gold-palladium catalyst (Figure 1).

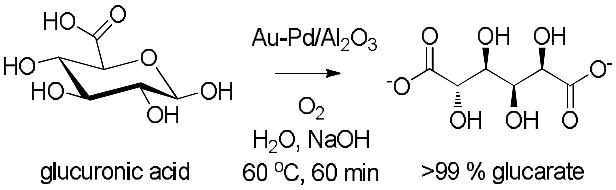

Figure 1. Catalytic oxidation of glucuronic acid to glucaric acid.

Experimental

The gold-palladium catalyst was prepared by impregnation on Al_2O_3. [6] The oxidation of uronic acids were carried out in aqueous media under controlled pH. As acid is produced in the reaction, the addition of sodium hydroxide was needed to neutralize the acid and maintain constant pH. Dioxygen was bubbled at 100 ml/min through the reaction mixture. The products were identified by ^{1}H-NMR and GC-MS after trimethylsilylation.

Results and discussion

The gold-palladium catalyst selectively oxidized the aldehyde group of the substrate resulting in nearly quantitative conversion to e.g. glucarate in 60 min at 60°C and pH 9. The reaction of galacturonic acid proceeds slightly slower. At lower pH, the activity of the catalyst dropped and the reaction didn't reach full conversion. No side products were detected and no reaction occurred without the catalyst.

Conclusions

In summary, we have demonstrated that glucuronic and galacturonic acids can be selectively oxidized into the corresponding aldaric acids over gold-palladium catalyst. Almost quantitative conversions into glucarate and galactarate were achieved in mild conditions with oxygen bubbling.

References

1. Werpy, T.A., Petersen, G. 2004. Top value added chemicals from biomass. Volume I, U.S. Department of Energy (DOE), Golden, CO, DOE/GO-102004-1992.

2. Ibert, M., Marsais, F., Merbouh, N., Brückner, C. 2002. Determination of the side-products formed during the nitroxide-mediated bleach oxidation of glucose to glucaric acid. Carbohydr. Res. 337(11), pp. 1059–1063.

3. Mirescu, A., Prüße, U. 2007. A new environmental friendly method for the preparation of sugar acids via catalytic oxidation on gold catalysts. Appl. Catal., B 70, pp. 644–652.

4. Dirkx, J.M., van der Baan, H.S., van der Broek, J.M. 1977. The preparation of D-glucaric acid by the oxidation of D-gluconic acid catalysed by platinum on carbon. Carbohydr. Res. 59, p. 63.

5. Gírio, F.M., Fonseca, C., Carvalheiro, F., Duarte, L.C., Marques, S., Bogel-Łukasik, R. 2010. Hemicelluloses for fuel ethanol: A review. Biores. Technol. 101, p. 4775.

6. Herzing, A.A., Carley, A.F., Edwards, J.K., Hutchings, G.J., Kiely, C.J. 2008. Microstructural Development and Catalytic Performance of Au-Pd Nanoparticles on Al_2O_3 Supports: The Effect of Heat Treatment Temperature and Atmosphere. Chem. Mater. 20(4), pp. 1492–1501.

In situ polymerization of polyaniline in wood veneers

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Abstract

The present study describes the possibility to polymerize aniline within wood veneers to obtain a semi-conducting material with solid wood acting as the base template. It was determined that it is possible to synthesize the intrinsically conductive polymer (ICP) polyaniline in situ within the wood structure of Southern yellow pine veneers, combining the strength of the natural wood structure with the conductivity of the impregnated polymer. It was found that polyaniline is uniformly dispersed within the wood structure by light microscopy and FT-IR imaging. A weight percent gain in the range of 3−12 wt % was obtained with a preferential formation in the wood structure and cell wall, rather than in the lumen. The modified wood was found to be less hydrophilic with the addition of phosphate doped polyaniline as observed by equilibrium water swelling studies. While wood itself is insulating, the modified veneers had conductivities of 1×10^{-4} to 1×10^{-9} S cm^{-1}, demonstrating the ability to tune the conductivity and allowing for materials with a wide range of applications, from anti-static to charge-dispersing materials. Furthermore, the modified veneers had lower total and peak heat releases, as determined by cone calorimetry, because of the char properties of the ICP. This is of interest if these materials are to be used in building and furniture applications where flame retardance is of importance.

Introduction

Interest in intrinsically conducting materials has been prolific in the past few decades with the most recognition of the area being the 2000 Nobel Prize in chemistry for the development of conductive polymers awarded to Heeger, MacDiarmid, and Shirakawa. Traditional metals are inferior in terms of their mechanical properties and conductivity, while required high loading leads to heavier and inflexible systems.

Previous research, involving the coating of wood sawdust with polyaniline, has demonstrated that polyaniline coatings on wood and cellulose fibers can lead to increased fire retardancy. However, impregnating an aniline monomer solution into wood and synthesizing polyaniline in-situ, in order to take advantage of the complex and robust structure of wood itself, has received less attention.

The aim of this project is to use the complex structure of wood as a renewable material that is by nature a light yet strong material and modify with intrinsically conductive polymers in order to obtain a novel functional material. The proposed advantage is not only to obtain a conducting material but also to address other important restrictions for wood such as the effect of modification on the dimensional stability, strength, fire resistance, and morphology of the conductive polymer within the architecture of the wood structure.

Experimental

The crown cut/flat cut Southern Yellow Pine (Carolina pine) veneer was received from Specialised Veneers Ltd., Aylesburg, United Kingdom. After conditioning at 65% RH, the veneers had approximately 11 wt % moisture content and a density of 530 kg/m^3. The aniline (≥99.5% purity), phosphoric acid (85 wt % in H20, 99.9% trace metal basis), sulphuric acid (95–98%), dodecylbenzenesulfonic acid sodium salt, and ammonium peroxydisulfate (APS) (≥98%) were all used as received from Sigma Aldrich. The impregnated veneers resulted in 10 wt% dry polyaniline in wood.

Results and discussion

The modified veneers were found to be semi-conductive and the majority of polyaniline was determined to be located in the middle lamella. (Figure 1) The modified veneers also had better dimensional stability and were more hydrophobic than untreated wood.

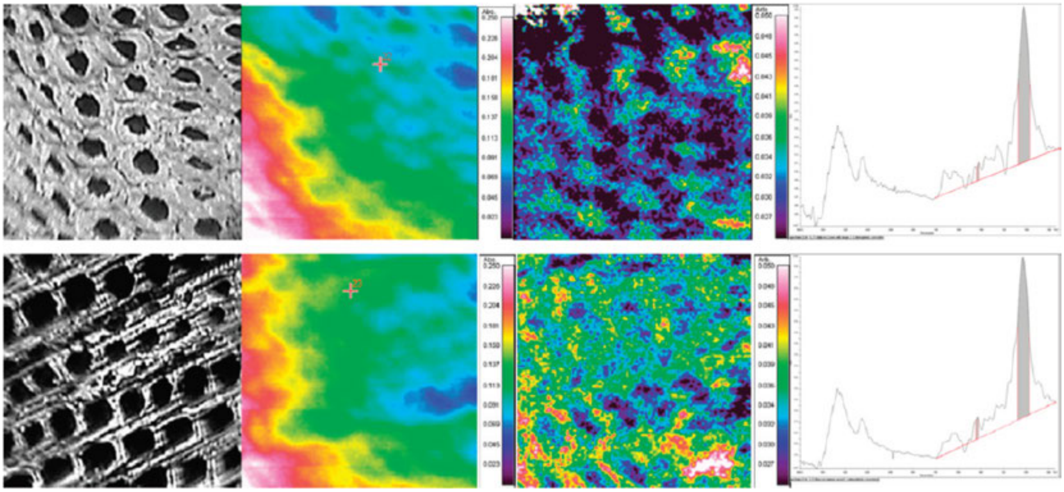

Figure 1. FT-IR imaging (each image 150 × 150 μm) of the cross-section of the unmodified veneer (top row) and 0.2 PANI-PA modified veneer (bottom row) with the visible image to the far left, the average absorbance second to the left, the band ratio image (1480:1080 cm-1) second from the right, and the band ratio illustrated in the selected spectra to the far right.

References

1. Trey, S., Jafarzadeh, S., Johansson, M. 2012. In situ Polymerization of Polyaniline in Wood Veneers ACS Appl. Mater. Interfaces 4(3), pp. 1760−1769.

Pre- and post-processing of solid biofuels and bio-ash into new construction materials

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Abstract

Ash derived from biomass combustion is composed of a complex heterogeneous mix of inorganic compounds. Many interesting properties such as leeching of elements and setting behavior with water strongly correlate with composition and structure. Ekolite has studied ashes with specific interest to self-hardening. The compositions and structures of ashes have been studied with XRF, XRD and SEM/EDS – methods. In addition the hydration behavior of ashes has been tested in a laboratory. Ekolite has also tested and verified a specific mechanical activation treatment for ashes in order to enhance their hydration behavior. Activation is based on high speed impacts of particles in the milling chamber. Collisions cause chemical and physical changes on material. Activation treatment is performed in a disintegrator mill. Ash quality is heavily depending on combusted biomass type and combustion conditions. Currently laboratory tests are being performed on enhancing ash quality and combustion properties with optimum biomass mixes and suitable additives.

Ashes produced by fluidized bed combustion of woody biomass mixed with different quantities of peat have been analysed. The major ash forming elements are Si, Ca, Al, Fe, Na, K and P. At temperatures below 900°C the ash does not completely melt into glass, but is also constituted by various mineral silicates along with sulphate and carbonate species, which would break done at higher temperatures into oxides. When the microstructure is observed by a SEM it is seen that silicates tend to form larger agglomerates. Carbonates and oxides form regular shaped smaller crystals or alternatively flakes adsorbed on the surfaces of the larger silicate agglomerates.

Significant differences were observed in the hydration behaviour of analysed ashes. This is believed to be the result of ashes containing different solid phases having different solubilities. The water to ash ratio upon hardening varied between 0,15 and 0,65. This water to ash ratio could be significantly reduced for all ashes by mechanical treatment of ashes in disintegrator – mill.

Introduction

Ekolite is presenting the ideas and some preliminary results, which are related to **the Sustainable utilization of ash, slag and pyrolysis residuals – TUULI Project**, a part of Tekes Green Growth Program. In the Tuuli project more than 10 industrial partners and research departments of Universities and Research Institutes are participating until June 2015.

Experimental

Ten different ash samples were collected from woody biomass utilizing Finnish heatplants. Analysed ashes were produced by plants using modern fluidized bed technology in which the operating temperatures are between 750 and 850°C. One sample was collected from a small scale heatplant using conventional moving – grate technology for reference. The biomass blend used for producing the ashes on all of the plants does not significantly change between plants. Woody biomass makes >80% of all used fuel while the rest is mostly peat.

The elemental and mineralogical composition of the collected ashes were measured using a Philips PW 1050 – XRD – apparatus. The microstructure of the ash samples was observed using a scanning electron microscope (SEM) coupled with a tip capable of electron dispersive scanning (EDS) for elemental analysis.

The hydration behaviour of the ashes was monitored in the laboratory by mixing the samples with water to obtain a dispersion of standard viscosity for all samples.

Results and discussion

Elemental composition

The elemental compositions of studied ashes vary. The most abundant elements found in the ashes are Si (30 w% to 60 w%), Al (10–20 w%) and Ca (10–40w%). The most silicon-rich ash sample is collected from a grate – boiler. A grate boiler also tends to have the highest content of unburnt carbon as indicated by a high LOI value. Gasification residues have also higher LOI values than fluidized bed combustors.

Mineralogical composition

The major crystal phases in the analysed ashes are feldspar – minerals and silicon dioxide as quartz or cristallobite. It is interesting to note that both calcite and calcia were found in the samples. This indicates that at least some of the calcium present in the woody biomass is reactive during combustion of these materials.

Microstructure

The microstructure is clearly very heterogeneous consisting of larger unevenly shaped particles or agglomerates and uniformly shaped spheres or rectangular crystals. Using EDS – technique it was found out that the larger unevenly shaped agglomerate particles consist mainly of silicate – type structures (feldspar minerals) and the uniform rectangular shaped crystals are calcium oxide or carbonate crystals. The even spheres that are sometimes seen are likely silicates in glassy form.

Hydration behaviour

Setting and hardening with water mixes differentiated greatly between samples. Within the ten collected samples ten different water-to-ash ratios were defined. Values range from 0,15 to 0,65. By mechanical treatment with disintegrator mill water to ash ratios were found to decrease on average by 30%.

Conclusions

Ten biomass ashes were analysed for elemental composition, mineralogical structure, microstructure and hydrological behaviour. Ashes composing mainly of Si, Al and Ca have a microstructure of small crystals of calcium carbonate or oxide and larger agglomerates of siliceous structures. Mixing with water creates hardened structures.

Carbon footprint of wood biorefinery products – case Forchem tall oil derivative products

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Abstract

Tall oil products are natural raw materials for many industrial processes which serve consumers in a variety of ways. They are used, for example, in paints and coatings, pulp and paper chemicals, printing inks and bio fuels, only to mention few. Tall oil is a residue of the chemical pulp industry. Pine, used as the raw material for tall oil, is a renewable natural resource which grows in northern forests.

Carbon footprint is one important element of sustainability of wood biorefinery products. Life-cycle assessment is the best currently available methodology for carbon footprint calculations of products. Gaia's experts calculated the carbon footprint of Forchem's products, including bio-fuel Fortop600, Tall Oil Fatty Acid, Tall Oil Rosin and Distilled Tall Oil. According to Gaia's calculations, the products have a minimal carbon footprint. Production of alternative products for same end-usage would cause 12–35 fold emissions compared to those of Forchem's products.

Methods

Carbon footprint calculations were conducted following the best available methodologies, i.e. life cycle assessment standards (ISO 14040 and ISO 14044). Emissions are calculated for year 2010. The presented results include emissions from raw material production, transportation and operations in Rauma refinery (cradle-to-gate).

Primary data was collected and used for all processes under the control of Forchem. Secondary data was collected from available databases (mostly Ecoinvent v. 2.1) and used to estimate the emissions of raw material production and transportation. When more accurate data was available in literature, the database data was further modified e.g. with national information for transportation emissions. Emissions of crude tall oil production (CTO) were assumed to be 3.5% of the emissions of sulfate pulp production. This is based on the average amount of CTO produced as side-product in sulfate pulp processes in Finland (mass basis). The direct emissions (e.g. electricity and fuel use) were allocated to different products based on actual utility consumption for each product. Transportation emissions and raw material emissions, including process water, were allocated to different products on mass basis (production amounts). Emission factor for average Nordic pulp mill is utilized here, as 90% of the CTO originates from Nordic pulp mills. The calculation was conducted for business-to-business purposes.

Results

Forchem TOFA Tall Oil Fatty Acid has lower carbon footprint compared to alternative materials such as soybean oil in e.g. paints and coatings. The carbon footprint of Forchem TOFA is only 78 gCO_2eq./kg, whereas soybean oil fatty acid has significantly higher carbon footprint with 1457 gCO_2eq./kg. This makes greenhouse emissions of vegetable oil alternatives as high as 12-fold compared to emissions of Forchem TOFA.

Forchem DTO Distilled Tall Oil has lower carbon footprint compared to alternative materials such as soybean oil in e.g. paints and coatings. The carbon footprint of Forchem DTO is only 76 gCO_2eq./kg, whereas soybean oil has significantly higher carbon footprint with 920 gCO_2eq./kg. This makes greenhouse emissions of vegetable oil alternatives as high as 12-fold compared to emissions of Forchem DTO.

Forchem TOR Tall Oil Resin has a lower carbon footprint compared to production of gum rosin. Its carbon footprint is only 71 gCO_2eq./kg, whereas gum rosin has a significantly higher footprint with 980 gCO_2eq./kg. This makes greenhouse emissions of gum rosin as high as 14-fold compared to emissions of Forchem TOR.

Fortop600 is a liquid biofuel, which replaces heavy fuel oil (HFO) in customer applications. Carbon footprint for Fortop600 is 71 gCO_2eq./kg, significantly lower compared to carbon footprint of HFO, 430 gCO_2eq/kg. When effective heat values are taken into account, carbon footprint for production of Fortop600 is 1,9 gCO_2eq./MJ, whereas production of HFO causes six times higher emissions. Combustion of biofuels is classified to be carbon-free in the EU emissions trading scheme. Taking this into account the greenhouse gas emissions of HFO are as high as 35-fold compared to emissions of Forchem Fortop600.

The main results of carbon footprint calculations are summarized in a figure below.

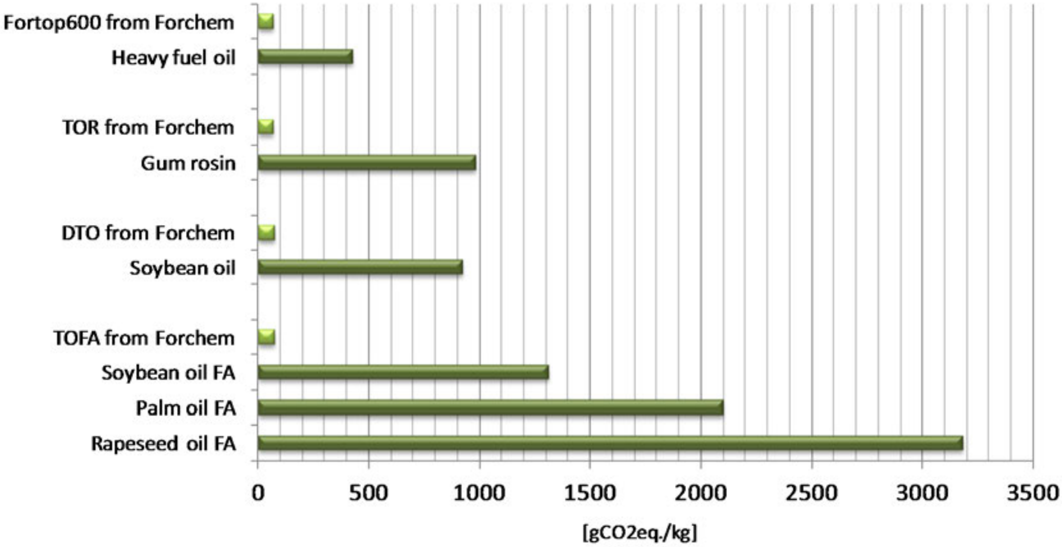

Figure 1. Carbon Footprint of Forchem CTO derivative products and their substitutes.

Conclusions

According to Gaia's calculations, Forchem's tall oil derived products have a minimal carbon footprint. Production of alternative products for same end-usage would cause 12–35 fold emissions compared to those of Forchem's products.

Series title and number

VTT Technology 53

Title	**NWBC 2012** **The 4th Nordic Wood Biorefinery Conference**
Author(s)	Klaus Niemelä (Ed.)
Abstract	This proceedings book is based on a total of more than 120 oral and poster presentations in the 4th Nordic Wood Biorefinery Conference, held in Helsinki 23–25 October 2012. As a whole, the contributions clearly demonstrate the increasingly important role of the wood-based industry as a source of different renewable materials, chemicals and energy products (in addition to the more traditional products).
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Keywords	Biorefinery, innovation, wood, forest, biomass, pulp, biochemicals, biomaterials, biofuels, cellulose, lignin, hemicellulose
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