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NWBC 2015

The 6th Nordic Wood Biorefinery Conference

Helsinki, Finland, 20–22 October, 2015

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Preface

Eemeli Hytönen
Chairman of the NWBC 2015 Organising Committee

These proceedings highlight the latest advances in the wood-based biorefining related R&D&I and form a "snapshot" of the state of the art today. The most discussed topics include lignin based products and sugars; wood fractionation, enzymatic hydrolysis, filtration, and extraction processes; Kraft pulping process integration; and lignin separation from spent cooking liquors. The organizers sincerely hope that the selected presentations form an interesting and balanced cross-section of the current topics and point the way to future topics of interest to both industry and academia.

The organisers of the NWBC 2015 wish to thank everyone involved in the preparation process of this conference; the programme advisory committee members and session chairs for their contribution in planning and setting up the conference agenda. Not forgetting of course all speakers, poster presenters and their co-authors for their valuable contributions to the contents of the conference without whom this event would be impossible.

The organisers wish to express special thanks to Erja Schlesier, the technical editor of this book of proceedings.

Enjoy the conference!

Contents

Policy

Sustainable Growth from the Bioeconomy – Implementing Finnish Bioeconomy Strategy

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Introduction

The Finnish Bioeconomy Strategy was drawn up in a project launched by the Ministry of Employment and the Economy in 2012. It was a collaborative effort involving several ministries and a broad range of stakeholders. The Bioeconomy Strategy and the Government Resolution concerning bioeconomy have been implemented as part of the Strategic Programme for the Forest Sector (MSO) since the beginning of 2014. The strategy has been implemented in close cooperation with the Ministry of Agriculture and Forestry, the Ministry of the Environment, the Ministry for Foreign Affairs and other operators in the sector. Implementation measures have focused on generating new investments, exerting influence in the EU, improving the operating environment and promoting exports.

Implemented actions

Accelerating and supporting new investments and innovation

The Government growth package in 2014 included EUR 100 million of additional capital to the Finnish Industry Investment Ltd for developing the bioeconomy and other areas with growth potential. For Tekes, Finnish Funding Agency for Innovation, the package included an additional permanent annual authorisation of EUR 20 million to be used on the bioeconomy and cleantech. The Finnvera authorisation for export funding has also been increased.

Current and planned investments in bioproduct and pulp mills amount to EUR 3.5 billion. Various other kinds of bioeconomy investments have also been announced. Their total value is in the order of one billion euros. At this point, it is difficult to estimate how many of the investments will be realised, but the numerous new plans are a positive sign. In addition to participating in several investment projects, the MSO has also promoted their implementation.

In 2014, the programme organised an international biorefinery competition to promote new business and investments in bioeconomy. A diverse array of proposals took part in the competition, representing different areas of the bioeconomy. They varied in size from demonstration facilities worth less than a million euros to biorefineries requiring hundreds of millions of euros in investment. The combined value of the investments entered in the competition was approximately EUR 1.5 billion. The winning entry was Spinnova Ltd’s new textile fibre production technology. The other two award-winning proposals were Biovakka Suomi Oy’s concept for combining the production of biogas, nutrients, and transport fuel, and the Kemijärvi Consortium’s proposal for the production of new biomaterials and biochemical using novel Finnish technology. The Ministry of Employment and the Economy has assembled a funding group representing public entities to coordinate and help the three top proposals obtain public funding for the investment phase.

In accordance with its operational programme, the MSO has focused on finding development and funding models for enterprises and solutions for the realisation of investments. To boost growth enterprises, pilot projects have been launched to test new models for cooperation between large companies and SMEs. Cross-sectoral activities and new symbiotic relationships between industries have been promoted by organising separate events for large companies and SMEs and joint events for different sectors.

Providing a competitive operating environment in Finland and the EU

The most important national measure has been the project examining the legislative and administrative obstacles to promoting bioeconomy. The project was launched with funding from the Prime Minister’s Office, and it is coordinated by the Ministry of the Environment. It should be completed during 2015.

Work has also started on the Biomass Atlas, a tool that combines public data on biomass resources. The work is coordinated by the Ministry of Agriculture and Forestry.

In the European context, the aim has been to have a stronger and more proactive influence on the preparation of EU legislation, policies, decisions and actions concerning the forest industry and the forest bioeconomy at large.

Finnish priorities for the EU in the bioeconomy were defined in 2014. These priorities were: 1) Enhance competitiveness and growth by a shared vision and a favourable and predictable operating environment, 2) Create demand for biobased products by strengthening of people’s awareness and creating a level playing field, 3) Finance of R & D & I towards financing of first of its kind investments, pilots and demonstrations, and 4) Ensure acceptability, availability and sustainability of biomass use.

Numerous events have been organised in Brussels, and EU-officials and Deputy Permanent Representatives of EU Member States have been invited to Finland to see and personally experience forest bioeconomy. The purpose of the visits is to present Finland as a leading bioeconomy country with an ability to utilise forest-based biomass and the diversity of nature in a versatile and sustainable manner. The significance of collaboration in the development of Finnish and European bioeconomy was also emphasised.

Promotion of exports of biobased products and technologies

The MSO has engaged in close collaboration with the Ministry for Foreign Affairs and Finnish embassies to promote the bioeconomy and Finnish exports. Bioeconomy has systematically been integrated in Team Finland activities and Finland's country brand activities. The materials produced in the Stories of Wood project were presented and the importance and opportunities of the Finnish bioeconomy explained at the annual meeting of Finnish Heads of Mission in 2014.

At the beginning of 2015, the MSO began preparing a growth programme for bioeconomy, in collaboration with Finpro and different operators from the sector. As part of the growth programme, the parties have drawn up a three-year export programme for sawmills, aiming to support Finnish sawmills in exporting their products to China and other growing markets. The goal is to better understand the markets and customer needs and to enable growth in exports. The programme was launched in spring 2015. In addition to the sawmill industry, export oriented growth programmes are being drawn up for agrotechnology, packaging materials, bioenergy and energy production from waste. Together with Finpro, Tekes and enterprises, a growth programme is planned for innovative biomaterials, focusing on promoting exports, creating new business and organising “Invest in” activities.

Communication and promotion of the bioeconomy for stakeholders and general public

In 2013 and 2014, the MSO implemented the Stories of Wood project to promote the bioeconomy and its image and to increase its impact. The project included improvements to the bioeconomy website bioeconomy.fi and produced videos, brochures, a briefcase of product examples and presentation material in different languages, in collaboration with stakeholders, the Ministry of Agriculture and Forestry, the Ministry for Foreign Affairs and the Ministry of the Environment. Opportunities of the forest sector and the bioeconomy have been actively communicated and this has in many ways contributed to improving the image and attractiveness of the sector.

Outcome from the strategy process and its implementation

After one year of implementation, we have noticed several positive outcomes from the strategy process. Firstly, it has helped to form a strong national will to develop the bioeconomy. This can be witnessed in the governmental programme of the recently elected Government, where the bioeconomy is one the five spearheads. The process and the actions have created a positive outlook for the future which can be seen in increase of investments both from the private and public sectors. We are also seeing an increased interest from non-forest industries to utilise biomass, and an increased public acceptance for use of biomass.

New Zealand a Bioeconomy but with no National Bioeconomy Strategy: Contrast to Other Nations

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Introduction

New Zealand is an island with a small population, 86% of whom live in urban areas. Urban areas cover 5% of the land mass, 33% is conserved (primarily covered in native forest), 7% in plantation forests, 3% in crops/horticulture and the remainder (52%) is devoted to production of animals. The challenge of both producing food and fibre/bioproducts/biofuel is relatively easy as there is plenty of available land. The greater challenges are maintaining clean water, and building emerging industries while increasing food and fibre productivity and intensification. 80% of food produced is exported, and about 50% of wood fibre production is exported. By contrast, most chemicals, transport fuels and materials are imported. Challenges include safety of food including packaging needs and building new industry clusters outside the dominant primary food producers in a society dominated by SMEs. New Zealand focusses on the international environment and needs, and makes an interesting test bed for new ideas and access to Asia. While it is a very biologically based country, and sells mostly biological products it has no overarch- ing Bioeconomy Strategy.

Does this matter?

The New Zealand Government does have, however, a growth strategy. This is to increase the ratio of exports to GDP to 40% by 2025, from a base of 30% in 2012. This requires the real value of exports to double over the 13 years (from $60 billion to around $120 billion), a real export growth between 5.5 and 7% per annum. Of necessity, based on the economic activity of New Zealand, biobased products (food and other materials) and manufacturing associated with this will be the predominant sources of growth. However, there have been little or no direct subsidies to support growth. For example, it introduced technology development grants for firms that invest significantly in research and development in 2012 rather than giving direct subsidies.

There is one strategy that has been put in place, but without direct incentives or drivers to ensure rapid progress. This is the New Zealand Energy Strategy, first released by the Government in 2007: Towards a sustainable low emissions energy system; as well as a parallel document; New Zealand Energy Efficiency and Conservation Strategy. At that time there were to be initiatives to “champion renewable energy across power generation and transport and the development and deployment of sustainable energy technologies”. The government then set a target for 90 per cent of electricity to be generated from renewable sources by 2025, based on an already high renewable energy content in the national energy framework. At that point, New Zealand had a renewables energy content of ~70%. The Strategy was updated in 2011, and included growth from export of oil and gas (possibly 4th greatest in merchandise export) and at this point (September 2015) 82.8% of New Zealand’s electrical energy was renewable, with demand also up for power, especially by the major biobased export industries. However this growth is NOT due to biomass technologies.

Such a growth in renewables clearly would be expected to include the development of biorefineries. However the lack of a specific strategy and an industrial bioproducts strategy has meant that growth in biorefinery products and biobased materials and products has been slower than might be expected in a biobased economy. Rather than put in place incentives to drive growth, the government policy has been to try to encourage by setting up funds for companies or company clusters based in New Zealand to apply for to grow commercially oriented R & D.

New Zealand currently produces a small suite of bio-based industrial (and medical) products, primarily from plantation forests, seafood by-products, plant fibres, and animal tissues. However, this is beginning to change with a range of firms and sectors, notably the wood processors, showing increasing interest, as evidenced by the Vision 2050 document of the WPMA. Pine plantations represent a significant competitive advantage for New Zealand for the development of bio-based products. They are an abundant resource that doesn’t generally compete for land with food crops, harvesting and processing supply chains exist, and there is strong underpinning science capabilities associated with plantation management and processing. As such pine plantations have the potential to form the backbone of an advanced bioproducts system in New Zealand.

New Zealand has a diversity of groups and organisations interested in bioproducts research and development. The CRIs Scion, Plant and Food Research, AgResearch and IRL, along with the University of Canterbury and Massey University have particular strengths already aligned to bio-based products and biorefineries. There are however, a broader range of research, engineering and technology skills and capabilities within New Zealand (such as industrial enzyme development, life cycle analysis, and social science) that need to be tapped into to develop the critical capabilities that would support a bio-based industrial products sector. Critical challenges include the development of new value chains and their coordination, clarity of markets and opportunities, cost of production, and collaboration internationally as well as locally.

What of the Future?

New Zealand has multiple international agreements that encourage a future Bioeconomy. These include climate change agreements, trade agreements and energy agreements. An example is the requirement for compliance with the programme's 90-day oil stocks obligation which has, since 2007, been met through a combination of domestic commercial stocks and 'ticket' contracts for stocks held in other IEA member countries. As a further example, New Zealand has environment cooperation arrangements with Thailand, Singapore, Brunei, Chile, China, Malaysia, the Philippines, and Hong Kong, China. Negotiations are in progress for similar arrangements with South Korea and Bahrain.

Climate Change and the actions agreed globally and commitments by New Zealand, will mean that a way to encourage significant changes in New Zealand's current practises will have to be found. New Zealand's current target is to reduce greenhouse gas emissions to 5 per cent below 1990 levels by 2020. The new post-2020 target is equivalent to 11 per cent below 1990 levels by 2030. New Zealand will meet these responsibility targets through a mix of domestic emission reductions, the removal of carbon dioxide by forests and participation in international carbon markets. The post-2020 climate change target is to reduce greenhouse gas emissions to 30 per cent below 2005 levels by 2030. This means a more active participation in a Bioeconomy will be required, for example as the WPMA Vision 2050 imagines.

Industrial bio-based products in development or early commercialisation (not as biorefinery products) include:

- Biobased polymers electrospun into mats and applied in different ways to filters (eg Revolution Fibres)
- Microbes metabolising CO, H and CO2 to make a range of products including biofuels (eg Lanzatech, now moved headquarters to USA)
- PHAs used as substrates for additional proteins immobilised by metabolic linkages making bionanoparticles (eg Polybatics)
- Use of cellulose to 3D print absorptive media - new membrane filtration structures to segregate materials with altered flow properties (University of Canterbury)
- Wood (tree) waste transformed into densified products for heat generation (eg Natures Flame, SSF)
- Wood fibre plastics substituting for many short glass fibre composite products such as in automotive applications (eg Woodforce)
- Biopolymer substitute for foamed products (eg Zealafoam)

Lastly, New Zealand's Science Minister announced on 5 October 2015 a new National Statement of Science Investment 2015-2025. This sets out the 10 year strategic direction for science in New Zealand. It contains no statement on a Bioeconomy focus, rather indicates a maintenance in government funding for the primary sector, but focussed on discovery research, strengthening ICT research in fundamental areas, increase investment to support manufacturing, continuing to support environmental research and increasing investment in the health sector. Overall there is a desire to invest in high tech and knowledge intensive sectors.

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Canada's Forest Innovation Ecosystem – Accomplishments and the Path Forward

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Abstract

Canada's forest sector research has made great strides since the turn of the millennium towards establishing a strong, coordinated, resilient and flexible "Innovation Ecosystem". This presentation uses examples to describe the genesis of the Innovation Ecosystem and its current accomplishments. It also provides a description of an Innovation Framework that is being implemented to ensure continued competitiveness and sustainable transformation of the industry.

Introduction

In the early 2000's, Canada's forest sector research was fragmented across many different players: three non-profit research institutes, federal and provincial government departments and many university and college programs. While collaboration among these stakeholders occurred, no single organization was positioned to develop a common vision, a coordinated approach and a collective review of strategic science and technology investments across the entire value chain. The predictable result was research gaps in critical areas, duplication of effort in others and investment of scarce resources on projects with little potential for commercial impact.

FPInnovations and the Transformative Technologies Program

An important milestone in improving the alignment of research resources with regional and national industry needs was the 2007 merger of the three existing non-profit industry research institutes to form **FPInnovations**. Today, FPInnovations has an annual research budget of C$100 M and employs 600 staff across the country. A membership-based, collaborative business model ensures it is highly representative and atuned to industry needs across all parts of the sector.

In 2012, the Forest Products Association of Canada (FPAC) launched **Vision2020**. This initiative challenged industry, governments, academic researchers, policy thinkers and other stakeholders to drive the sector's transformation through an agreed set of strategic goals, which are to:

- Renew the workforce with an additional 60,000 new recruits;
- Improve environmental performance by 35%; and

- Generate an additional $20 billion in economic activity from new products and markets;
  …all by the end of the decade.

These goals reflected a stark reality that remains true today:

Canada's forest sector can only maintain and grow its competitive strength in the global marketplace and set the stage for long-term prosperity if we deliver more innovation to achieve the above goals and do so in an effective and efficient way.

One of the key shifts in this innovation space was that, in addition to alignment of priorities and capacities, there was an additional focus on innovation deployment and de-risking of new products and processes.

The federal government-funded Transformative Technologies Program was designed to support FPInnovations in leveraging industry investment to achieve this outcome. As examples, this resulted in three new technologies for traditional and non-traditional forest products that will create significant economic development opportunities being brought to the verge of commercialization:

- A 30 ton/day plant implementing FPInnovations Lignoforce Technology™ for kraft lignin precipitation, which will start up in the fall of 2015 at West Fraser Timber's kraft pulp mill in Hinton, Alberta;
- A 5-ton/day demonstration plant for cellulose filaments started up in 2014 at Kruger Bioproducts' Trois-Rivières, Quebec mill; and
- A 1-ton/day demonstration plant implementing FPInnovations' cellulose nanocrystal production process, which started up at Celluforce in Windsor, Quebec in 2012. Celluforce has since launched several CNC products and has attracted additional equity investment from companies, such as Schlumberger International.

University Engagement and FIBRE

The developments above, while important, are built on the foundation of underpinning academic research and represent a small fraction of current forest products revenues. To ensure the continued competitiveness and transformation of the industry, a larger pipeline of potential new technologies, products and applications is required.

Universities and colleges are a rich source of creative ideas and it was with this in mind that, in 2009, Natural Resources Canada and FPInnovations developed a memorandum of understanding with Canada's Natural Sciences and Engineering Research Council (NSERC) to assist in identifying critical forest sector needs to be addressed by a 5-year, $34M program targeted at forest sector research and development.

Through a series of workshops the subject areas of four strategic networks, to be funded at $1M/year for five years, were established. When launched in 2010, these new networks joined four existing networks in which FPInnovations was already an industrial partner to bring a powerful array of university resources to bear on industry problems.

FIBRE – Forest Innovation By Research and Education – was a consortium of these university research networks, which was created in 2011 to improve collaboration, transfer of university research to industry and to give a coherent voice for the academic community within the Forest Sector Innovation Ecosystem. Its accomplishments include the training of over 500 Masters and PhD level scientists, almost 600 peer-reviewed publications, 43 patent disclosures and 2 start-up companies. Equally important, it has attracted top level scientists from many disciplines not usually associated with forestry to provide fresh perspectives on the conversion of forest biomass to value-added products.

The constituent networks of FIBRE will all have come to the end of their 5-year mandates by the end of 2015. This provides an opportunity for the stakeholders in the Forest Innovation Ecosystem to evaluate its performance – what worked, what didn't, how can it be improved – and use this to devise new means to engage academic research more effectively into industry transformation.

An Innovation Framework for the Future

To manage future transformation processes, FPInnovations, Natural Resources Canada, and FPAC developed a national **Forest Industry Innovation Framework** in 2014. This common Framework, outlined in Figure 1, was designed to guide innovation needs and identify opportunities to deliver transformation while aligning the sector on agreed upon goals. The framework should allow the sector to better assess the balance and direction of its research and development portfolio. It will also help Canadian research providers to design research methodologies and partnership models that deliver purpose-built solutions more efficiently:

- align business performance and industry impact metrics between stakeholders;
- strengthen sector-level mobilization of key strategic opportunities; and
- support investment in post-secondary institutions and funding requests to federal and provincial government investment programs.

The Framework summarizes both **what** must be done to achieve transformation to a new, vibrant and competitive forest sector and **how** it should be done:

- The left side of Figure 1 captures the three key Functional Goals (i.e. research outcomes) to make the sector grow and prosper sustainably:
    - A Sustainable Fibre Supply requires not only resilient and productive forests, but also that the management of these is integrated with the needs of the larger natural environment and that the fibre is harvested and transported responsibly.
    - Value is added to this fibre supply through Innovative Manufacturing and Products. Efficient and adaptive manufacturing is needed to maintain cost

    competitiveness, find new markets for existing products and to develop new wood-fibre based materials and applications.
  - These two elements are connected through Integration Enablers: decision support systems, optimized supply chains and new business and investment models.

It is important to realize that Figure 1 carries no assumptions about who within the Innovation System is best placed to deliver each of these Functional Goals. Rather, it provides a structured framework to classify current activities, identify gaps and to think strategically about where future resources should be deployed.

- The right side of Figure 1 captures the key mechanisms to deliver successful innovation. It is perhaps the more difficult part of the Innovation Framework to grasp and to put into action. However, it is also the most important as these mechanisms will be routinely used to determine what the Functional Goals are and drive a cross-sectoral Culture of Innovation Excellence:
  - To develop Fit for Purpose Solutions, one must endeavour to make effective use of market intelligence and future foresight, apply principles of design and engage meaningfully with our customers' customers to understand deeply market needs.
  - A Leading Edge R&D Capacity requires that we engage the efforts of multiple disciplines and infrastructures through effective partnership vehicles to create sustainable resourcing across the R&D value chain.
  - Linking these two elements through Efficient Delivery will require use of technoeconomic modelling, capturing both new and existing intellectual property (*i.e.*, avoiding a not-invented-here perspective) and finding ways to engage end users' investment and deployment capacity.

Critically, it is hoped that each of these mechanisms will be consistently deployed in the planning of major research initiatives and throughout their execution, rather than as an after-thought once a detailed research program is well underway.

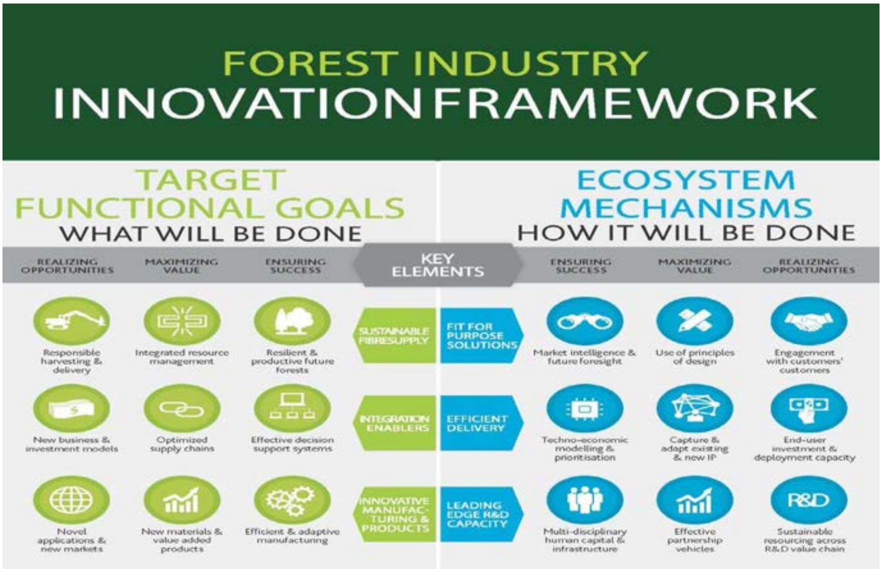

Figure 1. Forest Sector Innovation Framework.

Innovation Framework in FPInnovations' Strategic Action Plan

The adoption of the Innovation Framework as a perspective to shape activities cannot be forced from above. As a way to demonstrate its commitment and facilitative leadership, FPInnovations has placed the Innovation Framework at the core of its **5-year Strategic Action Plan** and has built key performance indicators around it. FPInnovations is now leveraging the Framework in a variety of ways:

- Best-practice, evidence-based approaches and advisory processes are guiding our research and development programs and informing those of our partners and investors. Furthermore, we are capitalizing on comprehensive market intelligence and future fore-sighting, including our unique Industry and Technical Advisor network, to actively inform all of our investments and research.
- Standardized techno-economic analysis, stage-gating, value proposition development and intellectual property mining tools are being promoted for use by our R&D partners and stakeholders. We have structured our research programs to take advantage of the efficiencies that come with working on a national scale, while maintaining a focus on regional benefits for economic growth and job creation.
- Using a "best teams" philosophy, we are continuing to embrace the capabilities of colleges, universities and other research providers. This has enabled us to coordinate an integrated, multi-partner portfolio representing the majority of Canada's total forestry sector investment in fundamental and applied pre-commercial research and development.

- We are co-authoring at least two significant white papers per year on recommended investment, technology and market strategies for industry, and federal and provincial governments. In addition, FPInnovations is acting as an intermediary to connect existing sector members with emerging participants, such as aboriginal businesses, bio-chemical manufacturers and green consumers.

Conclusion

The Canadian Forest Innovation Ecosystem has been through major changes over the last 8 years. Those changes have helped all stakeholders to:

- Define national sectoral vision and priorities;
- Align innovation capacities;
- Create synergies within the innovation ecosystem; and
- Attract new investments.

FPInnovations is committed to playing the role of **Facilitative Leader** and **Efficient Innovator** within this Ecosystem – and work with national and international partners to improve the competitiveness and transformation of the forest sector.

National and international activities

AERTOs Stimulates the Bio-based Economy in Europe

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Abstract

Seven European research organizations have started a joint project BBE-Biobased Economy within an AERTOs (Associated European Research and Technology Organisations) framework. The aim of the project is to stimulate the development of the bio-based economy in Europe. It will also overcome technical hurdles in the innovation value chains.

The project focuses on the development of lignocellulosic biomass processes for modern biorefineries. The aim is in particular to create new, valuable lignin products and cheap technical sugars for the production of bio-based chemicals. Besides lignocellulose algae biomass is the other focus of the project. Extraction methods both for macro and micro algae will be developed. Various product options from algae biomass will also be evaluated. Besides the technical research questions bioeconomy scenario work and market analysis will be carried out.

The AERTOs BBE – Bio-based Economy – project will strengthen the collaboration of European research organizations in the field of bioeconomy and improve the mobility of researchers. It combines different technologies available from the following partners: VTT Technical Research Centre of Finland, Tecnalia, Fraunhofer, Sintef, VITO, TNO and SP. T

The R&D work in the programme will be funded by the partners. The total budget is EUR 3.5 million.

CLICing Bioeconomy and Cleantech into Global Biorefinery Solutions

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Introduction

In September 2015 two Finnish Clusters, Finnish Bioeconomy Cluster FIBIC Ltd and the Cluster for Energy and the Environment CLEEN Ltd merged to form CLIC Innovation Ltd. The mission of CLIC is to create comprehensive solutions with global business impact far beyond the capabilities of individual actors. CLIC addresses systemic challenges that arise from the scarcity of natural resources.

CLIC will speed up the commercialization of new knowledge by initiating and orchestrating solution orientated project portfolios covering the entire innovation chain from basic research to demonstrations. Bioeconomy and clean solutions are the key drivers behind the activities.

Background

The Strategic Centres for Science, Technology and Innovation (SHOKs) was an initiative launched in 2006 by the Finnish Research and Innovation Council (1). A key role of the SHOKs was to increase the competitiveness of the Finnish research and innovation system, by developing industry-driven research activities, and by focusing resources on selected areas important for the Finnish economy, By 2009 six SHOKs representing different sectors where established. Together they include 80% of Finland's export business,

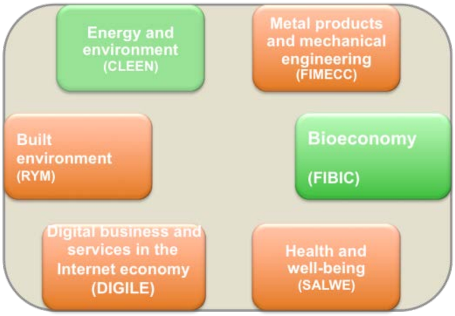

Figure 1. The Finnish Cluster (SHOK) network.

Forestcluster, which in 2012 changed focus and became Finnish Bioeconomy Cluster FIBIC, was the first SHOK to start in 2007. FIBIC's mission was to offer businesses and research organizations a new way of engaging in close, long-term cooperation with the aim to build the future, sustainable bio-based economy.

The Cluster of Energy and the Environment CLEEN Ltd was designed to bring focus and industry lead to the energy and environmental research.

In 2014 a process to deepen the cooperation between these two Clusters was initiated, and in September CLIC Innovation was born as a result of a merger between FIBIC and CLEEN. The merger was based on the desire by the industry to create a company with activities covering the whole R&D&I chain from basic research to demonstrations and commercialization. In addition, synergies between the Strategic Research Agendas of CLEEN and FIBIC were evident.

Strategic Scope and Focus

The Strategic Research Agendas of both CLEEN and FIBIC form the starting point for the activities of CLIC Innovation. The merger will not effect the existing programme portfolios of CLEEN and FIBIC, on the contrary, the existing programme portfolios will be finalized and the exploitation of the results will be ensured. The strong framework created as a result of the merger will enable a rapid and extensive utilization of research results.

Table 1. Starting point for the CLIC project portfolio.

CLEEN SRA Themes	FIBIC Competence Platforms
Architecture of sustainable future Energy systems	Biomass-based energy production
Sustainable production, handling and uses of gases for energy production	Biorefinery concepts and processes
Healthy urban living	Fibre and cellulose products
Sustainable use of natural resources	Sustainable biomass supply

CLIC is aiming at creating something completely new in the field of bioeconomy and cleantech with a determined objective of global impact. A major next step is to build up the future project portfolio. This will include long term competence building as well as demonstration activities to boost tnew business opportunities. As a first example, a feasibility-study was carried out, to study the possibilities of flexibly linking different future energy system options and creating a platform in Åland. By creating a versatile platform, demonstration of smart energy technologies, enabling a high share of renewables can be made in a real environment. The smart energy system of the future combines Finland's strengths and future global needs, i.e. the bioeconomy, cleantech and digitalization, with other functions of society, such as electric transportation, the food chain and waste management, in a natural and sustainable way. Åland provides an opportunity to prove that it is possible to solve future energy challenges today by pooling together different interests and fields of excellence.

Another example is an initiative comprising of several company-lead consortium projects glued together by a joint research platform, with the aim to develop new fibre-based products for different applications.

Actors with impact

The core of CLIC comprises of 30 world-leading companies in their sectors and the most significant national research institutions (17) for which bioeconomy and cleantech are the main business drivers and source for scientific inspiration.

The aggregated sales of the companies involved are over 100 billion euros and they employ more than 150 000 people. Together they spend annually more than 1 billion euros on R&D. CLIC will for building cross-industrial and multidisciplinary competence network to address.

All major Finnish universities and research institutes with activities in the field of Bioeconomy and clean solutions are taking part in the CLIC network. In addition, CLIC is connected to extensive international networks. European networks have been most important in the field of bioeconomy, whereas Asia has been the main direction for clean solutions.

CLIC aims at becoming an importanta node for bioesonomy and cleanteoch research, development and innovation actions.

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Programmes and projects to follow in the future

Norwegian Biorefinery Laboratory (NorBioLab); Developing the Processes for Tomorrows Biobased Society

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Abstract

The Norwegian Biorefinery Laboratory (NorBioLab) is a national laboratory for development of novel biorefinery processes for conversion of biomass to environmentally benign biochemicals, biomaterials and bioenergy products. The vision of NorBioLab is to be the fundament for developing novel, advanced biorefinery processes at top international level.

Introduction

The NorBioLab project was established in 2014. The project is included in the Norwegian Roadmap of Research Infrastructures. This roadmap gives a listing of prioritized national infrastructures that are considered the most strategically important investments in Norwegian research. NorBioLab is the only infrastructure in this roadmap focusing on biomass conversion/biorefinery processes. The national research infrastructures are funded by the Norwegian Government through the Research Council of Norway. The aim is to have all research infrastructures installed by end of 2016 – some are already in use. The NorBioLab project, involving also the use of the installations, will last until 2021, but the intention is that the infrastructure user phase will last far beyond this.

Through NorBioLab a number of novel research tools – not commercial off the shelf units – are being established, complementing existing infrastructures. The aim is to establish flexible units that can be applied to different raw materials and that can address a large variety of processing schemes, both for biochemical and thermochemical conversion of biomass (see Figure 1).

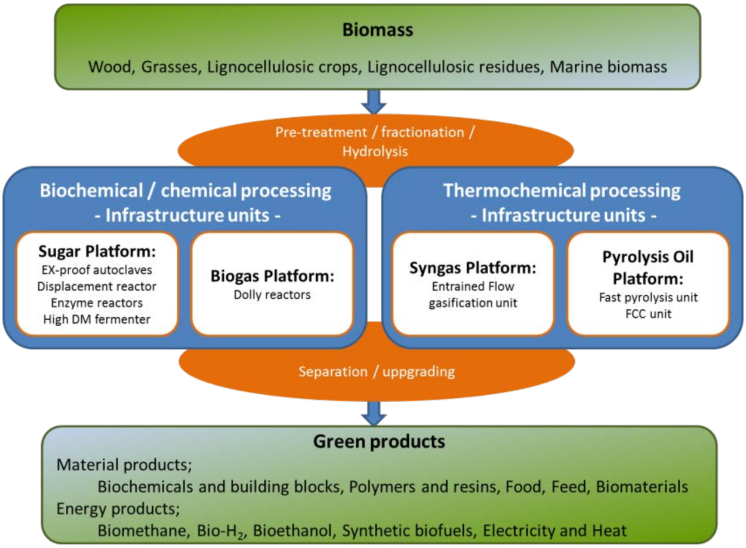

Figure 1. The NorBioLab Infrastructure Project layout.

NorBioLab objectives

The main goal of NorBioLab is to be a **national infrastructure for biorefining,** accessible to national and international stakeholders for the development of processes for the sustainable conversion of Norwegian land and marine based biomass to novel, environmentally benign biochemicals, biomaterials and bioenergy products.

Through the establishment of NorBioLab we aim to:

- Establish a unique laboratory infrastructure for biomass conversion
- Be the national fundament for developing environmentally friendly processes and products
- Position the research partners at an international level
- Stimulate both national and international industries, researchers and students to use the infrastructures
- Position Norway as an attractive R&D partner in international research projects

The NorBioLab infrastructures

NorBioLab addresses both the C6/C5 sugar platform, the Biogas Platform, The Syngas Platform and the Pyrolysis Oil Platform (cf. Figure 1).

Equipment suited for biochemical conversion routs include i) advanced, EX proof reactor systems for pretreatment and fractionation of biomass (e.g. high pressure, rapid heating, novel sampling systems), ii) units for enzyme production and hydrolysis, iii) advanced high dry matter fermenters with novel product separation system, iv) reactors for biogas production, and v) multiple autoclave system for liquid phase catalytic conversion of biomass to platform molecules.

Equipment for thermochemical conversion of biomass includes i) fast pyrolysis reactor suited for production and ex situ upgrading of pyrolysis oil, ii) reactor for production of hybrid bio-fossil fuels through co-processing in fluidized catalytic cracking (FCC), and iii) entrained flow gasification reactor with interchangeable in-feed modules.

The total infrastructure will allow for simulating and testing most conceivable conversion routes in laboratory to pilot scale. NorBioLab infrastructures will be accessible to – and welcomes – both national and international research partners and industries.

The NorBioLab partners

NorBioLab gathers central Norwegian stakeholders in the biorefinery area, and unites existing and new research infrastructure and national competence, allowing for internationally leading research on new, innovative biorefinery processes. NorBioLab is headed by PFI, in close collaboration with The Norwegian University of Science and Technology (NTNU), The Norwegian University of Life Sciences (NMBU) and SINTEF (Table 1). Through this gathering of competences we aim to lay a foundation for internationally leading research on new, innovative biorefinery processes.

Table 1. NorBioLab partners.

Partner		Description
PFI	Paper and Fibre Research Institute	PFI is a centre og expertise for wood fibre, pulp, paper, new biobased materials and biofuels.
NTNU	Norwegian University of Science and Technology	NTNU is Norway's primary institution for educating the nation's future engineers and scientists.
NMBU	Norwegian University of Life Sciences	NMBU's focus is on sustainable development, human and animal health, renewable energy, food production, and land- and resource management.
SINTEF		SINTEF is a broadly based, multidisciplinary research institute, and is the largest independent research organisation in Scandinavia.

Acknowledgement

We greatfully acknowledge the Research Council of Norway (grant no. 226247/F50) for financial support to establishing NorBioLab.

Australian Bioprocessing Advanced Manufacturing Initiative (BAMI)

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The Bioprocessing Advanced Manufacturing Initiative (BAMI) is a national industry transformation research hub (ITRH) resulting from the partnership from the major Australasian Bioresource processing manufacturers and technology companies with the Australian Research Council (ARC) aiming at diversifying manufacturing through innovation and technology. BAMI has two platforms: 1) Advanced materials and 2) Green chemicals.

Novel applications of nanocellulose and paper in biomedical diagnostics, high performance nanocomposites and packaging are investigated as part of the material platform. In one project, nanocellulose is analysed as a barrier to decrease moisture and oxygen permeability when used as coating on paper based packaging. In a second project, the properties of novel nanoparticles-nanocellulose composites are explored. The special focus is to control the composite structure at the nano and the micro scales. This is achieved by engineering the co-flocculation of nanocellulose and nanoparticles using various polyelectrolytes. The variables controlled include the type of polyelectrolyte (CPAM, PEI), its charge density and molecular weight as well as the polymer concentration or its surface coverage. Thin and flexible composites are built using the papermaking process. Of special interest are the nanocellulose composites at high nanoparticle content (50-80%). SAXS (laboratory and synchrotron) and electronic microscopy (SEM and TEM) are used to characterize the composite structures. Using nanosilica (8 nm) with microfibrillated cellulose, two different structures were found based on the nanoparticle content. A packed bed structure is reported at concentrations up to 50%; in this regime, the nanoparticles aggregates are lodged within the porosity created by fibers and do not affect sheet structure. Beyond 50%, nanoparticles pack in a closer structure and form aggregate bigger than the natural pore size formed by nanocellulose fibers; this means composite volume/thickness increases. The effects of the structure on the properties of the composites are discussed in terms of mechanical properties and permeability.

In a third example, bioactive paper is investigated for low cost diagnostics for blood typing application (A, B, D). The concepts behind the commercialization of the Group Legible Immunohaematology Format (GLIF) will be reviewed. GLIF represents a disruptive technology in blood analysis. It is faster, cheaper and much easier to use than the current gel card technology, while achieving similar reproducibility and sensitivity. Best, it does not require any modern blood analysis laboratory, trained technician or even water or electricity to function. Antibody anti-A, anti-B and anti-D are printed in letters over paper and dried. For blood analysis, a blood droplet (40 µL) is deposited over the bioactive part of the test, let 1minute to incubate, before a saline solution is used to wash non agglutinated blood (40 drops). The blood group simply appears as a red letter (A, B, AB, O with +/- to indicate the rhesus). When in contact with its specific antibody, blood agglutinates. This test relies on blood agglutinate to print letters. Paper serves many functions in this diagnostic. A first is as filter to separate blood aggregates (positive) from un-agglutinated blood cells (negative). Paper also store and stabilises the antibodies, and store a copy of the results.

The platform of green chemistry focuses on the catalytic conversion of cellulose and lignin into chemical intermediates. A first project is the catalytical and biochemical breakdown of lignin into controlled oligomers and their upgrading into chemical intermediates or through polymerization into thermo-processable polymers. Also of interest is the conversion of cellulose into fine chemicals through catalysis and the production of nanocellulose fibers.

Mobile and Flexible Processing of Biomass – EU Project Mobile Flip

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Abstract

EU project MOBILE FLIP in the SPIRE program aims at developing and demonstrating mobile processes for the treatment of underexploited agro- and forest based biomass resources into products and intermediates. The processes are evaluated in terms of raw material flexibility, as the biomass resources are typically scattered and seasonal. Process concepts have been designed around the key technologies pelletizing, torrefaction, slow pyrolysis, hydrothermal pretreatment and carbonisation. The products vary depending on the process concept, being typically fuels as such or for co-combustion (pellets, torrefied pellets, biocoals), biochars for soil remediation, biodegradable pesticides for agricultural or forestry use or chemicals for wood panel industry and sugars and hydrolysable cellulose as intermediate for the sugar platform. The concept evaluations are supported both by research and industrial (SME and large industries) partners in the whole value chains. Dissemination, communication and exploitation activities are an integral part of the project. Life-cycle analysis and a wide sustainability evaluation (economic, environmental and social assessment) are carried out for the process concepts in order to clarify their potential for flexible raw material valorisation. The partners are represented by the coauthors in this presentation: four SMEs, two large companies, six research organizations. The project duration is four years and total budget approximately EUR 10 million.

Objectives

MOBILE FLIP aims to develop technologies for simple and robust processes that are applicable to small scale. The specific aims of the project are to demonstrate at least three of the following technologies as a mobile unit

- biomass pre-treatment steps (comminution, drying, fractioning)
- hydrothermal treatment and saccharification
- hydrothermal carbonization
- torrefaction
- slow pyrolysis
- feasible compaction technologies for solid products (pelletizing and briquetting)

Approach

Sustainability, feasibility and social aspects are handled in dedicated work packages that support and provide feedback to the technical work packages as illustrated in **Figure 1** that presents the project structure. The process concepts being developed are presented schematically in **Figure 2**.

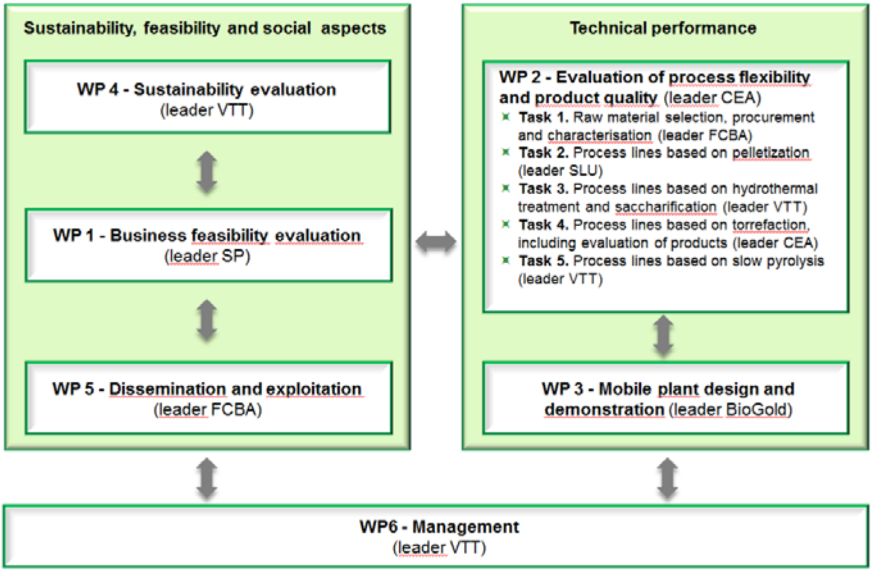
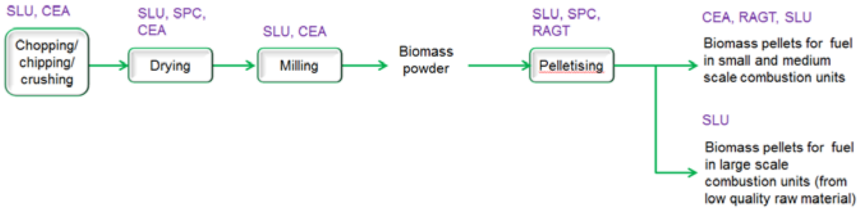
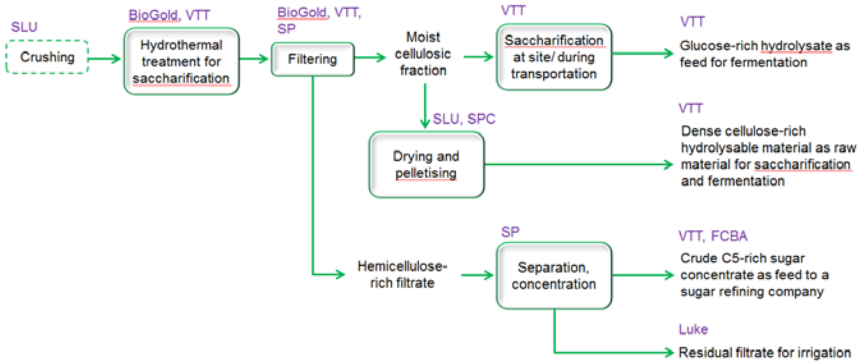


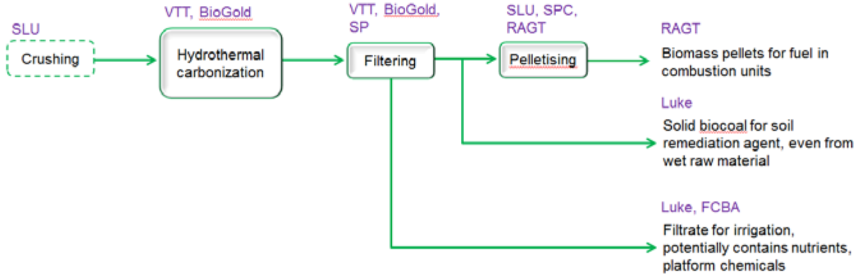
Figure 1. Strucure of MOBILE FLIP.



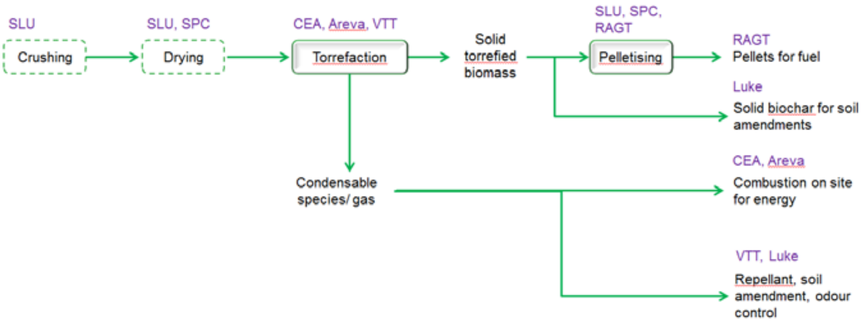
Pelletizing



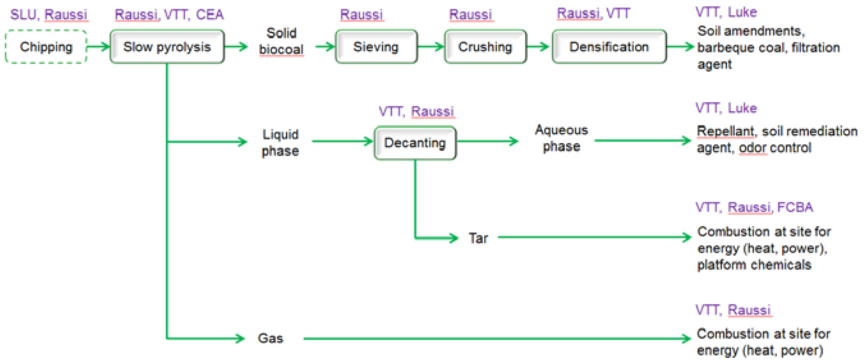
Hydrothermal treatment for saccharification



Hydrothermal carbonization



Torrefaction



Slow pyrolysis

Figure 2. Process concepts studied in MOBILE FLIP.

Acknowledgements

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REACH Registration of the Biorefinery Products

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Abstract

According to the provisions of the REACH Regulation any substance manufactured in or imported into EU has to be registered. The costs of one registration can sum up to 1,000,000 euro (while the typical REACH costs, however, are much less) and take up to one year.The registration obligation concerns any substance in quantities of one tonne or more per manufacturer or importer, unless covered by any of the exemptions. For example chemically unmodified natural substances, by-products which are not placed on the market as such or certain separately determined other substance groups are exempted from the registration.

The REACH registration process includes several strategic decisions. The registrants of the same substance are obliged to share at least the vertebrate animal test data. Typically the registrants of the same subtstance form a REACH Consortium which commissions the necessary laboratory and animal studies, prepares the Chemical Safety Assessments and prepares a Joint Registration Dossier.

In biorefinery concepts both main product(s), intermediates and by-products may be subject to the REACH registration. While the cooperation with the co-registrants is a possibility to reduce the costs of the REACH registration, it also means that the competitors have to share e.g. the details of the composition of their substance with each others. Actually, the substance identification can be an important strategic decision, too. It may be possible to define one biorefinery product as a one UVCB substance (Substance of Unknown or Variable composition, Complex reaction products or Biological materials) or as mixture of several substances.

REACH strategy is an issue of expenses but there are also several stages in the REACH registration process where specific attention has to be paid to the protection of the confidential product and process information. At the same time the requirements of the fair completion laid down in the competition law have to be kept in the mind.

The questions and challenges related to the development of new bio-based products typically include:

- Substance identification
- Interpretation of the “unmodified natural substance” definition
- The REACH obligations for the by-products and the decision on the by-products to be placed on the market
- Possibilities to apply the PPORD registration exemption ((product and process oriented research and development)
- Protection of the Confidential Business Information
- Competition Law compliance.

ACel Program: From Pulp Cellulose to Novel Products

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Abstract/Introduction

Advanced Cellulose to Novel Products (ACel) research program of FIBIC (CLIC Innovation from 1.9.2015) addresses the opportunity which is created by the fact that both the use of materials and the request of sustainable renewable raw materials is growing globally. In Finland, the world leading competence in cellulose production and conversion enables the further development of wood-based cellulose materials to novel application markets. The program is expected to have a major impact on the renewal of the forest cluster and generation of new Finnish networks in textile and composite value chains.

Background

The FIBIC FuBio programs (2009–2014; program books at http://fibic.fi/results) have generated knowledge and tools related to wood cellulose dissolution and modification to functional materials. An impressive set of novel ionic liquids has been synthesized, characterized and preliminary tested for partial or total dissolution of wood and cellulose fibres. In addition, basic knowledge on the chemical modifications of cellulose as dissolved or in fibre form in both water-based systems and in ionic liquids and the properties of resulting fibre-based cellulose materials has been generated.

The FIBIC research programs and the respective consortia have also invested in research environments during recent years. A dry-wet spinning equipment line (in Aalto University) for research use has been developed. Together with the basic knowledge and method development, a new knowledge platform in the area of dissolving cellulose processing especially to fibres has thus been built to Finland. Similar research environments and knowledge platforms have been created also for composites and thermoformable materials.

The rising interest on cellulose materials requires transferring the research from fibre properties to creating the properties of materials and polymers and to making use of them on case by case basis. This necessitates a completely new set of scientific approaches and understanding.

ACel objectives

ACel program aims to promote wood cellulose fibre based material opportunities in three product areas: textile fibres, thermoformable composites and cationic chemicals. Innovative methods to activate and modify and process cellulose with and without dissolution to target materials and chemicals with desired properties will be developed. The program also aims at creating a new concept for doing material testing together with converting and end user companies. The target is to facilitate the implementation of the research results during the course of the program.

ACel activities

ACel program activities contribute to the following four main topics:

- Development of advanced scientific methods for analysing fibre cellulose reactivity.
- Advances in new ionic liquid based process to produce high quality textile fibres from wood cellulose.
- Generating new strategies to efficiently produce thermoformable and thermoplastic composite materials for packaging, automotive, furniture and construction applications. Considerations of the cellulose reactivity will be combined with chemical, biotechnical and mechanical approaches for cellulose modification. Furthermore, efficient synthesis routes for cationic cellulose chemicals in novel solvents will be studied.
- Creating a Finnish application research network in cellulose materials. In practice, end user companies are invited to test the cellulose materials generated in the ACel program. Furthermore, a discussion platform for future wood cellulose-based textile and clothing R&D will be aimed at.

Knowledge generated in the program is published in scientific and technical papers as well as in open ACel research seminars. The materials of the first open seminar held in June 2015 with the title of “Cellulose reactivity and recycling of ionic liquid recycling” can be found at: http://fibic.fi/programs/on-going-programs/acel

ACel facts

Basic information of the ACel program has been collected to Table 1.

Table 1. ACel program facts.

Partners	9 companies & 6 research organisations
Duration	2+1 years, first period 1.6.2014–31.5.2016
Budget	6.1 million € / first period
Funding	Tekes, industry & research organisations
Contacts	Anna Suurnäkki, VTT
Net site	http://fibic.fi/programs/on-going-programs/acel

Overview of the Project ValChem

Value Added Chemical Building Blocks and Lignin from Wood

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This project has received funding from the Bio Based Industries Joint Undertaking under the European Union’s Horizon 2020 research and innovation programme under grant agreement No 669065

Abstract

ValChem (Value added chemical building blocks and lignin from wood) is an ambitious project combining the competences of forest, chemical and bio-technology industries to realise a sustainable and innovative integrated process to convert wood to a selected platform chemical and lignin based performance chemicals. The aim of the project is to demonstrate the technical and economic viability of an integrated biochemicals process as well as the whole value chain.

Funding and Partners

The consortium conducting the ValChem project received EUR 13.1 million funding from the Biobased Industries Joint Undertaking (BBI JU) under the EU´s Horizon 2020 program in June 2015. The project will be conducted over a period of four years in co-operation with Sekab E-Technology, METabolic EXplorer and the Technische Universität Darmstadt (Figure 1). The total budget of the project is EUR 18.5 million.

The BBI JU is a new EUR 3.7 billion partnership between the EU and the Bio-based Industries Consortium (BIC) aiming at increasing investment in the development of a sustainable bio-based industry sector in Europe.

Figure 1. Valchem Partners.

Objectives of the ValChem project

The aim of ValChem is to demonstrate technical and economic viability of a sustainable and integrated process from wood to bio-MPG and lignin based performance chemicals. The project will demonstrate that the integrated process can produce wood-based chemicals that are competitive with fossil-based identical (MPG) or similar-in-application (lignin) products in terms of quality and production cost. The demonstration activities aim to provide the final proof of technological and economic feasibility of a process and products before moving into a commercial phase. The target of ValChem is to be ready to make an investment decision for a flagship plant by the project-end.

ValChem utilises the existing demonstration plants of the project partners to produce wood-based chemicals. SEKAB's CelluAPP® technology for wood to sugars and to crude lignin conversion process has been verified in demonstration scale for ethanol production, however, in this project it will be combined with METabolic EXplorer's sugar to MPG process.

The largest markets for MPG are unsaturated polyester resins, paints and coatings, industrial use and personal care. High value added lignin applications will be developed jointly by UPM and Technische Universität Darmstadt. Their end-uses are for example in the field of lignin-based reactive resins and composites.

References

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Assessments and markets

Synthesis and Verification of Accumulated Experience and Results from Lignocellulosic Ethanol Research

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Abstract

A synthesis analysis of Swedish research undertaken and underway in the field of lignocellulosic ethanol has been carried out. The analysis was based on research in the Swedish Energy Agency's Ethanol Program conducted in Sweden, starting 1993. In the program different research groups has focused on optimizing both different parts of process, but also the overall process. An analysis and synthesis of results is particularly of interest now that the Ethanol Program is about to end. The result of the project is a summary of both of results and continued need for research and development in the field and for the commercialization and implementation of technology in production scale.

The result of the research that has been conducted has been compiled, both in terms of achievements in the various process steps and how these results can be translated into a future commercial process. Different process concepts has been evaluated and the advantageous and disadvantages of each process concepts has been summarized. The process options for softwood and straw that gives the highest ethanol yield, maximum energy efficiency or is optimal from an economic perspective has been analyzed and compared. Verification in demo scale will be conducted for the chosen process for each raw material as well as a techno-economic evaluation. The goal of these processes was that they must achieve an overall energy yield of ethanol and biogas at least 80% of theoretical based on the energy content of the carbohydrates in the raw material and that the concentration of ethanol after fermentation must be at least 5% to reduce energy consumption in the distillation process.

The analysis was conducted in close cooperation with stakeholders involved in the program, from universities and industry. A compilation of the international state of knowledge in the field was also conducted, both in terms of individual process steps and overall processes to be able to put the Swedish results into an international perspective.

Introduction

The synthesis analysis is based on the Ethanol Programs conducted in Sweden since 1993. Within the programs various research groups often focused on optimizing different parts of process.

Within the last Ethanol Program a similar synthetic work with the aim of compiling, evaluating and designing an enzymatic process based on the research results was performed. This led to a suggested process, primarily for softwood, and identification of important issues that remained to be solved. Several of these issues and others have been studied thereafter, e.g. within the current Ethanol Program. Thus, it was is important to resume the so-called synthesis project and update it with the new results that have been produced later based on research, pilot and demo trials and verifications.

An overall analysis and evaluation of the results are of particular relevance now that the Ethanol Program is about to end. Both for continued research and development and for the commercialization and implementation of technology in the production scale, it is important to conduct a summary of the international research front in relation to the Swedish developments.

Summary of research results

A summary of research results within the Energy Agency’s last two Ethanol Programs in the field: “Ethanol from cellulose” (2007-2011) and “Ethanol Processes” (2011-2015), was carried out. The focus was on the latter program. Results from the available final reports have been included in the compilation and for ongoing projects information from applications or interim reports was included. The purpose of this was to show in what areas it can be expected to get more results within the research program.

The research results have been compiled for each area / process steps: Raw material, Pretreatment and acid hydrolysis, Detoxification, Enzymatic hydrolysis, Yeast propagation, Fermentation, Process Concepts, Process integration with other processes and Techno - economic analysis.

International outlook

An analysis of research and development internationally was carried out both for individual process steps such as pretreatment, enzymatic hydrolysis, fermentation (including pentose fermentation) with respect to technologies, yield, concentrations etc., and of various process concepts with respect to overall yield, energy efficiency and economy, based the available literature.

Process concept for future verification

The summary of the research and the experience of a broad reference group was the basis for design of process concepts. Different process concepts for both softwood and wheat straw were compared based on ethanol yield, energy efficiency and an economic perspective. Verification in demo scale will be conducted for the chosen process for each raw material as well as a techno-economic evaluation. The goal of these processes is that they must achieve an overall energy yield of ethanol and biogas at least 80% of theoretical based on the energy content of the carbohydrates in the raw material and that the concentration of ethanol after fermentation must be at least 5% to reduce energy consumption in the distillation process.

Results and discussion

Summary of national research projects in focus areas

Raw materials

Lignocellulosic raw materials that has been used in different research projects are e.g. wheat straw, spruce, sugar cane bagasse, birch, pine, poplar, barley straw, corn stover and wheat bran. The first three: wheat straw, spruce and sugar cane bagasse has been by far the most common raw materials. Other raw materials used, mainly for yeast propagation and in studies involving the integration of first-generation ethanol process, are e.g. wheat flour and molasses.

Pretreatment and acid hydrolysis

Research projects that has studied pretreatment has focused on effects of pretreatment on different types of raw materials and mixes of raw materials, effects of pretreatment parameters such as raw material size, temperature and time and on choice of catalyst (e.g. H2SO4, SO2, NaOH, organic acids). Pilot and demo scale pretreatment has also been in focus.

Fermentation

Great focus has been on development of yeasts that also convert pentoses to ethanol. Common pentose sugars in lignocellulosic biomass are xylose and arabinose, but focus has been on increasing xylose fermentation since it is the predominant pentose in most lignocellulosic raw materials. Inhibitor tolerance has also been a focus, often in combination with development of yeasts able to ferment xyose. Yeast has been the most common microorganism, but also other types have been studied. Upscaling has been studied and thus also identification of common contaminators.

Process concepts
Several projects have studied various process configurations in order to use higher dry matter content in the hydrolysis and fermentation in order to reduce water use. This has also lead to development of detoxification processes to avoid inhibition at high dry matter content and pre-hydrolysis prior to SSF to reduce viscosity. Process concepts have also been developed in order to optimize pentose fermentation.

International outlook

The international outlook can be summarized in the following trends: 1) more focus on upscaling in terms of pilot and demo plants, 2) focus on processes able to handle a high dry matter content 3) genetically modified yeast able to ferment several of the different sugar monomers in lignocellulosic materials 4) process integration with other processes and 5) biorefinery concepts in which ethanol and other products are produced from the lignocelluloisc biomass.

Design of processes for future demo scale study

Demo scale using wheat straw

The process for production of ethanol from wheat straw consists, after decomposition of the raw material, by pretreatment with H2SO4 and then the pretreated material is separated into a solid phase and a liquid fraction. The separated liquid consists mainly of pentose sugars from hemicellulose. A portion of the liquid fraction is used with together with molasses for yeast propagation. The advantages of this is that yeast to some extent will be adapted to better cope with the inhibitors present in the fermentation stage, that by reducing the amount of dissolved sugar in the fermentation reduces product inhibition of the enzymes and that it will increase the simultaneous consumption of hexoses and pentoses. Another advantage is that by separating off the liquid, the fermentation can be performed at a higher dry matter content and thereby obtain higher ethanol concentrations. Enzymatic hydrolysis and fermentation are carried on the solid fraction in an SSF with purchased enzymes. After fermentation the material is distilled for separation of ethanol.

The remaining material after distillation is separated into a solid and a liquid fraction. There are various alternative uses for these fractions. The solid fraction which consists largely of lignin can be dried and sold for further processing or combustion. Alternatively, it can be incinerated for on-site production of electricity and heat. The liquid fraction of stillage can be digested to produce biogas before the liquid goes to water purification and / or recycling. To produce electricity, heat and biogas from the waste stream will increase the energy yield.

Demo scale using spruce as raw material

The process for the spruce is largely similar to the process for straw. The major differences between these materials are their different optimal pretreatment parameters and content of various sugars. Unlike straw, spruce contains greater proportion of hexose sugar monomers. Thus, the need for effective pentose fermentation and an efficient process could instead be based on a robust genetically unmodified yeast strain.

In the process pretreated material is hydrolyzed and fermented in a SSF with purchased commercially available enzymes and yeast. As for the straw process, there are different options for the solid fraction after distillation: to dry the lignin, or to produce electricity and heat from it, while the liquid fraction is digested.

Future research and development needs

The analysis resulted in suggested process concepts that will be demonstrated in demo scale and evaluated in a techno-economic evaluation. It has also led to identification of future needs to continued research and development. The following areas of research need has been identified: 1) Pretreatment (new types of raw materials and mixed raw materials, 2) propagation of pentose fermenting yeast 3) Processes that yields high ethanol concentration (e.g. processes with initial enzymatic liquefaction, development of new feeding strategies, improved process control and on-line measurements, improved control over inhibitors), 4) Development of robust strains able to ferment all sugars present and process concepts for optimal use, 5) Downstream processing (drying, production of pellets and combustion of lignin for heat and/or power production, other uses of stillage and evaluation best use, continuous digestion of stillage, 6) System and process design (integration with other biorefinery processes, system analysis, techno-economic evaluation, LCA etc. incl. biomass availability, logistics and storage, water cleaning and water recirculation).

Acknowledgements

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Simultaneous Assessment of Technical Performance, Economic Viability and Environmental Footprint of Forest Biorefinery Systems: I-BIOREF Tool

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Introduction

In 2012, the market for bio-based products excluding biofuels, was estimated at about $200Billion (Bn), of which polyols, bioplastics and biocomposites represent $28Bn. The annual growth of the entire bio-based products market is projected to be in the order of 6 to 8%, with the highest growth by bioplastics and biocomposites. Despite such significant market growth, the bio-based industry is still at the infant stage, facing major issues and hurdles to mitigate the technology and market uncertainties: economics (still highly dependent on of biomass price, only few companies are willing to pay green premium, new plants versus depreciated plants, etc.); value-chain acceptance (the downstream integration of new biochemicals and biocomposites is still not straightforward, the product functionalities are yet to be tested and proven); technology limitations (conversion yields and selectivity are not yet optimal); sustainability (energy intensity and LCA-based environmental footprint metrics need to be developed). Thus, the forest industry recognizes the potential market from the conversion of lignocellulosic biomass into high-value added bioproducts and the need for the technology shift. However, it remains cautious about the integration of novel technologies into their existing processes. Also, the industry is interested in diversifying its production with minimal interferences in its current facilities. Therefore, the industry and the end-users need tools that enable them to perform the benchmarking of their selected biorefinery option against other well-established alternatives. The proposed tool to be presented with a demonstration of its capabilities is the I-BIOREF software that is under development by CanmetENERGY of Natural Resources Canada. Two case studies are considered in this paper to demonstrate the features and functionalities of I-BIOREF as well its robustness and its self-adaptability at the software architecture level: **(a)** the first case study is based on integrating the LignoBoost^{TM} technology into a median Canadian bleached kraft pulp mill, that is limited by the recovery boiler capacity; **(b)** the second case study is based on a stand-alone organosolv biorefinery.

I-BIOREF Tool

The I-BIOREF tool is a solution that enables the modelling and benchmarking of any established biorefinery process or pathway, and simultaneous assessment of its technical performance, economic viability and environmental footprint. I-BIOREF incorporates graphical capabilities to aid visualization of the main unit operations involved, and make it possible to develop a detailed process flow diagram of biorefinery technologies, integrated into an existing mill or as a standalone system. Each unit operation includes default values for process data and associated economic data. It also incorporates pulp and paper process models and a comprehensive library of well-established biorefinery technologies – which can be combined or not –, for the simulation of a wide range of plausible "what-if" scenarios. Models available and under development in I-BIOREF include: pulp and paper processes (kraft pulp and thermomechanical); biomass pre-treatment processes (steam explosion; liquid hot water; acid hydrolysis; instant controlled pressure; organosolv; subcritical and supercritical fluids; ionic liquids; torrefaction); pre-extraction processes (hot water; enzymatic hydrolysis and supercritical fluids e.g. CO_2); lignin recovery processes (LignoBoost^{TM}; LignoForce^{TM}); conversion processes for lignocellulosic sugars (detoxification; fermentation; separation/purification); and thermochemical processes (gasification; pyrolysis; catalysis). Each model is supported by a detailed mass and energy balance and related key process characteristics, which include electricity, steam, water, biomass, fuel, chemicals, and effluents. An automatic control functionality is incorporated, to reconcile, diagnose and communicate inconsistent data or specifications to the user, ensuring that valid data is entered when creating process flow diagrams. The key features of I-BIOREF are provided in Table 1.

Table 1. Summary of I-BIOREF key features and related benefits.

I-BIOREF KEY FEATURES	BENEFITS
Comprehensive library of pulp and paper mill models	
Kraft pulping processes	- Represents an existing mill, as it is currently operated - Provides an overall understanding of the mill structure and operations - Provides the opportunity to embed any model associated with the existing mill or a new one
Thermomechanical pulping processes	
Comprehensive library of biorefinery models	
Over 15 biorefinery technologies included	- Modelling a wide range of industrial biorefinery processes, including utilization of electricity, steam, water, biomass, fuel, and chemicals - Quick simulation of a wide range of “what-if” scenarios for integrated or standalone biorefinery systems
Readily available process data	
Flow sheet of selected biorefinery technologies can be selected	
Input unit prices available	
Detailed mass and energy balances	
Appropriate coverage of materials and energy entering and leaving a mill site, as well as the mill’s processes, systems or equipment	- Provides a structure for examining interactions between the different components of an operation - Explores the relationship between energy use and the variables that may influence it, using data collected at appropriate intervals - Evaluates how much energy is being used, wasted or lost, and where this occurs - Examines chemical recovery and reuse opportunities
Systematic accounting for energy and chemical flows and transformations	
Multi-criteria decision-making	
Technical performance metrics (e.g. yield, purity of the products)	- Instantly determines the economic impacts of process designs or scenario decisions - Identifies revenue opportunities - Instantly determines the environmental footprint of a biorefinery system
8 key economic metrics included	
17 LCA-based metrics included	

Case study 1

The potential implementation of a LignoBoost$^{\text{TM}}$ technology within a Canadian softwood kraft pulp mill producing up to 1,100 air-dry-tonne/day of bleached pulp was considered (Fig. 1). To do so, a pulp production increase of up to 20% along with a lignin recovery of up to 100 dry-ton/day from weak black liquor have been targeted. The technical information obtained includes the impacts on the chemical and utility requirements for the pulp mill due to its integration with the LignoBoost$^{\text{TM}}$ technology along with the chemical and utility consumption for the LignoBoost$^{\text{TM}}$ technology. Computed economic metrics include internal rate of return (IRR), return on investment (ROI), return on capital employed (ROCE), net present value (NPV), earning before interest, tax, depreciation and amortization (EBITDA), access to biomass (CAB), and resistance to market uncertainty (RTMU). CAB and RTMU are new metrics that represent the ability to guarantee a supply of biomass over the long-term while providing a competitive value to biomass producers, and the sensitivity of the integrated biorefinery to the fluctuation in market value due to raw materials and energy price variations, respectively (Fig. 2).

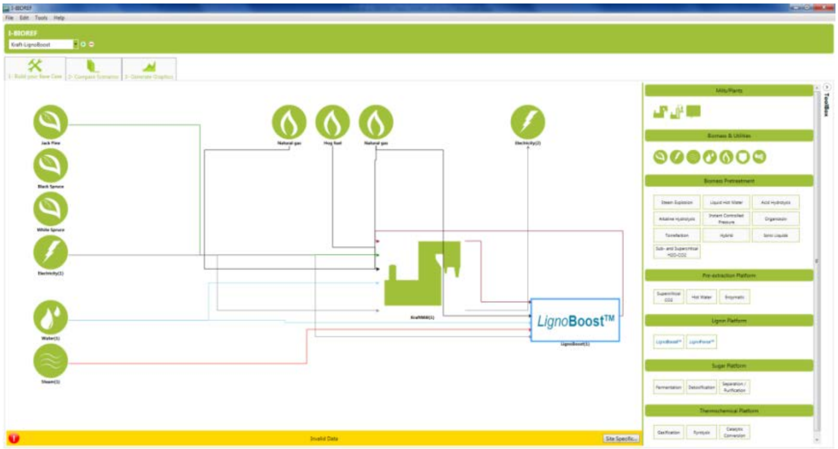

Figure 1. Integrated kraft pulp mill-LignoBoost biorefinery.

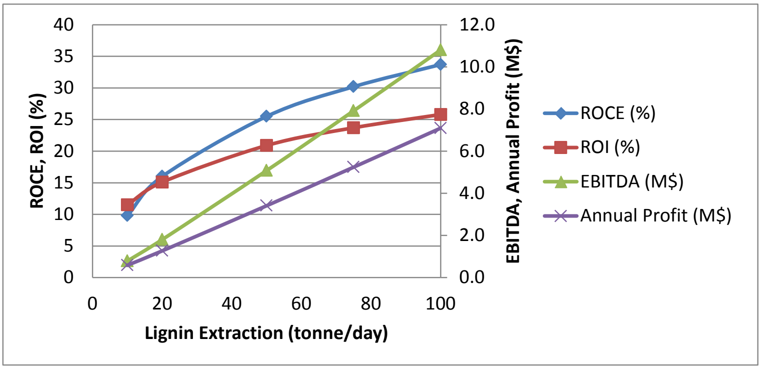

Figure 2. Economic viability of integrated kraft pulp mill-LignoBoost biorefinery.

Case study 2

The conversion of lignocellulosic biomass (LCB) into biofuels and biochemicals has a huge potential but it is more difficult and cost intensive than alternative feedstock such as corn starch. Partitioning of LCB into its constituents (hemicellulose, cellulose) for subsequent hydrolysis into sugars and the lignin fraction is difficult because of its complex and rigid structure, which makes it recalcitrant to bioconversion. Some degradation products formed during its pre-treatment are also fermentation inhibitors. The Ethanol-based organosolv process (Fig. 3) consists of separating lignin prior to enzymatic hydrolysis and preserving the native chemical functionalities of lignin. The case study considered in this work is based on the processing of yellow birch biomass. The ethanol/liquor ratio utilized is 0.65, while the liquor/LCB ratio is 10. The sensitivity analysis is based on a processing capacity varying from 500 to 2500 oven-dry-tonne of biomass. Accordingly, the water consumption varied from 10,926 to 23,823 tonne/day while steam consumption varied from 223 to 1,114 GJ/h. This correspond to a production capacity of 113 to 565 tonne/day of sugars, 169 to 846 tonne/day of cellulose pulp, 64 to 321 tonne/day of pure lignin, and 8 to 36 tonne/day of furfural as a co-product. Fig. 4 shows that the economic viability of this biorefinery option is relevant beyond 1400 air-dry-tonne of LCB per day.

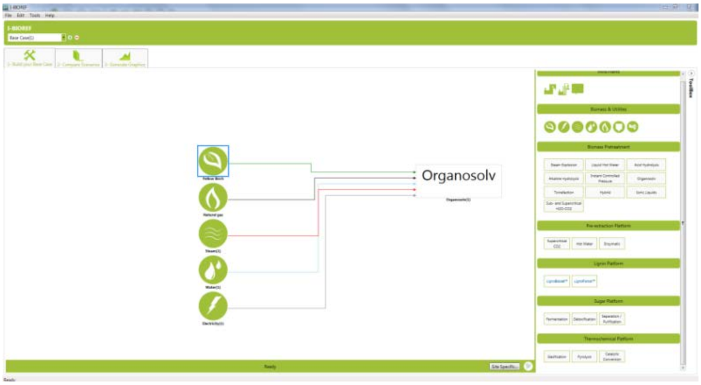

Figure 3. Stand-alone organosolv-based biorefinery.

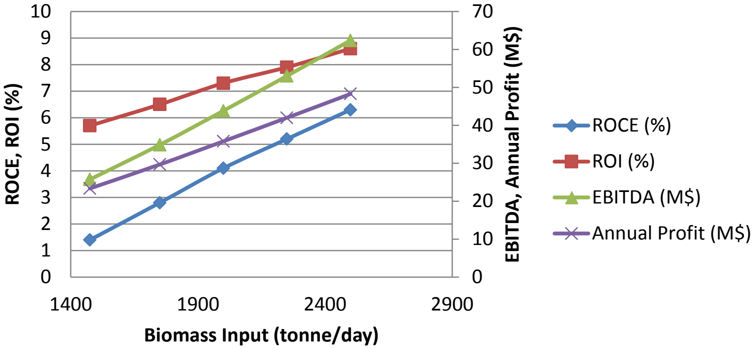

Figure 4. Economic viability of standalone organosolv biorefinery.

Concluding remarks

Multi-criteria analysis gives insights into the performance of biorefinery projects from different perspectives and helps decision-makers to assess the technical, economic and environmental impacts of different implementation strategies. I-BIOREF is a tool built on the basis of multi-criteria analysis for assessing the performance of biorefinery projects and analyzing the impacts of biorefinery implementation on an existing mills in terms of chemical and utility consumption. I-BIOREF brings together the power of process simulation and optimization to deliver a unique combination of biorefinery technology models and rapidly evaluate trade-offs that reflect the best biorefinery compromises for the production of bio-based products and commodities, from the technical, economic, and environmental standpoints. The two case studies illustrate the reliability of I-BIOREF in performing prefeasibility assessment of both integrated and stand-alone biorefineries.

Acknowledgments

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The “Biorefinery Fact Sheet” and its Application to Wood Based Biorefining - Case Studies of IEA Bioenergy Task 42 “Biorefining”

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Abstract

The IEA Bioenergy Task 42 “Biorefining” with its 11 member countries (A, AUS, CA, DK, G, I, IR, J, NL, NZ, USA) has the following definition on biorefining: “Biorefining is the sustainable processing of biomass into a spectrum of bio-based products (food, feed, chemicals, and materials) and bioenergy (biofuels, power and/or heat)”. Wood as a renewable and sustainable resource offers great opportunities for a comprehensive product portfolio to satisfy the different needs in a future BioEconomy. Worldwide many different wood based biorefining concepts are investigated and realised, of which the development status and the perspectives for implementation are quite different. Task 42 developed a “Biorefinery Fact Sheet” for the uniform and compact description of the main characteristics of these biorefineries and their whole value chain. The “Biorefinery Fact Sheets” are initially applied for a first selection of 15 interesting biorefinery systems identified by IEA Bioenergy Task 42, of which 6 are based on wood. Based on these fact sheets an easy and uniform comparison of the different wood based biorefinery concepts is possible. The “Biorefinery Fact Sheet” assists various stakeholders in finding their position on wood based biorefining in a future BioEconomy.

Introduction

The IEA Bioenergy Task 42 “Biorefining” with its 11 member countries (A, AUS, CA, DK, G, I, IR, J, NL, NZ, USA) has the following definition on biorefining: “Bio-refining is the sustainable processing of biomass into a spectrum of bio-based products (food, feed, chemicals, and materials) and bioenergy (biofuels, power and/or heat)” [1], [2]. A key driver for the necessary sustainable development is the implementation of the BioEconomy. Wood as a renewable and sustainable resource offers great opportunities for a comprehensive product portfolio to satisfy the different needs in a future BioEconomy. Worldwide many different wood based biorefining concepts are investigated and realised: Currently many wood based biorefineries are commercially operated (e.g. P&P industry), some concepts are realised as pilot and demonstration plants (e.g. gasification of black liquor for synthetic biofuels and chemicals) while others are developed on a conceptional basis (e.g. coproduction of bioethanol and phenol in particle board industry).

Goal and scope

As the development status and the perspectives for implementation and development of these wood based biorefineries are quite different the IEA Task 42 developed a “Biorefinery Fact Sheet” for the uniform and compact description of the main characteristics of these biorefineries: Part A: “Biorefinery plant” with the key characteristics of the biorefinery plant and Part B: “Value chain assessment” with the sustainability assessment based on the whole value chain of the biorefinery. The “Biorefinery Fact Sheets” are initially applied for a first selection of 15 interesting biorefinery systems identified by IEA Bioenergy Task 42 [1], [3], [5], of which the following 6 are based on wood:

- “3-platform (black liquor, pulp, electricity&heat) biorefinery using wood chips for pulp, paper, turpentine, tall oil, bark, electricity and heat”
- “2-platform (syngas, electricity&heat) biorefinery using wood chips for FT-Biofuels, electricity, heat and waxes with steam gasification“
- “3-platform (pulp, syngas, electricity&heat) biorefinery using wood chips for FT-biofuels, electricity, heat and pulp“
- “3-platform (C6 & C5 sugar, lignin, electricity&heat) biorefinery using wood chips for bioethanol, electricity, heat and phenols“ (Figure 2)
- “4-platform (hydrogen, biomethane, syngas, electricity & heat) biorefinery using wood chips for biomethane (SNG), hydrogen and carbon dioxide“
- “4-platform (C6 & C5 sugar, lignin & C6 sugar, electricity & heat) biorefinery using saw mill residues, wood chips and sulphite liquor for bioethanol, pulp & paper, electricity and heat“

The naming of the wood based biorefineries follows the classification system developed in Task 42 [2]. The classification of a biorefinery consists of the following four features (Figure 1): platforms, products, feedstocks and processes. With the combination of these four features, different biorefinery configurations can be described in a consistent manner. In Figure 2 the classification of a “3-platform (C5&C6 sugars, electricity&heat, lignin) biorefinery using wood chips for bioethanol, electricity, heat and phenols” is shown.

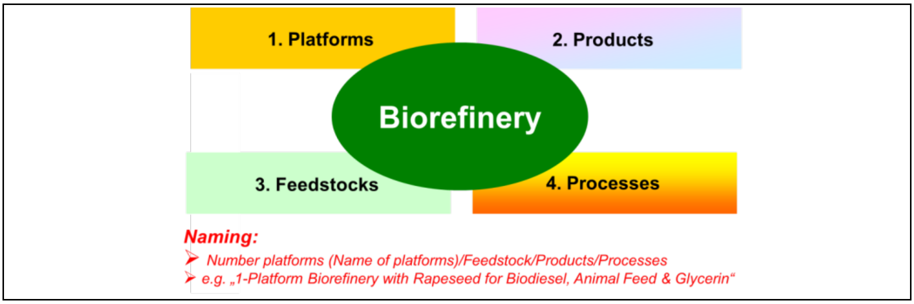

Figure 1. The 4 features to characterize a biorefinery system -and nomenclature of biorefineries in IEA Bioenergy Task 42 [2].

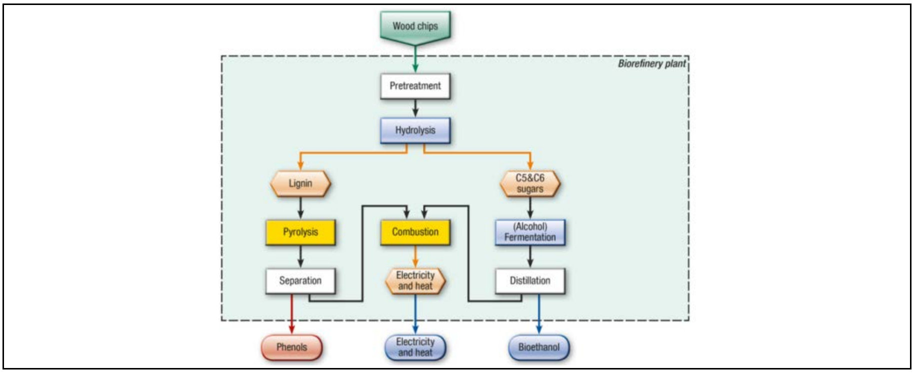

Figure 2. Classification system of a “3-platform (C5&C6 sugars, electricity&heat, lignin) biorefinery using wood chips for bioethanol, electricity, heat & phenols” [2]

The “Biorefinery Fact Sheet”

Due to the development status and the perspectives for implementation and development of biorefineries the IEA task developed a “Biorefinery Fact Sheet” for the uniform description of the key facts of a biorefinery [6]. Based on a technical description and the classification scheme the mass and energy balance is calculated for the most reasonable production capacity for each of the selected biorefineries. Then the three dimensions – economic, environmental and social – of sustainability are assessed for each biorefinery and documented in a compact form in the “Biorefinery Fact Sheet” by using the following methodologies

- Economic assessment with Life Cycle Costing (LCC),
- Environmental assessment with Life Cycle Assessment (LCA),
- Social assessment with Social Life Cycle Assessment (sLCA) and
- Overall assessment with Sustainability Life Cycle Assessment (SLCA).

The “Biorefinery Fact Sheets” consist of three parts (Figure 3):

1. Part A: Biorefinery plant
2. Part B: Value chain assessment and
3. Annex: Methodology of sustainability assessment and data

In Part A the key characteristics of the biorefinery plant are described by giving compact information on classification scheme, description of the biorefinery, mass and energy balance, share of costs and revenues.

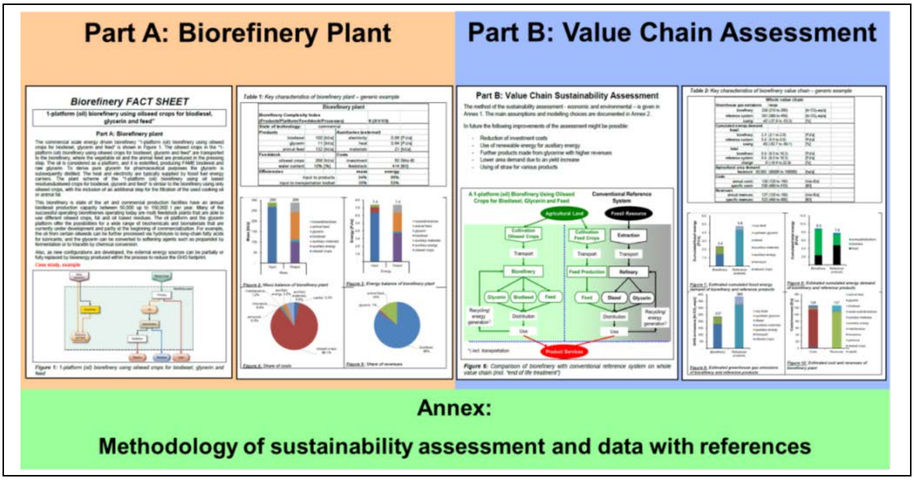

Figure 3. The three parts of the “Biorefinery Fact Sheet” [12].

In Part B the sustainability assessment based on the whole value chain of the biorefinery plant is described by giving compact information on system boundaries, reference system, cumulated primary energy demand, greenhouse gas emissions, costs and revenues. In the Annex of the “Biorefinery Fact Sheet” the main data for the sustainability assessment are documented.

Case studies

Based on the Case studies of the above 6 listed wood based biorefineries the Biorefinery Fact Sheets are made, of which some highlights are presented here. In Figure 4 the value chain and reference system of “3-platform (black liquor, pulp, electricity&heat) biorefinery using wood chips for pulp, paper, turpentine, tall oil, bark, electricity and heat"; in Figure 5 the mass and energy balance of "3-platform (C6 & C5 sugar, lignin, electricity&heat) biorefinery using wood for bioethanol, electricity, heat & phenols" and in Figure 6 the GHG emissions, costs & revenues of "2-platform (syngas, electricity&heat) biorefinery using wood for FT-Biofuels, electricity, heat & waxes" are shown

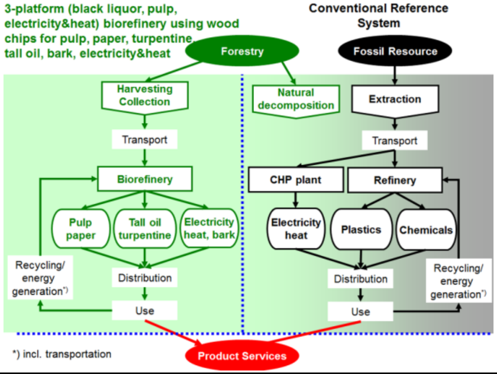

Figure 4. Value chain and reference system of "3-platform (black liquor, pulp, electricity&heat) biorefinery using wood chips for pulp, paper, turpentine, tall oil, bark, electricity and heat" [6].

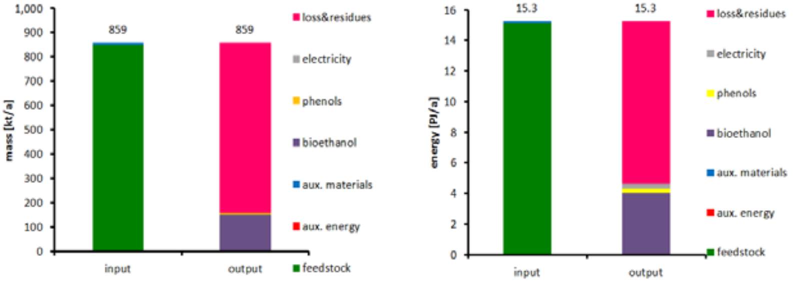

Figure 5. Mass and energy balance of "3-platform (C6 & C5 sugar, lignin, electricity&heat) biorefinery using wood for bioethanol (100 kt/a), electricity, heat & phenols" [16].

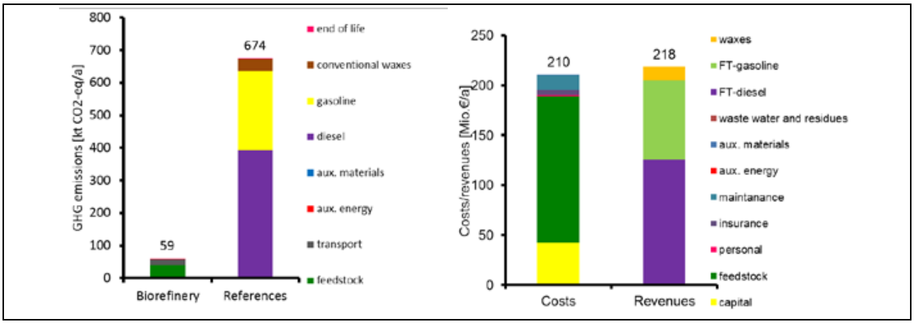

Figure 6. GHG emissions, costs & revenues of “2-platform (syngas, electricity&heat) biorefinery using wood for FT-Biofuels (200 kt/a, electricity, heat & waxes“ [6].

Conclusions

Based on these Biorefinery Fact Sheets an easy and uniform comparison of the different wood based biorefinery concepts is possible. The “Biorefinery Fact Sheet” assists various stakeholders in finding their position on wood based biorefining in a future BioEconomy. Further Fact sheets are under preparation and the IEA Task 42 offers the service to make these fact sheets for further biorefineries as part of a continuous process of an international stakeholder involvement.

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Pre-treatment/Fractionation

Sugars from Biomass – High Cellulose Hydrolysability of Oxygen Alkali Treated Spruce, Beech and Wheat Straw

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Abstract

Norway spruce (Picea abies (L.) Karst), common beech (Fagus sylvatica L.) and wheat straw (Triticum L.) were fractionated by VTT's modified oxygen/carbonate process in varying conditions. Main focus of the study was to obtain a solid fraction in high yield having high hydrolysability of carbohydrates. In addition to evaluating the cellulosic fraction in enzyme hydrolysis, some characteristics of the lignin fractions in spent liquors were determined as well.

The process parameters (reaction temperature and time) were adjusted for the different raw materials used according to their chemical characteristics. Beech proved to require somewhat milder process conditions for efficient treatment than spruce. A yield of about 60% was obtained for the fibre fraction (calculated on the original o.d. raw material) at a lignin content of 9% for beech and at a lignin content of 15% for spruce. Wheat straw was processed at clearly milder conditions giving a fibre fraction yield of 56% at lignin content of 3%.

All the samples showed high hydrolysability by enzymes. A very high degree of hydrolysis (up to 95% in 24 h) could be reached in laboratory conditions with moderate enzyme dosages. Longer hydrolysis times enabled significant reduction in enzyme dosage, as compared to e.g. typical fibre fractions from steam explosion.

The main component in the spent liquors was oxidized sulphur-free lignin with a molecular weight (Mw) range < 10000. Part of the original hemicelluloses was also dissolved and found in the oligo/polysaccharides form. Substantial amounts of low molecular weight carboxylic acids, most likely derived from hemicelluloses and lignin were detected as well.

Introduction

New technology to produce low-cost sugars from biomass are urgently needed to open the way for feasible biorefineries in industrial scale. Fractionation of lignocellulosic raw materials under oxygen/alkaline conditions is an efficient method to produce fibre fractions for enzymatic hydrolysis to monosaccharides which can be used as raw materials of fermentation processes for sugar platform chemicals, e.g. ethanol. Contrary to steam-explosion, oxygen alkali treatment does not produce furanoic compounds that inhibit fermentation. In addition, it is a delignifying treatment, yielding a cellulose-enriched fibre fraction and a fraction with dissolved lignin having interesting technical properties.

Experimental

Process conditions

The pretreatments for enzymatic hydrolysis were carried out according to the developed 2-stage AlkOx concept (Fig 1). Norway spruce (Picea abies (L.) Karst), common beech (Fagus sylvatica L.) and wheat straw (Triticum L.) were used as starting materials. Spruce and beech were used as chips and straw chopped to particles with suitable length.

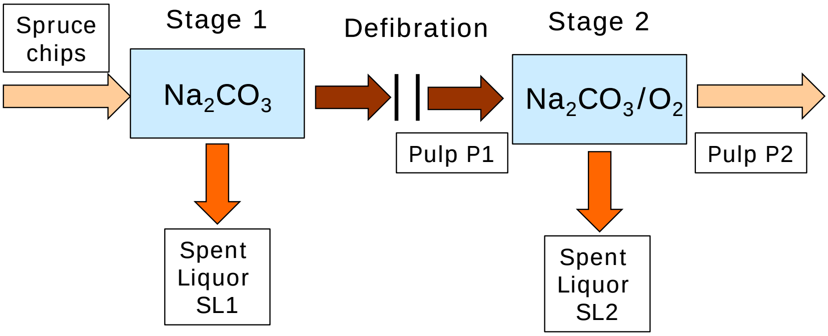

Figure 1. The 2-stage AlkOx concept.

The first stage was done in 15 litre electronically heated rotating autoclaves employing only sodium carbonate: Constant carbonate charge (2 mol/kg) and a liquor to wood ratio of 4 to 5 l/kg, or 10 l/kg for low lignin spruce, were used. The mild process was performed in a temperature of 130 °C and a reaction time of 1 to 2 h and the severe one in a temperature of 130 to 165 °C and a reaction time of 2 h.

The solid fractions were defiberized in an athomispheric 8” Bauer disk refiner in three stages with disk clearances 2 mm, 1 mm and 0.5 mm.

The second stage of the process was carried out using 1st stage refined pulp. The treatments were made in a pressurized 40 L Zirco reactor equipped with a mixer. Constant carbonate charge (2 mol/kg), oxygen pressure (10 bar at room temperature), liquor to solids ratio (10 l/kg) and reaction temperature (140 °C) were used. Reaction time for the mild process modification was from 1 to 2 h and for the severe one from 2 to 3 h.

Analytical methods

The solid fractions were analysed for kappa number (ISO 302:2004, indication of lignin content) and brightness (laboratory sheet, ISO 2470). The content of extractives and lignin were analysed from air dried samples by extracting the pulp samples with n-heptane in a Soxhlet extraction system. The lignin content was analysed from the extracted samples by acid hydrolysis with 70% sulphuric acid. Klason lignin was obtained by analysing the acid insoluble residue after drying and soluble lignin by analysing the UV absorbance with at wavelength 203 nm. An extinction coefficient of 128 L/g/cm was used for the calculation.

The carbohydrate composition of the pulp fractions was analysed after total acid hydrolysis [1] or using enzymatic methods according to [2] in cases in which the acid hydrolysis method gave low analytical yields (fibre fractions from 2nd stage). The resulting monosaccharides were analysed by high performance anion exchange chromatography (HPAEC-PAD) as described in [3].

The reducing sugars released during the pretreatments were monitored using the DNS method with glucose as standard [4]. The composition of the soluble polymeric carbohydrates was determined after acid hydrolysis of the neutralized samples by adding 0.5 ml 70% H2SO4 to 10 mL of sample and autoclaving for 1h at 120 °C. After filtration (0.45 μm) the sample was diluted to 25 ml and analysed according to [3]. The lignin content was measured from the liquors by UV spectroscopy at 280 nm using an absorptivity of 24 L/g/cm [5]. Carboxylic acids in the spent liquors were analysed by capillary electrophoresis [6].

The liquor samples were analysed for molecular weight distribution of the dissolved lignin by size exclusion chromatograpy (SEC). The analyses were performed in a Waters HPLC system by two Ultrahydrogel columns (pore sizes 250 Å and 120 Å) linked in series. The detection was carried out with an UV detector at 280 nm. Isocratic chromatography was performed using 0.1 M NaNO3 as the eluent, pumped through the columns at a rate of 0.5 ml/min. The samples were diluted with a ratio of 1:10 (v/v) with the eluent and filtered with 0.45 μm disposable filters prior to the injection of 50 μL into the SEC system. The analysis temperature was 30 °C. The molecular weight distributions (MWD) and the average number and weight average molecular weights (Mn, Mw) of the lignin were calculated using pullulan standards (5900–21200 Da).

The enzyme hydrolysis of pulp fractions was studied in a small scale laboratory experiment at 45 °C in 50mM sodium acetate buffer (pH 5) in a dry matter content of 10 mg/ml. Enzymes used were a commercial cellulase mixture Celluclast 1.5L (10 FPU/g dry weight) and a commercial β-glucosidase Novozym 188 (200 nkat/g dry weight). For dose response analysis, the cellulase dosage was varied in the range of 2–10 FPU/ g dry matter. The suspensions of 5 ml were incubated with magnetic stirring for 24 or 48 hours and the amount monosaccharides released were analysed by the DNS method [4] or by according to Tenkanen and Siika-aho [3]. Hydrolyses were run as triplicates.

Results and discussion

Process yields varied from 50% to 60% of the original o.d raw material (Table 1). The various raw materials were delignified differently, spruce being the most difficult and wheat straw the easiest one. The lignin contents of the solid fractions were close to the level of normal unbleached kraft pulp. Spruce and beech needed, however, severe conditions to reach it.

Table 1. Properties of the solid fraction after the 2-stage AlkOx treatments.

Raw material	Spruce			Beech		Wheat straw
Process type	Mild	Severe	Low lignin	Mild	Severe	Mild
Total yield, %	59.4	50.5	46.6	59.1	54.0	55.7
Kappa number	69.8	35.0	17.6	42.6	15.7	12.7
Lignin, %	14.0	6.9	4.4	8.1	3.5	3.8
Brightness, %	19.6	24.9	41.1	49.8	58.2	46.9

The severity of the treatment can be seen in the modification of carbohydrates of the fibre fraction (Table 2). With spruce material more galactoglucomannan is solubilized when the severity increases. The content of xylan remained more or less unchanged, whereas the content of cellulose increased when the lignin content decreased. The xylan content of beech and straw material remained or even slightly increased as a result of the treatment.

Table 2. Composition of carbohydrates of the solid fraction after 2-stage AlkOx treatment.

Material		Ara g/100 g	Gal g/100 g	Glu g/100 g	Xyl g/100 g	Man g/100 g	As monos. g/100 g	As polym. g/100g
Spruce	Mild	0.7	0.5	69.8	6.9	7.8	85.8	77.1
	Severe	0.7	0.3	77.9	7.4	5.6	92.0	82.6
	Low lignin	0.6	0.1	86.1	7.3	4.4	98.6	88.6
Beech	Mild	0.1	0.1	67.7	22.7	0.8	91.4	81.8
	Severe	0.0	0.0	72.0	23.9	0.5	96.5	86.4
Wheat straw	Mild	2.4	0.2	58.0	27.3	0.0	87.8	78.4

The AlkOx treatment resulted in an easily hydrolysable fibre fraction (Figure 2). The increasing severity improved the hydrolysabilty in the standard set-up. The cellulose of straw was practically totally hydrolysed within 24 h in the test conditions. The hydrolysability was clearly higher that that observed typically after steam explosion, which normally ranges from ca. 70–90%.

A specific feature of fibre fractions from alkaline oxidation is that the hydrolysis is not inhibited or stagnated with low enzyme dosages. Consequently, given longer residence time, high degree of hydrolysis can be obtained in very low enzyme dosages (Figure 3). This can result in significant savings in enzyme cost if the AlkOx process is used as pretreatment of a sugar based bioprocess.

The spent liquors after the 2nd stage contained substantial amounts of sulphur-free lignin (11–16 g/l as UV-lignin). In the case of spruce, the molar mass of the lignins was 6000–7000 g/mol, values slightly higher than those of commercial kraft lignins. The molar mass was slightly higher in the lignins recovered from the spent liquors by acid precipitation. No monosaccharides were detected in the spent liquors, which typically contained small molecular weight carbocylic acids (8–12 g/l for spruce) and some carbohydrate as oligosaccharides (2.5–3 g/l).

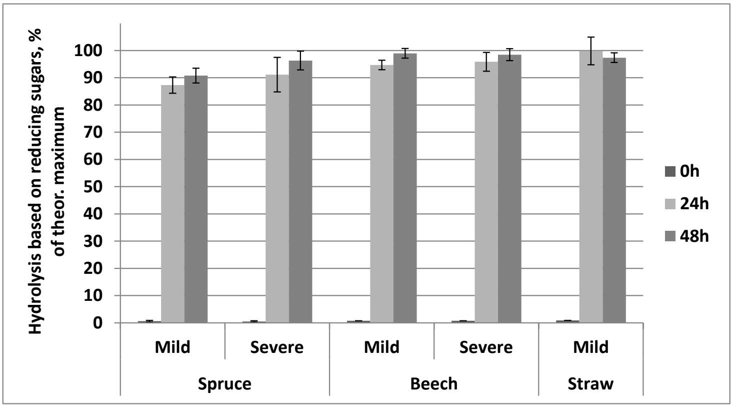

Figure 2. Hydrolysability of the fibre fractions.

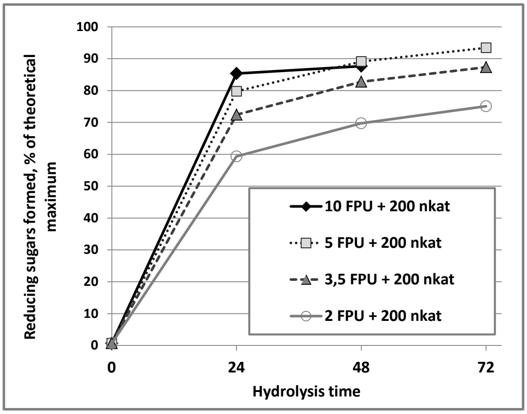

Figure 3. Hydrolysis of the low lignin fibre fraction from AlkOx with low cellulase dosages.

Conclusions

Alkaline oxidation (AlkOx) is a fractionation method based on the use of Na_2CO_3 and oxygen in moderate reaction conditions. It produces cellulosic fraction containing also the major part of xylan and considerable fraction of of galacto-glucomannan of the raw material. In addition, it produces liquid fraction, containing major part of lignin in oxidized form. The degree of solubilisation of lignin and hemicellulose depends on the severity of the treatment.

It was shown that the 2-stage AlkOx process can be adapted to softwood (spruce) and hardwood (beech) materials. The degree of delignification could be easily adjusted by the treatment conditions. In addition, wheat straw was observed to be a material suitable for fractionation by the AlkOx process.

Cellulosic (fibre) fractions were shown to be highly hydrolysable by moderate enzyme dosages, with the degree of hydrolysis above 90%. The fibre fraction from softwood could be hydrolysed efficiently also with low enzyme dosages, especially if the hydrolysis time was increased. This can result in significant savings in enzyme cost in the production of sugars from biomass.

The liquid fractions contained sulphur free lignin, in the case of spruce with molar mass of 6000–7000 g/mol and a small amount (2.5–3 g/l) of oligosaccharides and small molecular weight carboxylic acids (8–12 g/l).

2-stage alkaline oxidation process is an efficient pretreatment technology for sugar route biorefineries based on wood or agricultural raw materials. More precise optimisation of the process concept and individual unit operations can still give substantial improvements in the performance of this fractionation technology.

Acknowledgements

This work was completed in AERTO’s Biobased Economy project. Johan van Groenestijn and Erwin Beckers from TNO and Moritz Leschinsky from Fraunhofer IGB are acknowledged for supplying the straw and beech raw materials.

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Organosolv-fractionation of Beech Wood – From Pilot Scale to Industrial Implementation

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Abstract

A pilot plant for fractionation of industrial wood chips based on the Organosolv process by Tayenthal and Kleinert [1] has been in operation since May 2013, at the Fraunhofer-Center for Chemical-Biotechnological Processes (CBP) in Leuna, Germany. The pilot plant, which has been planned and constructed by Linde Engineering, was designed to fractionate wood, e.g. beech-wood, by means of ethanol-water-mixtures with the aim to provide all major wood fractions (lignin and sugars/fibres) in sufficient amounts for the development of new bio-based chemicals and respective chemical value chains.

Based on the data obtained from the pilot plant, an engineering concept for a first-of-its-kind industrial-size production plant is currently under development. A modular approach was chosen to enable the examination of cost effectiveness and environmental acceptability of numerous plant configurations, including a complete green-field as well as “add-on” plant configurations.

In a next step, after identification of the most feasible configuration for an industrial size plant, a scale-down from the virtual production plant to a smaller demo plant will be carried out. The continuously working demo plant is essential to demonstrate the technical reliability of the implemented components as well as the overall plant concept.

In parallel to these efforts, process development and optimization work continues in the pilot plant in Leuna to ensure technical support during the implementation phase of the demo plant and beyond.

The CBP Leuna Pilot Plant

Implemented Process Steps

Heart of the Organosolv pilot plant is a 400 L batch digester with state-of-the-art displacement cooking technology, large enough to provide scalable results of process optimization efforts conducted. The digester is accompanied by a non-pressurized and two pressurized tanks for liquid handling at different temperatures and pressures.

The Organosolv-lignin can be precipitated from the cooking liquor either by dilution or distillation. Then, it easily can be removed from the residual cooking liquor and leaves the plant as 95% dry powder with high purity after drying. The obtained Organosolv liginin is ideally suited for further chemical conversion or direct use as powder in polymer processes.

The almost lignin-free remaining hemicellulose fraction of the cooking liquour is obtained at 70% w/w sugar contents after removal of residual ethanol and concentration.

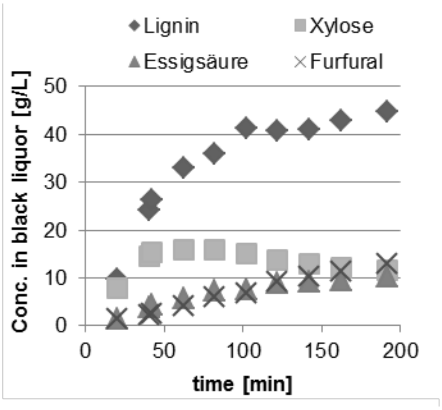
The fibre fraction is washed for further lignin and ethanol recovery and then processed by enzymatic hydrolysis to glucose, leaving the plant finally at 70% w/w sugar contents after concentration. It is suitable for e.g. fermentation processes. Alternatively, the washed fiber fraction can be used as highly valuable raw material for other pulp products like e.g. dissolving pulp.

The used solvent ethanol is recycled to investigate recovery rates of the different process steps and the accumulation of by-products. Other relevant process streams are examined regarding their potential commercial utilization and for the development of optimized treatment methods. **Figure 1** shows a picture of the digester plant in Leuna.

Figure 1. Digester circulation and pressurized liquor tanks in the pilot plant at Fraunhofer CBP, Leuna.

Results from the Pilot Plant

Since its commissioning the pilot plant in Leuna was operated to produce sufficient amounts of product samples for various application test on the one hand and to further optimize the ethanol-water fractionation process on the other hand. In order to improve the pulping process, a systematic kinetic study was started, where the influence of the parameters temperature and catalyst concentration on lignin yield, molecular weight and carbohydrate composition in the pulping liquor was investigated. The concentration curves of lignin and hemicelluloses were recorded for a multitude of temperatures and acid concentrations, an example is shown in **Figure 2**. Based on these results, the deligninfication rates of beech wood chips could be calculated. Together with the data from carbohydrate content and composition, process conditions for a maximum yield of lignin and hemicelluloses could be deduced.



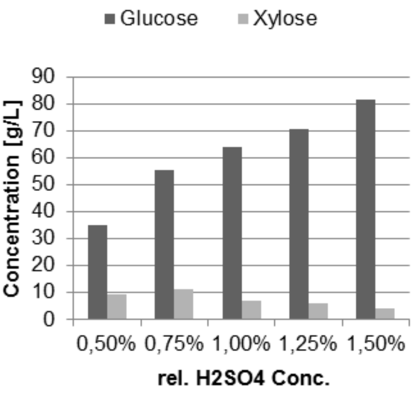


Figure 2. Composition of black liquor during an organosolv experiment.

Figure 3. Sugar concentration in filtrate after enzymatic hydrolysis at 50 °C and 10% solids concentration different concentrations of sulphuric acid (% w./w. o.d. wood).

Furthermore, the ability of the pulp fraction for enzymatic saccharification was investigated for several pulping conditions (**Figure 3**). Keeping all other conditions of pulping and enzymatic hydrolysis constant, the sugar yield during enzymatic hydrolysis of the resulting pulp fraction is highly dependent on the catalyst concentration during pulping. Under standardized hydrolysis conditions, the conversion of cellulose to glucose could be increased to yield almost 90% by dosage of 1.5% of sulfuric acid on dry wood. At the same time, the acetic acid and xylose impurities of the resulting glucose could be reduced. The data obtained from these optimization studies can be used to adopt the process conditions in a way to achieve the maximum economic value for different scenarios of product commercialization.

As an interesting outcome of a cooperation between European RTO's within the AERTO BBE program, experiments in the pilot plant conducted with finnish spruce chips provided by VTT, showed promising delignification results also with softwood (**Figure 4**). Pulping conditions published by Pan [2] for canadian pine could successfully be adopted to the pilot plant and showed even higher delignification rates for spruce than for beech. Further results of this study are expected in the AERTO BBE project.

Beside the optimization of the pulping process, progress on the precipitation of lignin from the organosolv spent liquor could be achieved. In a cooperation with the Max-Planck-Society a new process for the evaporative precipitation of lignin was developed. The new patented process avoids the formation of lignin deposition and fouling during direct spent liquor distillation. Using the new process, the consumption of important amounts of water for a dilutive lignin precipitation can be avoided and the recycling of ethanol becomes much more efficient.

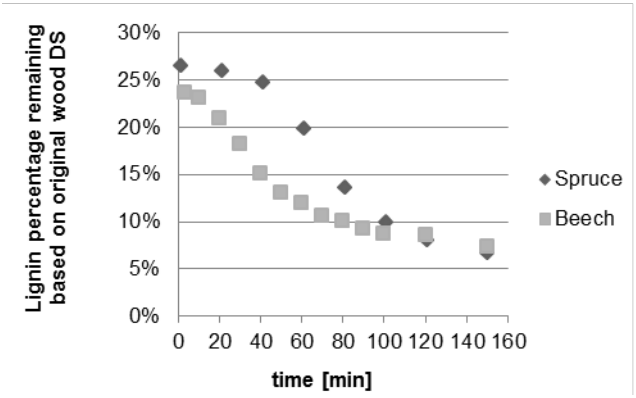


Figure 4. Comparison of delignification of beech and spruce wood.

The Scale-up to Production Process

Based on the optimum results of the pilot plant activities at that state, a scale-up study of the process was carried out. The aim was to investigate the technical and economic feasibility of a greenfield production plant at a hypothetical site, capable for processing 280,000 BDMT of beech wood per year. Thus, additional to the core technology of the Organosolv process as displayed in Leuna, further necessary process steps and utilities had to be taken into account; e.g. logistics, wood handling, chipping, sorting, waste water treatment and recycling, cooling facilities, power plant, administration, workshops, etc.

Production Plant Design

Consisting of the foresaid subsystems and functionalities, a modular plant design was set up, enabling an easier approach to cost structure evaluation and optimization. This modular approach also allows for later adjustment to potential real sites and plant configurations. A simplified block flow diagram of the plant structure is given in **Figure 5**.

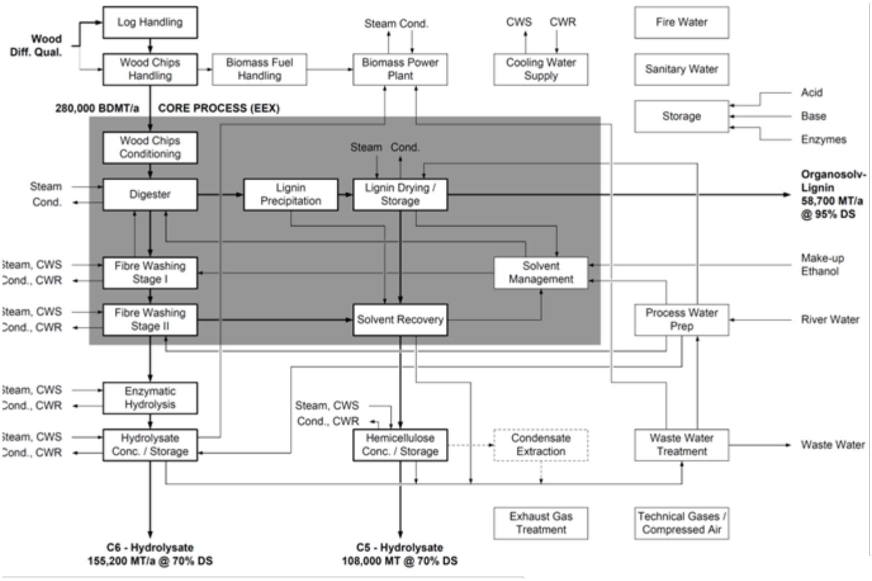


Figure 5. Simplified block flow diagram of the investigated plant configuration.

From the results in Leuna, annual yields of 155,200 MT of 70% DS C6-hydrolysate, 108,000 MT of 70% DS C5-hydrolysate and 58,700 MT of 95% DS pure Organosolv lignin per year can be deduced, if 280,000 BDMT of beech wood chips are processed within 8000 hours of continuous operation.

From the block flow diagram process flow sheets with complete heat- and mass-balances were derived. The main equipment was specified and inquired to have a reliable base for cost estimation ±30%, a big progress compared with former studies, based on simulations of only the process plant, using integrated cost data bases, and neglecting the side functions heaving a great impact on costs [3].

A possible layout of the whole plant at a hypothetical site was developed to determine realistic space requirements and costs related to construction etc. The achieved total footprint of the greenfield plant is 320 m x 670 m, half is needed for wood logistics and feedstock preparation. The core process (see **Figure 5**) needs 90 m x 80 m. The residual area is occupied by utilities and auxiliary functions.

Economic Evaluation of the Concept

IRR calculations showed that the decision for C6-hydrolysate as one main product is presently not favourable due to low oil and sugar prices. However, the production of dissolving pulp and related products deliver an IRR within a possible range of interest. The brown stock leaves the fibre washing process with kappa-numbers of approximately 30. This is within a suitable range for dissolving pulp.

Despite the question of utilization of the fibre fraction, lignin could in any case be produced with high purity at reasonable costs. The same is true for the C5-hydrolysate since its production is directly linked to lignin.

Conclusion and Outlook

The operation of the pilot plant in Leuna delivered scalable results of high quality and gave access to larger sample quantities and specifications of the main products for testing by potential offtakers/investors. This is of outmost importance for the necessary market development, especially for lignin and the C5 fraction.

On this sound basis it was possible to successfully design a first technically and economically feasible production plant design, leading a way to further optimization of the whole process and plant concept.

Nevertheless, due to technical uncertainties when scaling up the pilot plant process to production scale, especially at the digester and fibre washing line, a smaller demonstration plant, probably with a wood processing capacity of around 8,000 MT/a is strongly recommended to minimize the risk. Furthermore, a suitable bleaching process of the brown stock which fits into the Organosolv concept is to be developed.

Acknowledgement

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FPInnovations’ TMP-Bio for Lignocellulosic Biomass: Current State and Scaling Up

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Abstract

FPInnovations has developed a proprietary process (TMP-Bio), to convert cellulosic biomass into various value-added bio-products. The process includes a unique mild biomass treatment technology, a robust enzymatic hydrolysis technology, and various pathways to value-added products from both a mixed sugar stream and a near-native lignin stream (H-lignin).

During the last three years, we have successfully implemented a TMP-Bio pilot plant in Point-Claire (Quebec, Canada). This pilot plant allows us to conduct enzymatic hydrolysis at greater than 20% biomass loading, and carbohydrate conversions exceeding 90% can be obtained. During a 3-month pilot plant campaign, we were able to consistently produce sugar at a concentration of 120-140 g/L. A total of more than one tonne (OD) of high quality cellulosic sugars and 1.5 tonnes of H-lignin were produced.

This paper will update our progress on scale-up activities and further developments on pre-treatment and post-treatment technologies. Lab and pilot fermentation trials confirmed that both glucose and xylose from the TMP-Bio process can be directly fermented to lactic acid, succinic acid, ethanol and butanol without detoxification. Thus, these cellulosic sugars have great potential for replacing agricultural and food-based feedstocks that are currently used for the production of bio-based chemicals.

Introduction

About ten years ago, a biomass-based biorefinery was seen as something extremely futuristic. However, this position has definitely changed when four cellulosic ethanol plants were successfully established during the past two years [1]. Among them POET-DSM, Dupont and Abengoa all use corn stover; while Granbio uses bagasse as the raw material. The core biomass pretreatment technology of these four facilities is steam explosion or modified steam explosion. Although this technology works well with non-woody biomass such as corn stover and agricultural residues, the high capital cost and difficulties encountered when dealing with woody biomass, pose serious challenges for further commercialization of this technology, especially using woody biomass.

FPInnovations has developed the patented TMP-Bio process for lignocellulosic biomass [2]. The technology works particularly well on hardwood biomass. As shown in Figure 1, the core technology of the TMP-Bio process includes a unique mild biomass treatment technology, a robust high solid enzymatic hydrolysis technology, and various pathways for value-added products from the sugar and hydrolysis lignin (H-lignin) streams. With this technology, the cellulosic biomass can be fractionated into a clean, concentrated sugar stream and a sulfur-free, near-native H-lignin stream at large scale. Thus, the TMP-Bio process lays the foundation for producing various biofuels and biochemicals from a renewable non-food lignocellulosic biomass.

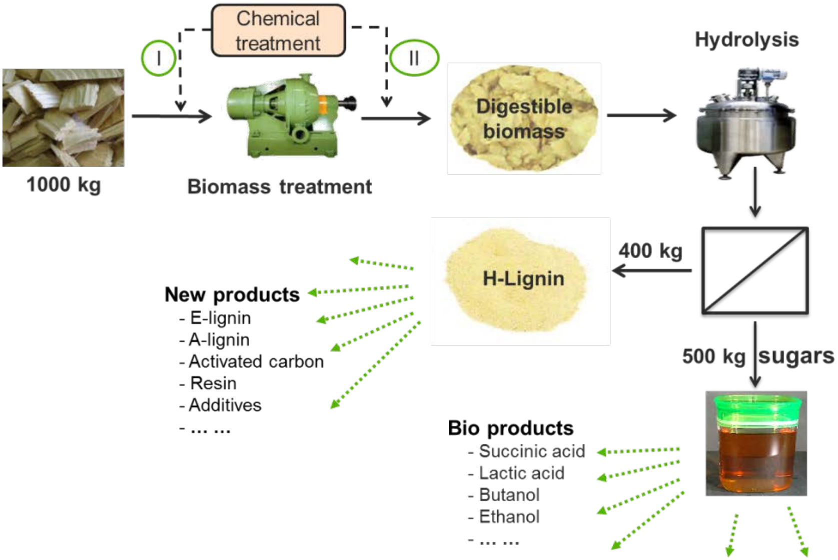

Figure 1. TMP-Bio process and pathways to value-added products. Option I: chemical pre-treatment; option II chemical post-treatment.

We have previously presented our core technology in the 4th Nordic Wood Biorefinery Conference in 2012 [3]. At that time, our research was focused on a mild chemical treatment on chips before refining (referred as pre-treatment, option I). In the subsequent three years, we have conducted research to evaluate the possibility of a post-refining chemical treatment (referred as post-treatment option II). This would greatly improve the flexibility of the process. More significantly, a TMP-Bio pilot plant has been successfully built at FPInnovations in Point-Claire (Quebec, Canada). This paper will mainly discuss our progress on further process development and scale-up activities.

Further development on process: post- treatment technology

The original TMP-Bio process is based on conventional chemi-thermomechanical pulping (CTMP) processes (Figure 1). For typical CTMP mills, pre-impregnators and low temperature digesters are available which can be readily adapted to the TMP-Bio process. Consequently, for the case of CTMP mills, the chemical treatment can be carried out on the chips before refining (option I). However, most thermomechanical pulping (TMP) mills don't have pre-impregnators and are thus unable to adapt the TMP-Bio process in its original configuration. Fortunately, these mills usually have bleaching facilities, which are typically operated under atmospheric pressure and could potentially be adapted to "post-treat" the mechanical pulp after refining but prior to enzymatic hydrolysis.

After extensive laboratory optimization, post-treatment conditions were identified, and post-treatment pilot trials were conducted in our TMP pilot plant to further evaluate the digestibility of the biomass compared to biomass generated by the original (i.e. pre-treatment) technology.

For the pre-treatment pilot trials, the chemical was introduced by the press-impregnator, and the chemical pre-treatment was conducted on chips in a pressurized digester. For the post-treatment trial, the chemical was loaded onto the fibrous biomass, and then retained in an atmospheric digester for treatment.

Biomass enzymatic digestibility was compared with biomass generated by the pre-treatment technology at enzyme loadings ranging from 5 to 20 FPU/g glucan. The results in Figure 2 indicated that similar carbohydrate conversion yields were obtained, and Glucose conversion yields reached >80% at an enzyme loading of 10 FPU/g glucan. The results confirmed that both pre-treatment and post-treatment can generate a highly digestible biomass. This further development greatly enhances the process flexibility of TMP-Bio technology, and allows us to easily retrofit our technology to both CTMP and TMP mills.

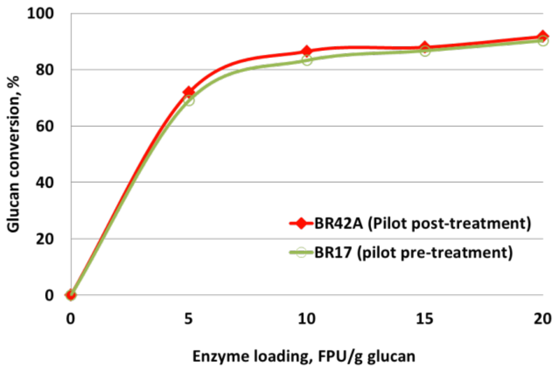

Figure 2. Glucan conversions of biomasses generated in pilot plant by pre-treatment and post-treatment technology. Hydrolysis conditions: 2 wt % solids, 72 Hrs, 50 °C, 50 mM sodium acetate buffer at pH4.8.

TMP-Bio Scale-up

To further validate the TMP-Bio technology and generate sufficient samples of cellulosic sugars and H-lignin for our partners to develop value-added products, we successfully built a pilot plant in Pointe-Claire (QC, Canada) in 2013. Figure 3 shows the simplified flow diagram of the pilot plant. The pilot plant has the capacity to convert 200 kg (OD) biomass per batch to mixed C5/C6 sugars and H-lignin. It is comprised of the following three sections: i) biomass treatment, ii) high-solid enzymatic hydrolysis, and iii) sugar/lignin separation and downstream processing. The major installations include retrofitting the existing CTMP pilot plant and adding new specific equipment, as shown in Figure 4.

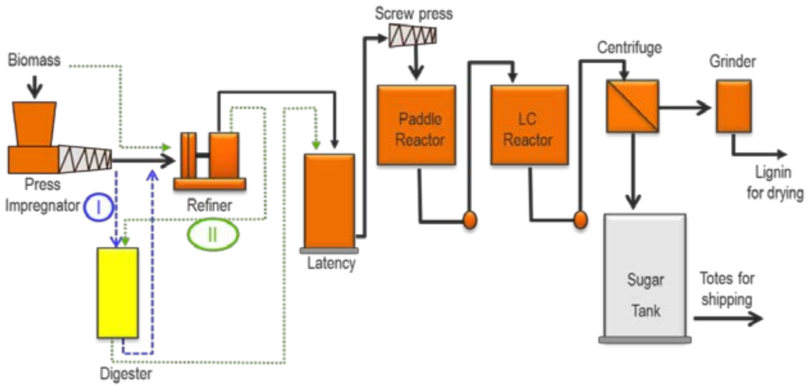

Figure 3. FPInnovations' 200 kg/batch TMP-Bio Pilot Plant. Option I: chemical pre-treatment; option II: chemical post-treatment.

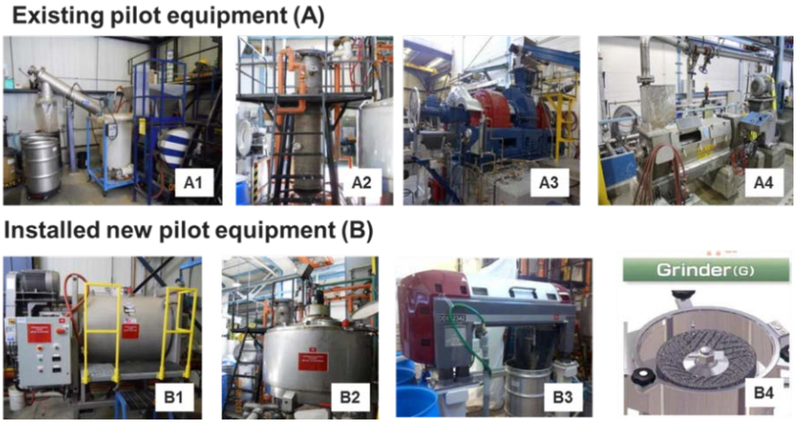

Figure 4. TMP-Bio pilot plant includes retrofitting the existing CTMP pilot equipment (A) and newly installed specific equipment (B).

Biomass treatment

This section uses all the facilities in our existing CTMP pilot plant. As is shown in Figure 4 (A1-A4), the major equipment used includes a press-impregnator (A1), digester (A2), disk refiner (A3) and biomass neutralization and thickening facilities (A4). This batch system allows us to conduct both pre-treatment (option I) and post-treatment (option II) on biomass. The capacity of this section is limited by the digester which has the capacity to process about 200 kg (OD) biomass per day. Highly digestible biomass after screw press thickening (A4) has a solids content of about 30%.

High solid enzymatic hydrolysis

A one cubic meter paddle mixer (Figure 4 B1) was designed and fabricated for high consistency enzymatic hydrolysis. This new reactor allows us to conduct enzymatic hydrolysis at greater than 20% solids loading. The reactor has a hot water jacket for temperature control, and it can be set for continuous or intermittent mixing during the enzymatic hydrolysis. In pilot plant trials, enzymatic hydrolysis was conducted at 20 wt % solids loading in a paddle mixer and a conventional mixing tank.

Figure 5 shows the general operation of this reactor in fed-batch mode. It takes about 5–6 hours to load all the biomass to the reactor (fed-batch), and the biomass usually is liquefied within 8–10 hours after completion of biomass loading. After liquefaction, it can either be pumped to the 2nd conventional mixing tank (Figure 4 B2) or remains in the paddle mixer to complete the enzymatic hydrolysis.

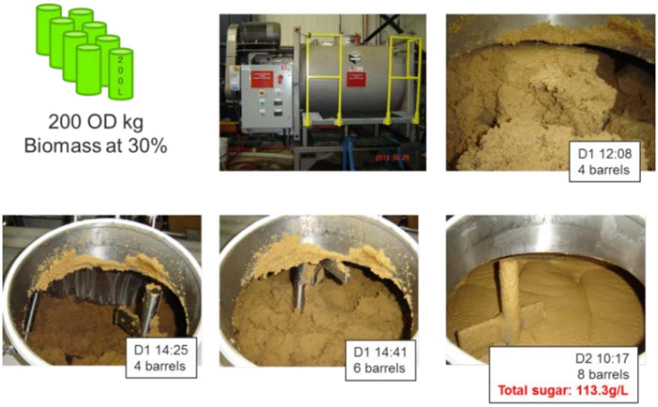

Figure 5. Fed-batch high solid enzymatic hydrolysis. Hydrolysis conditions: 20 wt % solids, 50 °C, 50 mM sodium acetate buffer at pH4.8.

Sugar/lignin separation and downstream processing

Our typical enzymatic hydrolysis pilot trials were conducted at 20% biomass loading. Total sugar concentration consistently reached 120–140 g/L and total suspended solids was at around 8% at the end of hydrolysis. A decanter centrifuge was used for sugar/lignin separation (Figure 4 B3).The H-lignin was then dried and ground (Figure 4 B4). The sugar solution was denatured, centrifuged to a clear sugar solution, and then concentrated to 400 g/L before shipping to our partners.

Pilot plant operation and sugar quality

During the 3-month pilot plant operation, we successfully produced one tonne OD dry cellulosic sugar from hardwood chips. Figure 6 showed that total sugar concentrations from various trials can consistently reach 130 g/L. The freshly produced sugar is basically free of inhibitors, and can be directly fermented to lactic acid as shown in Figure 7.

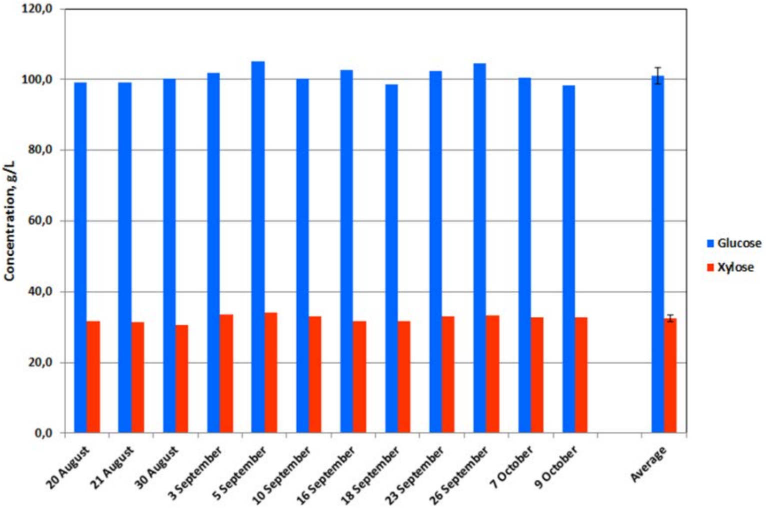

Figure 6. Sugar concentration from various pilot trials. Fed-batch, 20 wt % solids, 50 °C, 50 mM sodium acetate buffer at pH4.8.

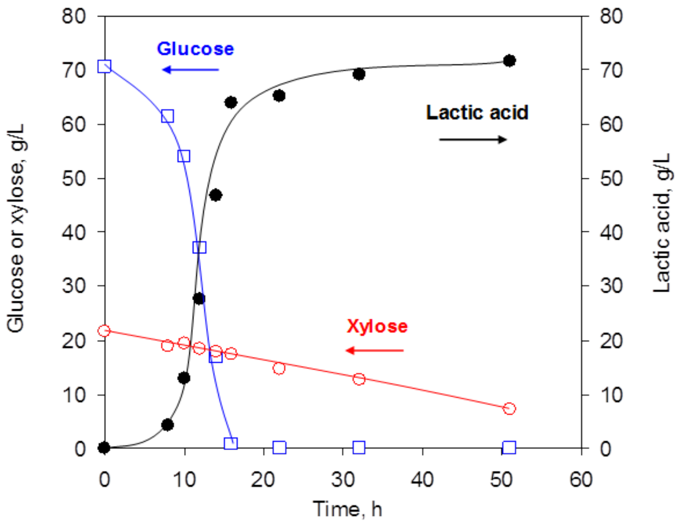

Figure 7. Fermentation of TMP-Bio sugar from aspen by *Bacillus coagulans* MXL-9. Initial total sugar concentration ≈ 90 g/L.

Nine hundred kilograms (OD) of this sugar was shipped to our partner for pilot fermentation trials. These fermentation trials showed that both glucose and xylose in the TMP-Bio solution were totally consumed in a high-yield fermentation to produce lactic acid [4], and a sugar free fermentation was achieved (both glucose and xylose was completely consumed). Other lab evaluations [3] showed that this clean and concentrated sugar stream can also be directly fermented to ethanol, butanol, and succinic acid with yields of 47%, 33%, and 76% respectively.

Conclusions

FPInnovations has developed a proprietary TMP-Bio technology based on the conventional mechanical pulping process. The technology includes a unique mild chemical treatment technology which can be carried out either before, or after the biomass refining stage. Our lab and pilot trials confirm that both pre-treatment and post-treatment technologies work equally well and generate a highly digestible biomass. This new development greatly increases our process flexibility, and allows us to be able to easily retrofit our technology to existing CTMP as well as TMP facilities.

We have successfully established a TMP-Bio pilot plant (200 kg/batch) in Point-Claire (Quebec, Canada). Our pilot plant campaign demonstrated that carbohydrate conversions exceeding 90% can be obtained, with the total sugar concentration consistently reaching 120–140 g/L. The pilot fermentation trials also confirmed that both glucose and xylose from TMP-Bio process can be directly fermented to lactic acid without detoxification.

Acknowledgement

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Towards a Wood Based Material Biorefinery - A Demonstrator

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Abstract

Wood, the most abundant ligno-cellulosic raw material available, is a key potential feedstock for production of more sustainable alternatives to fossil-based materials. However advances within the fields of extraction and treatment processes within what is often referred to as the biorefinery concept is essential to allow for such transition. In this study, several different methods for the extraction and separation of wood constituents have been combined in a single process with the purpose of achieving a high overall efficiency of material extraction and utilisation. The work builds on several activities within the Wallenberg Wood Science Center (WWSC). The aim is to present a laboratory-scale demonstrator that illustrates how the different constituents can be separated from the wood matrix for later use in the production of bio-based materials and chemicals. The process steps involved have been tested as integral steps in a linked process for a scale of operations that range from the kilogram-scale down to the gram-scale. Industrially chipped softwood, containing mainly spruce with some pine, was used as raw material.

Introduction

If renewable bio-based raw materials are to replace currently used fossil resources enabling a more sustainable production of materials, fuels and energy, an efficient use of these renewable resources are necessary since availability is being limited by yearly growth. That include utilising a wide range of different raw materials to their best potential and recovering waste and side streams for production of by-products. In line with green chemistry and green engineering principles usable/valuable structures in the starting material should be retained to minimize cost and environmental impact. This is of course more challenging the more complex and heterogeneous the starting material is, and is a considerable challenge for such raw material as wood. This is, however, also an important challenge to overcome since wood is the most abundant ligno-cellulosic raw material available making it a key potential feedstock for biobased products [1].

Within the Wallenberg Wood Science Center (WWSC), we have since 2008 been working on processes for the extraction and valorisation of wood components, which can be combined with pulping processes for the production of conventional paper-grade pulp, dissolving pulp and/or cellulose nanocrystals or cellulose nanofibrils. The aim has been to retain the polymeric structure of the extracted wood component to as large extent as possible. So far, individual process steps and certain combinations of a few of these steps have been investigated, and the results presented in a large number of publications (e.g. [2-8]).

The purpose of the present study is to combine the different process steps developed during our research activities, and to achieve a high overall material yield in the form of a demonstrator. The suggested process concept is simulated on a laboratory scale, linking together each operation such that the products from each step are used as raw material in the subsequent step, with flows ranging from a kilogram scale down to a gram scale.

Material and methods

The principal approach in developing the demonstrator was to utilise several primary separation steps to extract wood components from the wood matrix that subsequently can serve as raw material for the production of materials and chemicals. While the extracted soluble material is purified and fractionated, the solid remains are processed by conventional pulping methods. From this general outline, a process concept for a wood-based biorefinery is proposed, Figure 1. The numbering of the streams indicated in the figure is consistently used throughout this work with solid streams being indicated by an S and liquid streams with a L.

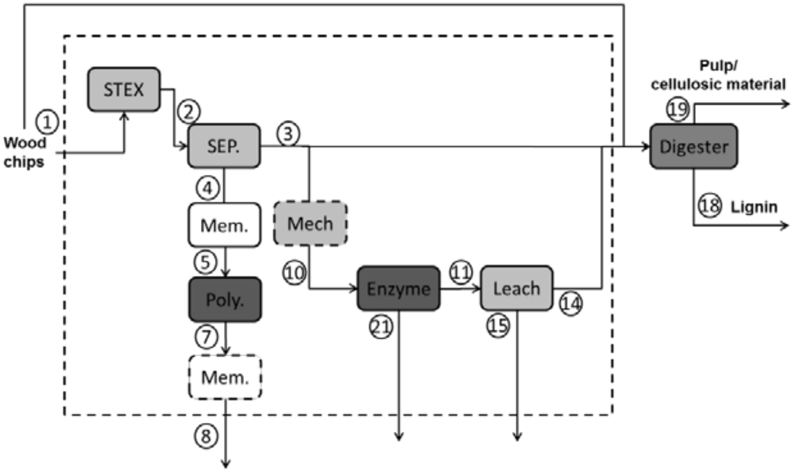

Figure 1. An overview of the process. The dotted area encloses the various primary separation steps utilised. Abbreviations: STEX: mild steam explosion Sep.: separation; Mem.: membrane fractionation; Poly.: upgrading of the polymers by crosslinking; Mech: mechanical treatment; Enzyme: enzymatic treatment; Leach: leaching; Digester: cooking with the sulphate pulp method; Oxygen: oxygen delignification.

The starting material was industrially chipped softwood, mainly spruce with some pine, which was dried and sieved. A fraction that passed through holes 30 mm in diameter but was retained on sieves with 3 mm holes was used as raw material for the subsequent process steps.

Mild steam explosion

The mild STEX equipment used in this study has been described by Jedvert *et al.* [8]. For each run, 500 g (dry basis) of wood chips (Stream 1S) were used. Prior to the steam treatment, the chips were impregnated with de-ionized water at a liquor-to-wood ratio of 10:1. In this study a steam pressure of 7 bars (165 °C) was maintained for twenty minutes before pressure release. The procedure was repeated until several kg of wood chips had been processed. Directly after the STEX treatment, the condensed steam was recovered by filtration through a Büchner funnel, and the steam explosion liquor was then frozen, (Stream 4L). The steam-exploded wood chips were rinsed with water and stored at 5 °C.

Mechanical treatment

Steam-exploded wood chips (Stream 3S) were subjected to mechanical treatment in a laboratory-scale 12” disc refiner (Sprout-Waldon). The chips were subjected to atmospheric steam for 15 min and treated in the refiner in a single pass mode, where an energy input of about 250 kWh/dry tonne was used.

Enzymatic treatment and leaching

The solid material in Stream 10S was subjected to enzymatic treatment prior to leaching, using gamanase from Novo Nordisk. 50mM acetate buffer pH 5.0 was added to the wood to a final wood consistency of 3% w/w. 20µl of gamanase (activity: 1000 VHCU/ml) was added to the mixture for each gram of dry wood. After 24 hr of incubation at 60 °C, samples were filtered through a fibre cloth with a mesh opening of 71 microns and 86 mesh count per cm from MONODUR. The cake was then washed with boiling water to inactivate the enzymes and the wash stream was recovered as Stream 21L. The gamanase enzyme cocktail utilised in the extraction experiments is not a pure mannan-degrading enzyme, but is contaminated with hydrolytic enzymes of various activities, and with quantifiable oligosaccharides of unknown structure.

The enzyme treated material was then leached with a mixture of 50% w/w methanol and water containing 5% alkali charge on wood. The liquor-to-wood ratio was 10. Leaching was performed in 2 L stainless steel autoclaves rotating in a vessel filled with polyethylene glycol as heating medium for two hours at 130 °C. The separated liquid was collected in Stream 15L.

For reference, the enzymatic-treatment step was also performed without active enzymes, and a reference wash (Stream 21L-ref) and leached material (Stream 15L-ref) was recovered.

Pulping

In the cooking process, two different cooking liquids and loads were used depending on the physical size of the wood material.

For wood chips (Stream 1S and 3S), 100 g (dry basis) of chips were placed in stainless steel autoclaves for each batch. The cooking chemicals, added as NaOH, Na_2S and Na_2CO_3, were added to a liquor-to-wood ratio of 4.5:1 (kg/kg). The effective alkali (EA) charge was 22%, the sulphidity was 35% and the concentration of carbonate in the white liquor was 0.1 M. For pulping of mechanically treated wood material (Stream 14S), 50 g (dry basis) of the material was used for each batch and the cooking chemicals were charged to a liquor-to-wood ratio of 9:1 (kg/kg). The EA charge was 29%, the sulphidity was 35% and the concentration of carbonate in the white liquor was 0.1 M.

The autoclaves used for the cooking process were placed in a pre-heated polyethylene glycol bath at 80 °C for 20 min. The temperature was then increased to 170 °C at 0.8 °C/min and was maintained for 20, 40 or 60 min. The autoclaves were cooled and the cooked chips were separated from the black liquor which was re-filtered once, and the filter cake was then displacement washed with twenty litres of de-ionized water. This was followed by disintegration in a laboratory defibrator (L&W Noram) at 3000 rpm and the filtrate was re-filtered once. The pulp was then subjected to a second wash with fifteen litres of de-ionized water.

Enzymatic crosslinking

The crosslinking was performed according to the Ecohelix technology described by Oinonen *et al.* [4]. A summery through a schematic representation of the enzymatic crosslinking process is shown in Figure 2. A 5 kDa retentate from membrane filtrations of the STEX 7 bar extract (Stream 5L) was used for the crosslinking experiments.

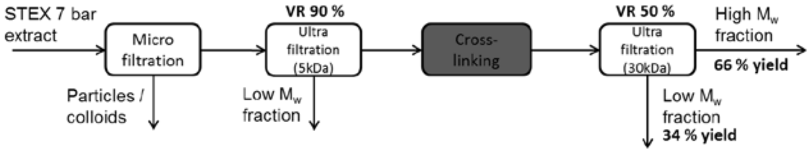

Figure 2. A schematic representation of the enzymatic crosslinking process.

Analytical methods

Klason lignin, acid soluble lignin and carbohydrate content was determined by the method described in [8] except for the data reported in Tables 3 and 5 where the composition presented was determined using Tappi-2003 or SCAN-CM 71:09 with slight modifications. Intrusion volume was investigated using mercury porosimetry (Auto pore IV, micromeritics). ISO Brightness, viscosity and kappa number was determined according to SCAN methods; SCAN-C 11:75, SCAN-C 15:62 and SCAN-C 1:77 respectively.

Results and discussion

Yields

The yield based on total mass for the soft wood chips treated with the 7 bar STEX and a 60 min digestion step are shown in Figure 3. A total of 5 kg of dry wood chips was used as raw material for this process.

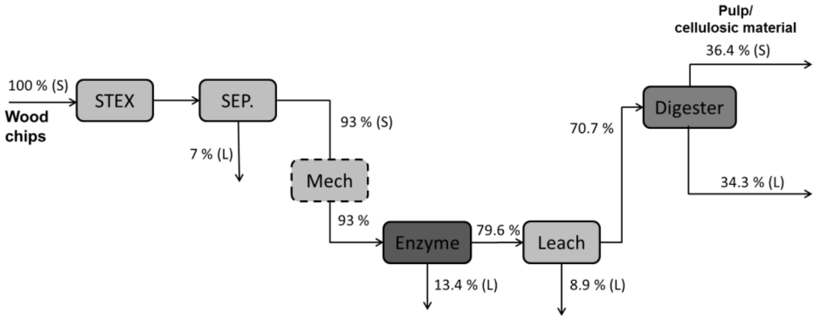

Figure 3. Cumulative yields for a 7 bar STEX pre-treatment followed by a digestion step (60 min at $\boldsymbol{T_{max} = 170\ °C}$). (S) or (L) marks solid/liquid streams.

After a pre-treatment with a mild steam explosion at 7 bar, followed by enzyme-assisted leaching steps, a total of about 29% (w/w) of the wood could be extracted.

Fractionation and upgrading of mild-STEX extracted components

The components released from the mild steam explosion (mainly hemicelluloses) were fractionated by membrane filtration, and Table 1 shows the sugar composition of several fractions recovered. These results show that arabinose was found mainly in the low molecular weight fractions. Since the 1-5 kDa fraction contains only 7.4 wt% arabinose, it is concluded that most of the arabinose is enriched in the < 1 kDa cut-off. As a side chain of xylan, arabinose can be easily cleaved from the polysaccharide backbone by autohydrolysis under harsh conditions, and hence enriched in the low molecular weight fraction. These results also show that the largest concentration of galactoglucomannan (GGM) was found as higher molecular weight material in the > 5 kDa fraction.

The Klason lignin content in the membrane-fractionated samples show that the amount of lignin was greater in the fraction with a lower cut-off, which indicates that the lignin extracted during hot water treatment is of lower molecular weight relative to the hemicelluloses.

Table 1. Anhydro sugar composition and lignin content of membrane-fractionated samples, extracted liquid after STEX 7 bar treatment (wt%).

	Arabinose	Galactose	Glucose	Xylose	Mannose	Klason lignin
<0.45µm permeate	7.4	5.2	8.2	7.4	22.4	13.0
0.45 µm – 5 kDa	3.6	5.3	9.8	7.0	27.8	10.0
5-1 kDa	7.4	5.7	5.7	10.7	19.4	12.9
5 kDa permeate	14.9	4.6	3.1	8.1	11.3	16.1
1 kDa permeate	19.2	3.8	1.7	6.3	6.1	17.6

Enzymatic crosslinking

To further upgrade the hemicelluloses that were recovered by the STEX treatment, enzymatic crosslinking according to the Ecohelix technology was employed, to produce Stream 8L. The polymer samples were successfully crosslinked using this approach, as shown by the size exclusion chromatography (SEC) data, Table 2. The table also gives an indication of the degree of polymerization of the 5 kDa retentate STEX extract, and suggests that the hemicelluloses released in this fraction have on average a degree of polymerization on the order of 30 sugar monomer units. The crosslinked sample was separated into two fractions, of comparatively high and low average molecular weight. The sugar compositions of the fractions are given in Table 3.

Table 2. Molecular weight distributions of fractions before and after cross-linking.

	M_n (Da)	M_w (Da)	M_w/M_n
Ultra filtration 5 kDa retentate	5590 ± 50	12900 ± 250	2.18 ± 0.03
After cross linking	6000 ± 60	17000 ± 350	2.82 ± 0.08
Low M_w fraction (Stream 8L)	4800 ± 10	9100 ± 50	1.90 ± 0.01
High M_w fraction (Stream 8L)	7600 ± 100	19800 ± 750	2.62 ± 0.06

Table 3. Anhydro sugar composition of crosslinked samples (wt%).

Sample	Arabinose	Galactose	Glucose	Xylose	Mannose
High M_w (Stream 8L)	4.3	6.5	10.4	8.0	42.5
Low M_w (Stream 8L)	1.5	6.0	11.3	5.3	42.8

The Ecohelix technology therefore seems promising for the crosslinking and upgrading of hemicelluloses derived from the steam explosion process.

Extracted and residual material after enzymatic treatment and leaching

After addition of monocomponent enzymes the amount of reducing sugar in the leached streams 15L, 15L-ref, 21L and 21L-ref was measured, see table 4. The relative changes in reducing sugar levels between Streams 15L-ref and 15L indicate that the gamanase treatment increases the amount of polysaccharides available for enzymatic hydrolysis, as all of the monocomponent enzymes tested (xyloglucanase, xylanase and mannanase) are able to release significantly more reducing sugar from Stream 15L than from Stream 15L-ref.

Table 4. Amount (g) of reducing sugar released by the enzyme per kg total dissolved solids in the sample, 7 bar STEX pre-treatment.

Enzyme:	15L-ref	15L	15L/15L-ref	21L-ref	21L	21L/21L-ref
endo-glucanase	0.98	6.16	6.3	6.05	6.33	1.0
endo-mannanase	1.17	8.73	7.5	7.27	5.94	0.8
endo-xylanase	1.47	8.74	6.0	7.33	5.64	0.8

This increased response to gamanase treatment could be explained by an increase in the concentration of polysaccharide, or simply by an increased polysaccharide accessibility. A general loosening of the lignocellulosic network by chain cutting of the glucomannan may have increased the accessibility of polysaccharides within the LCC network. The gamanase pre-treatment is not specific for inter-network connections but has mostly *endo*-type activities (cleaving polysaccharides at points along the backbone), so it is likely that the polysaccharides have been made more soluble by a reduction in chain length (degree of polymerization) by the degradative activity of the gamanase; this would lead to an increased concentration of shorter, dissolved oligosaccharides in these samples of leaching water.

The composition of the solid residue after enzymatic treatment and leaching can be found in Table 5. Glucomannan content in the solid residual is significantly reduced by the leaching step and the effect is enhanced by enzymatic treatment (compare Stream 14S and 14S-ref).

Table 5. Lignocellulosic composition after mechanical treatment and enzymatic treatment and leaching treatment respectively (wt%).

Sample	Cellulose	Glucomannan	Xylan	Klason lignin
Stream 10S	39.1	13.2	4.4	27.5
Stream 10S (rep.)	42.4	14.4	5.4	26.7
Stream 14S	47.5	8.6	4.8	27.6
Stream 14S (rep.)	48.4	8.7	4.9	28.5
Stream 14S-ref	47.4	10.5	5.0	27.5

Pulp production

The pulping (producing Stream 19S) followed reasonable trends, with lower kappa numbers and lower intrinsic viscosities after longer pulping times at the cooking temperature, see Tables 6, 7 and 8. Material subjected to mechanical treatment followed by enzyme-assisted leaching treatment (M.E.L treatment; Stream 14S) was also subjected to cooking, and yielded low pulp viscosities.

Table 6. No pre-treatment.

Time (min) at T_{max}:	20	40	60
Yield (%):	52	48.6	48.5
Res. Alkali (g/kg):	15.4	13	12.2
Kappa nr.:	71.7	41.2	29.9
Viscosity:	1110	1215	1125

Table 7. STEX 7 bar pre-treatment. Table 1. STEX 7 bar & M.E.L. pre-treatment.

Time (min) at T_{max}:	20	40	60
Yield (%):	50.3	45.8	43.2
Res. Alkali (g/kg):	13.9	12.8	12.7
Kappa nr.:	63.6	35.8	25
Viscosity:	1230	1115	1000

Time (min) at T_{max}:	20	40	60
Yield (%):	53	49	51.5
Res. Alkali (g/kg):	20.3	18.5	16.5
Kappa nr.:	72.5	35.5	29.8
Viscosity:	970	840	750

Applying the different treatments alone or in combination with each other, and controlling the intensity of the steps more carefully provides a toolbox where pulp grades ranging from a product closely resembling conventional Kraft pulp to a product approaching dissolving pulp, can be achieved.

Concluding remarks

The results within this work demonstrate the feasibility of combining multiple different methods of biomass treatment, extraction, separation and modification to create a palette of different fractions – a pulp fibre with acceptable qualities, and fractions of solubilized hemicelluloses and lignins. However, can the process be economically feasible? Firstly, it must be emphasized that all the methods used in this work can be scaled-up, and several of the individual stages have for a long time been used industrially. The enzymes and other chemicals used are of industrial grade. At the present time, the hemicelluloses and lignins produced in this process are of grades that have limited commercial value, however the value of compounds like these is expected to increase as the availability of non-renewable resources decreases. The most valuable product of the process today and in the foreseeable future is the cellulose fibre. It must also be kept in mind that this is a first attempt to develop a novel industrial process, and that it can be optimized in several ways.

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Upgrading 1

Heterogeneous Catalysis – A Powerful Tool for Upgrading of Forest Biomass to Value Added Products in Novel Biorefineries

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Introduction

Lignocellulosic forest biomass is the most abundant source of raw material for sustainable value added chemicals and fuels in bio-economy. Main constituents of this biomass, cellulose, hemicellulose and lignin, can be fractionated by using novel fractionation techniques including Organosolv processes and e.g. fractionation based on gamma-valerolactone [1]. Relatively pure fractions obtained from these processes can be upgraded by different techniques to value added products. A natural way is to apply fibres of cellulose in material applications. Alternatively, cellulose and especially hemicellulose can be utilized as C6 and C5 sugars. Moreover, the values of all biomass fractions in novel biorefineries, including lignin, have to be maximized. A potential alternative is to upgrade lignin by catalytic depolymerization to monoaromatics to be applied as fuel components or chemical intermediates.

Heterogeneous catalysis is a powerful tool for upgrading of lignocellulosic biomass components. Heterogenous acid catalysts can be applied for dehydration of C5 and C6 sugars to important bio-based chemical intermediates furfural and hydroxymethylfurfural (HMF). Typically homogeneous acid catalysts have been used for these reactions. However, the process based on homogeneous catalysts suffer from a wide variety of unwanted side products. Furthermore, separaration of homogeneous catalyst from the product can be a challenge. By using heterogeneous catalysts, side reactions can be suppressed in these reactions. Moreover, e.g. carbon-based solid catalysts tolerate well water solutions of sugars. [2] However, some other types of acidic heterogeneous catalysts including metal oxides and zeolites have also investigated for this application [3].

Furfural and HMF are potential intermediates for many chemicals e.g. by oxidation or hydrogenation routes. Futhermore, many other reaction routes from furfural and HMF are reported in the literature. [4] Some important specialty chemicals and chemical intermediates can be obtained by catalytic oxidation route including succinic acid from furfural [5] and 2,5-furandicarboxylic acid (FDCA) from HMF. FDCA is a potential monomer for the production of bio-based polymer polyethylene furandicarboxylate (PEF) to replace fossil-based polyethylene terephthalate (PET). [6] Moreover, furfural and HMF can be hydrogenated to high quality fuel components. By hydrogenation of furfural, a potential gasoline component 2-methylfuran (2-MF) with high octane number (RON 131) can be produced. However, maximization of yield and selectivity for 2-MF has turned out to be challenging. Traditionally, CuCr-based supported metal catalysts have shown good performance in this application. However, due to poisonity of chromium, environmentally friendly heterogenous catalysts with good activity and selectivity towards 2-MF have to be developed. [7]

Lignin is a challenging raw material for the production of monomeric components due to it's complex polyphenolic nature. Catalytic hydrogenolysis route is one of the most promising route for monomer production [8]. By using hydrogenolysis/solvolysis lignin can be converted into monoaromatics by using metal catalysts supported e.g. on carbon and zirconia. Monoaromatics can be further upgraded to aromatic fuel components or specialty chemicals by catalytic hydrodeoxygenation [9]. The final product is suitable to be used e.g. as bio-based jet fuel components. Alternatively, aromatics can be applied in e.g. resins to replace phenolic monomers. [10] Hovever, full monomer yield cannot be obtained by hydrogenolysis, but the residual lignin from this process is a potential raw material for materials applications [11].

The scope of this study was to investigate and verify potentiality of hydrotreatment route for upgrading of furfural to a potential gasoline component 2-MF as well as for the depolymerisation of lignin to monomeric intermediates to be upgraded to fuel components or specialty chemicals. Different supported metal catalysts were screened to discover catalysts with optimal performances.

Experimental

Furfural hydrogenation experiments

Catalyst screening experiments in furfural hydrogenation to 2-MF were carried out in a 50 ml high pressure autoclave reactor operating batchwise. Solid catalyst was placed in a Robinson-Mahoney type static basked. Reactor was heated to the reaction temperature and furfural as well as a solvent (2-propanol) were charged with hydrogen pressure. Typical conditions for a experiment were: T = 230 °C and p_{H2} = 40 bar. Liquid samples were withdrawn from the reactor during the experiment to be analysed with GC. A gas sample from reactor gas phase was taken to a bomb after the reactor was cooled down and analysed by GC.

Liquid samples were analysed by Agilent 6890 Series GC equipped with a Zebron ZB-wax Plus column and FID detector. Gas samples were analysed by Agilent 6890N network GC with gas feed valve, a three-column system and FID as well as TCD detectors.

Lignin depolymerisation experiments

Organosolv lignin from Fraunhofer was used as feedstock in the lignin depolymerization experiments. Experiments were carried out in a 100 ml high pressure autoclave reactor. 1 g of lignin was mixed with 50 ml of ethanol and charged into the reactor. The solid catalyst was placed in a spinning basket. The experiment was started by heating the reactor and charging the hydrogen. Typical conditions for an expement were: T = 300–400 °C and P_{H2} = 30–50 bar. Due solid material in the reactor, a liquid sample was taken from the reactor only after the experiment.

Product analysis of the lignin depolymerization experiment is a complex procedure. Basically, the product was divided into ethanol solubles and insolubles fractions and ethanol insoluble fraction was further divided into THF insoluble and solubles fractions. The molecular weight analysis of the lignin and the product were performed by GPC with an Agilent 1100 HPLC/VWD (Phenogel guard column and two Phenogel size exclusion columns of cross-linked styrene-divinylbenzen). The ethanol solubles fraction was analysed with an Agilent 7890A GC/MS (5975C) (HP-5 column). The amount of light compounds (monomers and dimers) of ethanol soluble fraction was determined applying the GC/MS and GPC results. Furthermore, pyrolysis-GC and elementary analysis were applied to characterize feedstock and products.

Results and Discussion

Furfural hydrogenation

A catalyst sceening of in-house prepared metal catalysts supported on steam activated carbon was performed in order to discover a catalyst with an optimal performance for the production of 2-MF. The catalyst applied in the screening and their propertied based on characterization are listed in Table 1.

Table 1. Properities of catalysts applied in furfural hydrogenation.

Catalyst	Metal content (%)	7 point BET (m^2/g)	Pore volume (ml/g)
Cu/C	1,6	516	0.313
Ni/C	1,9	710	0.281
CuNi/C	2.3/1.5	837	0.220
CuFe/C	2.4/1.5	765	0.150
NiFe/C	2.1/2.5	975	0.224

Based on the experiments, the reactions in furfural hydrogenation form a complex network with several competitive and consecutive reactions. 2-MF is formed in consecutive hydrogenation~~s~~ steps through furfuryl alcohol intermediate. Moreover, 2-MF can react further to many side products. A simplified reaction network is presented in Figure 1. Optimization 2-MF yield in such reaction complex network is a challenging task requiring a catalyst with optimized performance.

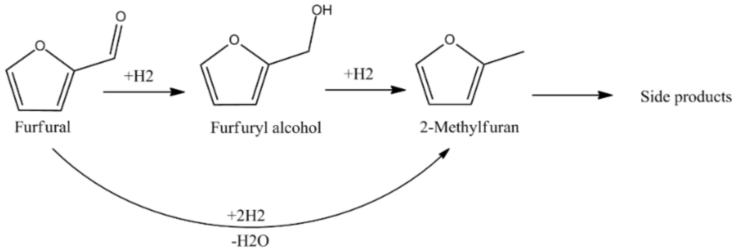
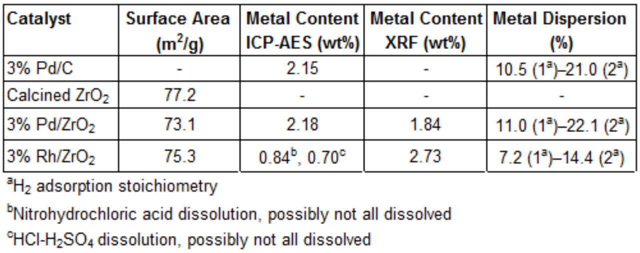


Figure 1. Reaction network in furfural hydrogenation.

A summary of the results of catalysts screening is presented in Table 2. Different catalyst gave quite different yields and selectivities for different product. E.g. with Cu/C catalysts, almost only furfuryl alcohol was obtained, whereas catalysts including nickel as an active metal turned out to give relatively high yields and selectivities for 2-MF. The best yield for 2-MF was obtained with 10% Ni/C. Compared to other studies on furfural hydrogenation, similar level of 2-MF yield was obtained as the best one reported in the literature [7]. As next steps, different carbon supports will be studied on order to further enhance 2-MF yield and selectivity. Furthermore, contiuous experiments will be performed to investigate the stability of the catalyst as well as to study a continuous process concept. It is expected that the product yield can further inproved by optimizing the contact time in the continuously operated system.

Table 2. Conversions and 2-MF yields in furfural hydrogenation experiments.



Catalyst	Surface Area (m^2/g)	Metal Content ICP-AES (wt%)	Metal Content XRF (wt%)	Metal Dispersion (%)
3% Pd/C	-	2.15	-	10.5 (1^a)–21.0 (2^a)
Calcined ZrO_2	77.2	-	-	-
3% Pd/ZrO_2	73.1	2.18	1.84	11.0 (1^a)–22.1 (2^a)
3% Rh/ZrO_2	75.3	0.84^b, 0.70^c	2.73	7.2 (1^a)–14.4 (2^a)

[a] H_2 adsorption stoichiometry

[b] Nitrohydrochloric acid dissolution, possibly not all dissolved

[c] $HCl-H_2SO_4$ dissolution, possibly not all dissolved

Lignin depolymerisation

Different supported metal catalysts were tested for the hydrogenolysis/solvolysis of Organosolv lignin. The supports applied were zirconia, alumina and activated carbon. Furthermore, palladium and rhodium were used as active metals. Both commercial and in-house prepared catalysts were applied. The characterized properties of the catalysts are presented in Table 3.

Table 3. Characterization results of catalysts for lignin polymerization.

Catalyst	**Highest furfural conversion achieved (%)**	**Highest 2-Methylfuran yield achieved (%)**
1% Cu/C	54.0	2
2% Cu/C	75.6	3
5% Cu/C	98.5	20
2% Ni/C	97.5	32
5% Ni/C	99.8	33
10% Ni/C	99.9	49
2%/2% CuNi/C	99.7	40
2%/2% CuFe/C	99.8	41
2%/2% NiFe/C	99.9	31
5%/2% NiFe/C	100.0	36
5%/5% NiFe/C	99.9	26

The catalysts were compared in the experiments at 300 ºC and 50 bar. Moreover, the effect of temperature in the range of 200–400 ºC and pressure 30–50 bar was investigated using Pd/C catalyst. The results obtained with different catalysts were compared with an experiment without any catalyst. The yields of product fractions with different catalysts are presented in Figure 2.

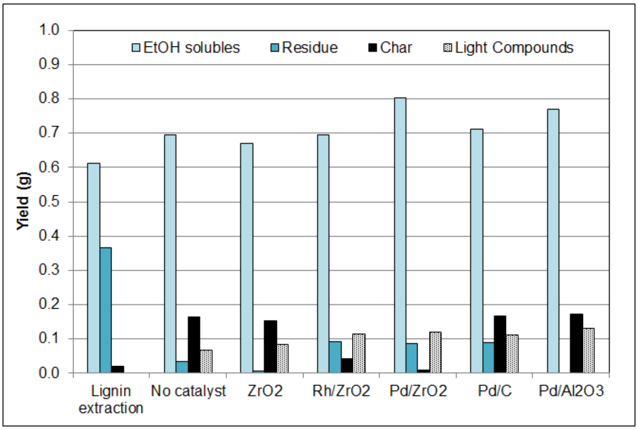


Figure 2. Yields of product fractions with different catalysts.

As can be seen from the figure, the best catalysts enhanced the yield of ethanol solubles fraction compared to non-catalytic experiment. The best yield of this fraction was obtained by 3% Pd on ZrO_2. Furthermore, the best catalysts being 3% Rh/ ZrO_2 and 3% Pd/ ZrO_2 suppressed the formation of char fraction. The value of char fraction can be considered low affecting negatively the yields of value added fractions. The yield of light compounds fraction based on GC-MS analysis can be considered to be higher with all the catalysts than without any catalyst. The highest yield was obtained with 3% Pd/ZrO_2 and 5% Pd/Al_2O_3. However, catalysts affected significantly the properties of light compounds fraction. It was possible to lower oxygen content and increase hydrogen content by applying solid catalysts. Based on literature the yield of light compounds fraction can be further enhanced significantly by raising the temperature near 400 C. The depolymerisation of lignin takes place mainly thermally and the main role of the catalysts and hydrogen donors is to protect the system from repolymerization leading to heavy useless residue formation. [12] A process concept can be developed based on catalytic hydrogenolysis/solvolysis. In this concept, light compounds are the main product and partly degraded ethanol solubles can be circulated back to the feed of the reactor section. Party degraded lignin can also be used in materials applications. The formation of char should be minimized.

Conclusions

Heterogeneous catalysts can be efficiently used for upgrading of fractions of lignocellulosic biomass. For upgrading of furfurals, hydrogenation route and supported metal catalysts can be applied. 2-MF is a potential fuel component to be produced through hydrogenation of furfural. By using Ni catalyst supported on carbon, 2-MF yield of ~ 50 % could be obtained corresponding best yields reported in the literature.

Organosolv lignin was depolymerized by metal catalysts supported on carbon and zirconia. The best performance was obtained by using zirconia as a support. The existence of a solid catalyst enhanced the yield of light compounds fraction containing monomers and dimers of phenolic components and suppressed char formation. Moreover, the solid catalysts improved the quality of this light compounds fraction as fuel component intermediate.

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Subcritical Water De-polymerization of Kraft Lignin: A Process for Future Biorefineries. Structural Characterization of Bio-oil and Solids

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Abstract

A 2D-NMR analysis was carried out on fractionated bio-oil in order to investigate the result of the subcritical water base catalysed de-polymerization of LignoBoost Kraft lignin (350 °C, 25 MPa). It was confirmed that the signals from aliphatic lignin inter-unit linkages, *i.e.* β-O-4’, β-β’, β-1’ and β-5’, had disappeared in all bio-oil fractions (light oil, heavy oil and suspended solids). This means that both aliphatic carbon-oxygen (C-O) and carbon-carbon (C-C) bonds in LignoBoost Kraft lignin have been broken and an effective de-polymerization has occurred. However, re-polymerization to higher molecular weight (Mw) fractions take place simultaneously. These higher Mw fractions (heavy oil and suspended solids) were found to be re-polymerized macromolecules (Mw distribution 5.4 kDa and 19.5 kDa resp.) with new structural networks based on guaiacol/disubstituted aromatic ethers and polyaromatic hydrocarbon structures tightly bound together. In this work it has been demonstrated that the subcritical water de-polymerization process of LignoBoost Kraft lignin does function; an effective de-oxygenation of LignoBoost Kraft lignin takes place, generating a bio-oil with a low content of atomic oxygen (15 wt.%) suitable for further processing at fossil-based oil refineries.

Introduction

The future development of new, integrated biorefineries requires new methods for refining the various components of wood: cellulose, hemicellulose and lignin. Lignin is a natural source of aromatic rings (phenols, guaiacols and syringols), making it a potential, renewable source not only for producing fuel and chemicals but also for replacing a part of today's demand for fossil fuels. New green process technology currently exists for separating and purifying Kraft lignin from the black liquor generated in the Kraft pulping process, *e.g.* the LignoBoost process [1]. However, additional processes for transforming the Kraft lignin into new, high value products are needed. One promising technique for the de-polymerization of lignin is the use of sub/supercritical water to generate bio-oil [2]. When close to its critical point (372.9 °C, 22 MPa), water gains unique properties and resembles an organic solvent, which then allows it to be used to dissolve organic structures. This, in turn, allows for the environmental-friendly de-polymerization of lignin by "green chemistry". The subcritical reaction pathway is thought to start with lignin being de-polymerized by hydrolysis and de-alkylation reactions to form aromatic monomers (phenol, guaiacol, catechol and cresol), larger oligomeric structures and smaller aliphatic reactive intermediates (aldehydes and alcohols). However, these reactive functional groups could also be located on aromatic monomers, as well as the larger oligomeric structures. The many reactive groups/fragments mean that unfavourable re-polymerization reactions accompany the de-polymerization of lignin and yields cross-linking to higher Mw fragments (*e.g.* residual lignin, heavy oil, char, solids, residual solids, phenolic char and polyaromatic char) [3-6]. Recent investigations in continuous reactors have shown that de-polymerization and re-polymerization are fast, and competing, reactions that both start immediately in sub/supercritical water [7]. However, a structure analysis of the bio-oil is necessary for a better understanding of the lignin de-polymerization process. One major issue of these sub/supercritical water depolymerization processes is that only one third of the bio-oil is characterized structurally by GC-MS (Mw 40-400, approx. 25-40%). On the other hand, non-volatile compounds and oligomers cannot be detected, which yields only partial information of the chemical structures in the bio-oils [8]. Nevertheless, fractionation of the bio-oils, together with the unique potential of ^{13}C, ^{1}H-correlated Heteronuclear Single Quantum Coherence NMR technology (2D-HSQC NMR) allows a structural characterization of the higher Mw fractions in the bio-oil to be made. This work therefore focuses on elucidating the composition of the various bio-oil fractions generated from LignoBoost Kraft lignin after base catalysed subcritical water de-polymerization, *i.e.* light oil [diethyl ether (DEE) soluble fraction], heavy oil [tetrahydrofuran (THF) soluble fraction] and suspended solids (insoluble THF residue).

Experimental

The pilot plant used for the subcritical water base catalysed process was reported recently by Nguyen *et al.* [9, 10]. It is a high-pressure catalytic reactor that uses ZrO_2 pellets. The suspension fed into the reactor was comprised of lignin (5.5%), phenol (4.1%), K_2CO_3 (1.6%) and KOH (0.2%), and the reaction temperature and pressure were 350 °C and 25 MPa, respectively. The bio-oil was fractionated by liquid fractionation into a DEE soluble (light oil), THF soluble (heavy oil) and THF insoluble (suspended solids) fraction. These fractions were characterized using GC-MS [10], elemental analysis [10], Gel Permeation Chromatography (GPC) and NMR. GPC was analyzed using PolarGel-M columns (8 µm, 50×7.5 mm and two 300×7.5 mm) with DMSO/LiBr (10 mM) as the mobile phase and calibrated with Pullulan standards to determine the molecular weight (Mw) and polydispersity index (PD). The ^{1}H, ^{13}C NMR and ^{1}H, ^{13}C-HSQC spectra were recorded at 25°C on a Bruker Avance III HD 18.8 T NMR spectrometer (Rheinstetten, Germany) equipped with a 3 mm TCI Cryoprobe operating at 800 MHz for ^{1}H and 201 MHz for the detection of ^{13}C. The ^{13}C spectra were recorded with an inverse-gated de-coupling sequence, 90° pulse angle, 12 s pulse delay and 3200 scans. The HSQC spectra were recorded with a standard Bruker pulse sequence “hsqcedetgpsisp2.3” with a 90° pulse, 0.25 s acquisition time, 3 s pulse delay, $^1J_{C-H}$ of 145 Hz, 16 scans and the acquisition of 8192 data points (for ^{1}H) and 256 increments (for ^{13}C). Data processing and plots were carried out using MestReNova v10.0.0 software.

Results and Discussion

The bondings most characteristic of lignin, *i.e.* β-O-4’ (β-ether), β-β’ (pinoresinol), β-1’ (diphenyl ethane), β-5’ (phenylcoumaran), α-O-4’ and dibenzodioxocine (5-5’-α, β-O-4’), are found in the 2D-HSQC NMR inter-unit aliphatic lignin region/oxygenated aliphatic region (δ_C/δ_H 52.5-90.0/2.8-5.7 ppm) [11]. However, LignoBoost Kraft lignin displays a modified chemical structure when compared with native lignin: β-O-4’, β-β’, β-1’ (weak signal) and β-5 were found (Figure 1). It is clear from visible inspection of the different bio-oil fractions’ 2D-HSQC NMR spectra in this region that all inter-unit linkages (the C-O linkages) from the LignoBoost Kraft lignin have disappeared (Figure 1). This means that the aliphatic C-O and C-C bonds have been broken under subcritical conditions, *i.e.* in the known lignin inter-unit structures β-O-4’, β-β’, β-1’ and β-5’, indicating that some type of de-oxygenation reaction has occurred in all of the fractions (light oil, heavy oil and suspended solids). The assumption can then be made that lignin is initially solubilized/hydrolyzed in the subcritical phase during the conditions employed (350 °C, 25 MPa), and that subsequent de-polymerization and re-polymerization reactions occur, yielding monomeric/dimeric molecules and re-polymerized macromolecules, respectively. If, in contrast, we had found intact C-O inter-unit linkages in the higher Mw fraction (*i.e.* heavy oil and suspended solids), it would be an indication of a non-homogenous reaction and partially-dissolved LignoBoost Kraft lignin, leading to higher Mw structures resembling Kraft lignin, *i.e.* residual lignin.

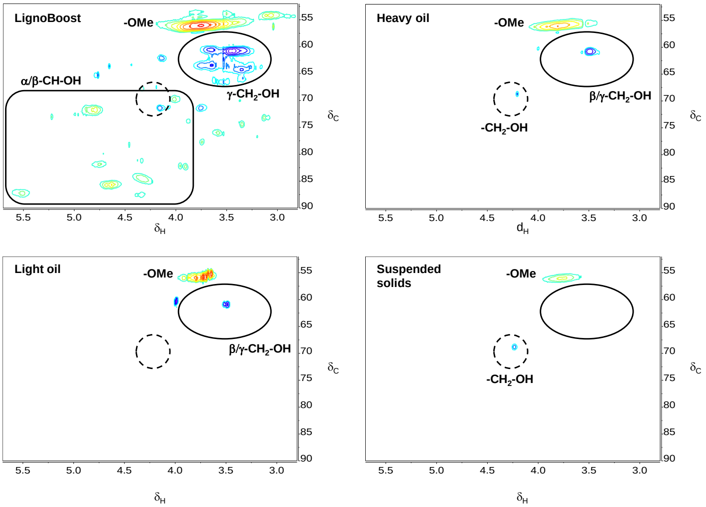

Figure 1. Inter-unit aliphatic lignin region δ_C/δ_H 52.5-90.0/2.8-5.7 ppm of 2D-HSQC NMR spectra of the subcritical oil fractions. Cross-peaks CH/CH_3 (green-yellow-orange-red) and CH_2 (blue). Black rings show the structural motifs of the lignin; dashed rings show new cross-peaks found in the bio-oil fractions.

Another intriguing finding was that the location of the C-O bonds in the heavy oil and suspended solids seemed to be mainly on aromatic rings: (a) Figure 1 shows that almost no aliphatic hydroxyl and ether bonds remain (2D-HSQC NMR). (b) ^{13}C NMR integration of the aromatic region revealed that the aromatic C-O bond was located almost exclusively in the di-substituted aromatic ether/guaiacol chemical shift region. (c) The methoxyl group (-O$\underline{CH_3}$) in ^{13}C NMR was found to be in a guaiacol-like environment. The conclusion that can thus be drawn is that C-O bonds in heavy oil and suspended solids are present as hydroxyl, methoxyl or aromatic ether in guaiacol, catechol or other aromatic di-substituted ether structures. It is interesting that this correlates with the literature in which guaiacol rings have been presumed to be responsible for polymerization reactions leading to higher Mw structures [3, 12]. The light oil fraction was, nevertheless, found to be composed of a mixture of phenol and guaiacol-like rings in a 2.4:1 ratio (^{13}C NMR).

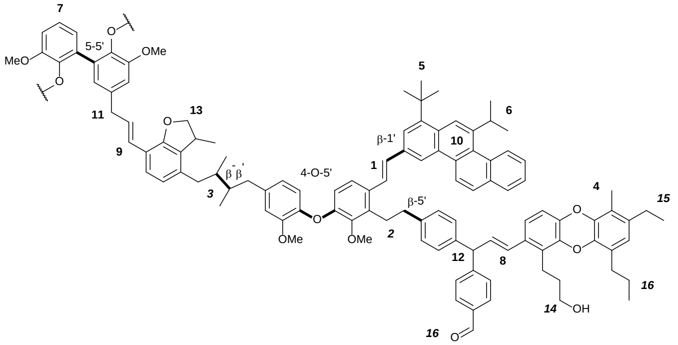

Figure 2. Hypothetical chemical structure of heavy oil/suspended solids based on the linkages found in 2D-HSQC NMR (*i.e.* not proportional to their natural occurrence in the macromolecule). Structural features only found in heavy oil are in italic and underlined; all other numbers represent linkages that could be found in both structures. C-C linkages from lignin are shown by bold lines.

Structural features found in the higher Mw fractions are visualized in Figure 2, which is a hypothetical, macromolecular, structural drawing that visualizes the various chemical fragments/linkages found using 2D-HSQC NMR. The bio-oil fractions, heavy oil and suspended solids have none of the inter-unit C-O bondings of the original lignin left in β-O-4', β-β' and β-5', although the C-C skeleton of β-β', β-5' and β-1' may still be present in linkages and side chains, *i.e.* stilbene (**1**) and aliphatic linkages (**2** and **3**) [13]. The aromatic carbon-carbon 5-5' and carbon-oxygen 4-O-5' linkages in lignin have been reported to be more resistant to subcritical de-polymerization and, as such, are expected to remain unchanged in the bio-oil fractions [4]. As shown in Figure 2, the structural features present both in heavy oil and suspended solids are: aromatic methyl groups (α-CH_3, **4**), branched β-CH_3 groups [Ar-$CH_{0\text{-}2}$-($\underline{CH_3}$)$_{2\text{-}3}$) *i.e. tert*-butyl (**5**) or similar (**6**)], aromatic-CH (**7**), vinylic (Ar-$\underline{CH=CH}$-R, **8**) and allylic (Ar-C-$\underline{CH=CH}$-R, **9**) connected aromatic substituents, stilbenes (Ar-$\underline{CH=CH}$-Ar, **1**) and condensed PAH-like structures (**10**) as well as aliphatic carbon bridge heads methylene (α-CH_2, **11**) and methine (α-CH, **12**) substituted directly onto aromatic rings. It should be noted here that none of these connections are connected to an oxygen atom. One new methylene linkage connected to oxygen (Ar-O-$\underline{CH_2}$-R, **13**) was found both in heavy oil and suspended solids; a fraction of methylene-γ-hydroxyls (Ar-C-C-$\underline{CH_2}$-OH/R, **14**) was also found in the heavy oil. In addition, it seems that heavy oil is built up to a great extent of a more flexible bond structure, with two carbon bridges (-CH_2-CH_2-, **2**), ethyl (**15**) and propyl groups (**16**). However, these structures cannot be found in suspended solids, which rather are substituted on one carbon bridge head (Ar-$\underline{CH}$-, **12**) and have linkages with unsaturated bonds (vinylic **8**, allylic **9** and stilbene **1**).

Light oil is dominated by monomer and dimer aromatic structures and, as such, is very interesting in the further development of fine chemicals and fuels (Mw distribution 0.06-0.24 kDa). GC-MS analysis of the light oil fraction yielded the main constituents as being phenol > anisole > *p*-cresol > *o*-cresol > *p*-ethyl-phenol > guaiacol; both xanthenes and phenolic dimers (Ar-CH_2-Ar and Ar-CH_2-CH_2-Ar) were detected [10]. Using 2D-HSQC NMR allowed the total composition of the light oil to be investigated and a good agreement with the GC-MS results was found. An additional finding of the NMR was that the light oil, in common with the other high Mw fractions, is devoid of aliphatic oxygen lignin inter-unit connections. Two cross-peaks corresponding to methylene-γ-hydroxyls (Ar-CH_2-CH_2-$\underline{CH_2}$-OH/R, Figure 1) were detected, however, thus indicating that a small fraction of aliphatic hydroxyl groups remain in the light oil. From the 2D-HSQC NMR is it clear that a larger fraction of the light oil is connected to diphenylmethane (Ar-CH_2-Ar) and diphenylethane (Ar-CH_2-CH_2-Ar) structures that have not been detected before by GC-MS. Also, other aromatic substituents, such as aldehyde and methyl ketone groups, were detected in smaller amounts.

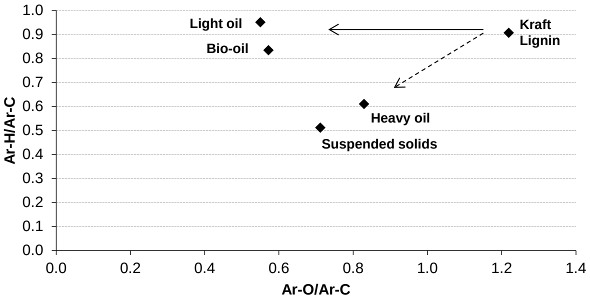

Figure 3. A van Krevelen plot calculated using ratios of Ar-H/Ar-C and Ar-O/Ar-C from ^{13}C NMR integration of the aromatic region (δC 106-162.5 ppm) from the subcritical bio-oil fractions and LignoBoost Kraft lignin. When measuring bio-oil with both monomeric and polymeric carbons in the same sample, the monomeric signals dominate: this is not a representative ^{13}C NMR ratio for describing the composition of the bio-oil. Abbreviation Ar = aromatic.

An additional way of visualizing the change in the structural composition of the bio-oil fractions compared to LignoBoost Kraft lignin is by plotting the Ar-H/Ar-C and Ar-O/Ar-C ratios from the aromatic region of ^{13}C NMR in a van Krevelen plot (Figure 3). The high Mw structures (heavy oil and suspended solids) found clearly displace the lower Ar-H/Ar-C and Ar-O/Ar-C ^{13}C NMR ratios than LignoBoost Kraft lignin. The H/C atomic ratios obtained from elemental analysis (that includes both aromatic and aliphatic carbons) also indicate a higher total carbon content for heavy oil (0.82) and suspended solids (0.70) with respect to LignoBoost Kraft lignin (0.87). This could be the result of the loss of C-H or C-O bonds in favour of the formation of C-C bonds, yielding a more substituted and/or condensed structure.

Conclusions

^{13}C NMR and 2D-NMR analyses have shown that LignoBoost Kraft lignin is de-polymerized/re-polymerized under subcritical base catalysed conditions (350 °C, 25 MPa), yielding a low and high Mw fraction based on new structural motifs. This knowledge can not only pave the way for improved understanding of the chemical reactions that proceed under subcritical conditions but also be used in the further development of the equipment used.

Acknowledgments

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De-polymerization – An Engineering Approach to Valorization of Lignin for Bio-based Chemicals and Materials

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Abstract

According to the International Lignin Institute, about 40-50 million tonnes of kraft lignin (KL) are generated worldwide each year in the form of “black liquor”. While combustion of black liquor to regenerate pulping chemicals and to produce steam and power is an integral part of the kraft process, a small portion of the lignin can be removed without compromising mill material and energy balances. This presents an opportunity for revenue diversification, if value-added applications for kraft lignin can be identified. The interest in kraft lignin has reached a critical juncture. A commercial-scale, 75 t/d, lignin plant has been in operation since 2013 at Domtar’s Plymouth, North Carolina mill, and projects with targeted capacities of 30 t/d and 142 t/d are under construction in Hinton, Canada and Sunila, Finland, respectively.

The production of platform chemicals (e.g., lactic, succinic and other organic acids) from sugars is growing and the next generation of these technologies seek to use cellulose-derived sugar feedstocks. For this to be realized commercially, value-added applications are needed for the hydrolysis lignin (HL) by-products that are generated from cellulose hydrolysis. Value-added lignn by-products are also needed if the struggling cellulosic ethanol industry is ever to become commercially viable.

Direct use of KL and HL in many biocomposite materials is difficult because the molecular weight is too high and because reactivity is reduced due to steric hindrance effects. Our approach to broaden the range of applications for both KL and HL has been to depolymerize the starting lignin to a mixture of monomers and oligomers. Compared with the original lignins, depolymerized lignins (DLs) are more chemically reactive as substitutes for petroleum-based chemicals (phenol, polyols and bisphenol-A) owing to their smaller molecular weights, reduced steric hindrance effects and more active functional groups. This paper presents some recent results achieved in the authors’ group on various technologies for lignin de-polymerization, focusing on hydrolytic de-polymerization and reductive de-polymerization, as well as production of bio-based phenolic resins, polyurethane

foam and epoxy resins using the DLs, and their applications in wood adhesives and composites.

Introduction

Due to increased concerns worldwide of declining petroleum reserves, energy security, climate change and sustainability, more attention has been focused towards the exploration of renewable resources such as agricultural and industrial wastes/by-products for fuels, chemicals and materials [1]. Lignin (20-30 wt% in wood) [2], a natural, aromatic three dimensional high molecular weight biopolymer composed of phenyl propanol units [3], is a potential candidate for the production of fuels, chemicals and bio-based materials. All native lignins are heterogeneous in nature and mainly composed of two types of linkages: condensed linkages (e.g., 5-5 and β-1 linkages) and ether linkages (e.g., α-O-4 and β-O-4) [4]. The percentage of ether linkages in soft- and hardwood lignins are 56% and 72%, respectively [5]. Aryl ether linkages can be more easily cleaved than the stable C-C linkages since the latter are stable and resistant to chemical depolymerization.

Kraft lignin (KL) is a major by-product produced in a large amount in the pulp and paper industry in the form of “black liquor”, amounting around 50-55 million metric tons per year, [6]. Black liquor is conventionally burned in recovery boilers to regenerate pulping chemicals and to produce steam and electricity for mill operations. While most KL is thus not available for isolation, a special case exists in the 60-70% of North American kraft mills that have production bottlenecks due to the thermal capacity of their recovery boilers. An interesting solution to this problem is to extract some of the lignin in black liquor by precipitation. The removed lignin can be further utilized as a raw material for value-added bio-products which would diversify the mill’s economic base.

Hydrolysis lignin (HL) is a by-product from pretreatment processes in cellulosic ethanol plants. FPInnovations has developed a proprietary hardwood fractionation process for bioproducts (or called “TMP process”) [7], where HL is expected to be produced in large quantity after commercialization of this process. HL is a solid residue [7] from the enzymatic hydrolysis of woody biomass and is mainly composed of lignin (56-57 wt.%), unreacted cellulose and mono and oligosaccharides. Compared with sulfur-containing kraft lignin (KL), HL is a sulfur-free lignin and an environmentally benign biomass. Several chemical modifications of HL have been carried to make effective uses of this abundantly available bio-polymer, however, the majority of the HL was disposed of or utilized as a solid fuel because either the required modifications were too expensive or the material did not function well enough in the applications. These are the same problems that researchers are facing today for effective uses for HL.

Direct utilization of lignin as a green substitute for chemicals such as polyols or phenol/bis-phenol A (BPA) would be challenging due to lignin’s large molecular weight, less functionalities, lower hydroxyl number, poor solubility in many solvents and the lower reactivity towards isocyanate/formaldehyde/epichlorohydrin in the resin synthesis process. Depolymerization of lignin is a viable route for the preparation of low molecular weight products i.e., depolymerized lignin, with more functionalities, higher hydroxyl number and better reactivity, making them promising feedstock for the preparation of bio-based polyurethane (BPU), bio-based phenol formaldehyde (BPF) and epoxy resin/foam materials.

Experimental

Materials

Softwood kraft lignin (KL) used in this study was provided by FPInnovations-Thunder Bay Bioeconomy Technology Centre and was completely soluble in aqueous alkali (pH >10). The relative weight-average molecular weight (M_w) of KL is ≈10,000 g/mol (PDI ≈2.0) based on our GPC-UV analysis. The dried sample contained 0.57 wt% ash (on dry ash free basis). Hardwood hydrolysis lignin (HL) was also provided by FPInnovations, a by-product from its proprietary hardwood fractionation process for bioproducts (i.e., “TMP-bio” process) [7]. The HL contains >50-60 wt.% lignin balanced by the residual cellulose and carbohydrates. The molecular weight was believed to be >20,000 g/mole, but not measurable due to its insolubility in any solvent. Other chemicals used were all of CAS reagents and used without further purification.

Depolymerization of lignin

In this study, the depolymerization of KL and HL was carried via either a high pressure process or a proprietary low-pressure/low-temperature process. The high pressure process operates under reaction conditions of 200-350 ^{o}C for 30-120 mins at 5-16 MPa in a solvent (water, alcohol, acetone or their mixtures) with a catalyst and N_2 or H_2 atmosphere. KL/HL was also effectively depolymerized via a proprietary low-P/low-T process operating under pressure of <300 psig at 150-250 ^{o}C for 30-120 min in the presence of a solvent, catalyst and N_2 atmosphere. The high or low pressure lignin de-polymerization process resulted in high yields of depolymerized lignin, being >90 wt.% for DKL and >70 wt.% for DHL. lignin depolymerization process is shown in Figure 1.

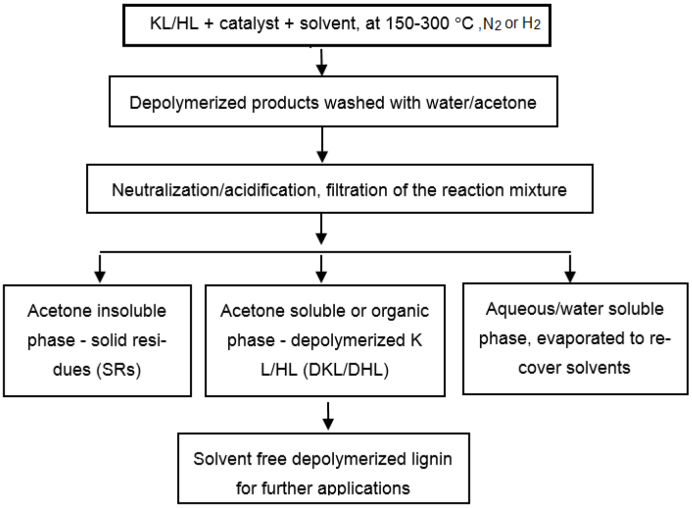

Figure 1. Depolymerization scheme for KL/HL.

The relative molecular weights of lignin and lignin derived products were measured using Waters Breeze GPC-HPLC (gel permeation chromatography-high performance liquid chromatography) instrument (1525 binary pump, UV detector at 270 nm, Waters Styrylgel HR 1 column at a column temperature of 40 °C) using tetrahydrofuran (THF) as the eluent at a flow rate of 1 ml/min with linear polystyrene standards for calibrations. The functional groups of lignins and lignin derived products and materials were also analyzed by Fourier Transform Infrared Spectroscopy (FTIR). Hydroxyl numbers were evaluated using both quantitative ^{1}H NMR analysis and potentiometric titration.

Results and Discussion

Either DKL or DHL products were soluble in organic solvent like acetone. Thus, we were able to determine their molecular weight distributions and (M_w, M_n and PDI) by GPC-UV using THF as the eluent. Comparison of the performance of various depolymerization processes for KL and HL is presented in Table 1.

Table 1. Comparison of the performance of various depolymerization processes for KL and HL.

Lignin type	Depolymerization process	Depolymerized lignin yield (wt.%)	Solid residues (wt.%)	M_w (g/mole)	OH_{Total} (mgKOH/g)
KL	Original	-	-	10,000	275
	High-P hydrolytic	77.0	1.0	1700	686
	High-P reductive	90.0	0.5	1270	466
	Proprietary low-P/low-T	90.0	0.3	1000	670
HL	Original	-	-	>20,000	-
	High-P reductive	70.0	10.0	1000	442
	Proprietary low-P/low-T	70.0	10.0	1500	247

The resulting DLs with a lower molecular weight and hence improved reactivity have been employed as bio-substitutes for polyols, phenol or bis phenol A in the preparation of valuable biomaterials such as bio-based PU resins/foams, phenolic resins/foams/adhesives and epoxy resins at a high substitution level (>50 wt%). The resulting bio-materials/products, as depicted in Figure 2, showed superior or comparable physical, mechanical and thermal characteristics when compared to the commercially available petroleum-derived products. Therefore, depolymerization serves as a cost-effective engineering approach to valorization of lignin for bio-based chemicals and materials.

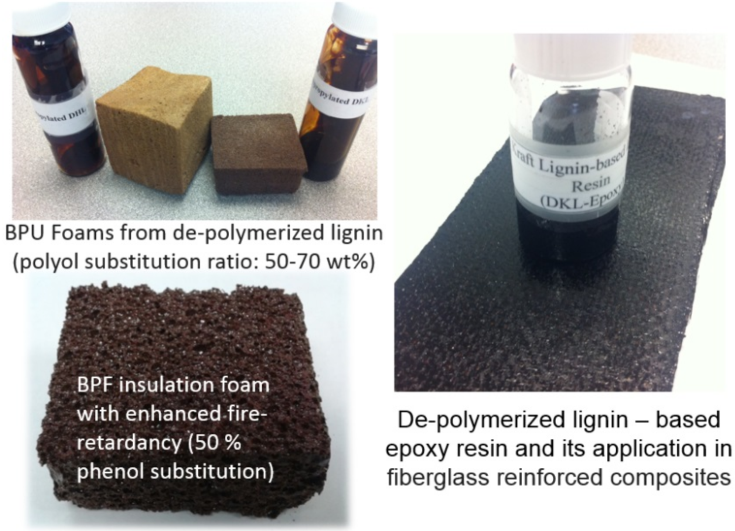

Figure 2. Bio-based PU resins/foams, phenolic resins/foams/adhesives and epoxy resins from DLs.

Conclusions

Although bio-based materials can be produced using crude lignin as a bio-substitute, the substitution ratios in the final products were generally low (<20-30 wt.%) due to its poor solubility in solvents, low reactivity and steric hindrances. In this work, depolymerisation of KL/HL led to the production of low molecular weight depolymerized lignin products (DKL/DHL) at a high yield (>70-90 wt.%). The DKL/DHL obtained proved to be highly reactive bio-substitutes for petroleum-based chemicals (phenol, polyols and bisphenol-A) for the production of bio-based PU/PF resins/foams and epoxy resins at a high substitution ratio (≥50 wt.%).

Acknowledgements

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Upgrading 2

Biomass to Lactic Acid and Platform Chemicals – A New Way of Thinking

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Introduction

The vast majority of processes to convert biomass to biomaterials extract cellulose and hydrolyse it to fermentable glucose. The operating costs of these processes are often dominated by the energy and / or enzyme required to hydrolyse the strong cellulose molecule, and by the purification steps required to deliver fermentable monosaccharide streams.

Plaxica's Versalac® technology takes a radically different approach. Firstly, we focus on the hemicellulose content of biomass. This is easier to extract and hydrolyse than cellulose, leading to a much lower operating costs. We have a particular focus on the hemicellulose-rich streams created as the by-product of the conversion of Kraft pulp mils to produce dissolving pulp.

Secondly, instead of fermentation, we use robust, chemical processes to convert these low-cost C_5 and C_6 sugar mixtures to lactic acid, whilst removing the acetic acid and lignin in the biomass as valuable co-products.

Plaxica

Plaxica was formed in 2008 to commercialise lactic acid technology originally developed by Dr Ed Marshall and Professor Vernon Gibson at Imperial College London. The company now operates laboratories and a pilot plant in Wilton, UK and employs 25 people.

Plaxica's business model is to license its lactic acid technology. In 2015 Plaxica concluded a strategic partnership with INVISTA Performance Technologies in which INVISTA will support the development, commercialisation and deployment of the Plaxica technology.

Market focus

Declining demand for paper due to the digital revolution is forcing mill operators to consider strategies to improve profitability and maximise the value of the mill asset. Many are beginning to view their mills as "bio-refineries", which can use forest resources to produce valuable chemicals.

One approach to re-purpose a mill is to convert it to produce dissolving pulp ("DP", also known as specialty cellulose) which is used in the production of viscose staple fibre – a high growth market. The conversion of the mill involves the installation of a pre-hydrolysis process prior to the Kraft cook which produces a hemi-cellulose-rich pre-hydrolysis liquor ("PHL") by-product. PHL also contains wood acids (mainly acetic), acid-soluble lignin and numerous lignin-derived impurities.

Plaxica's Versalac process isolates the lignin and acetic acid (as butyl acetate) from the PHL prior to converting the hemicellulose to lactic acid. Lactic acid is a valuable and versatile green chemical, which can be converted into products with diverse applications including biopolymers (polylactic acid), personal care and de-icing (propylene glycol) and super-absorbents (acrylic acid).

The butyl acetate produced in the pre-treatment process has numerous market applications, with the greatest demand being in the fields of paints and coatings. In the medium term, it is expected that a market for lignin will develop as a result of success in the numerous research projects looking to convert lignin into chemicals.

PHL is currently incinerated in the mill's boiler – Plaxica's proess has the potential to convert 80% of the carbon in this PHL waste stream into high value chemicals with existing proven markets. This transforms the financial performance of DP conversions.

Technology

Plaxica's Versalac uses a chemical technology – avoiding fermentation, the mainstay technology ingreen chemicals production. Process yields are unaffected by the impurities in the feedstock, making the process ideal for feedstocks such as PHL with significant levels of impurities which make them impossible to ferment.

The process equipment is relatively standard, and reaction conditions are not particularly harsh, with no use of excessive temperature or pressure. This reduces the risk of scale up, and allows the use of industry standard modelling techniques such as Aspen® to support process design. Plaxica has proven the use of PHL from dissolving pulp plants across the globe –the process has run successfully in all cases.

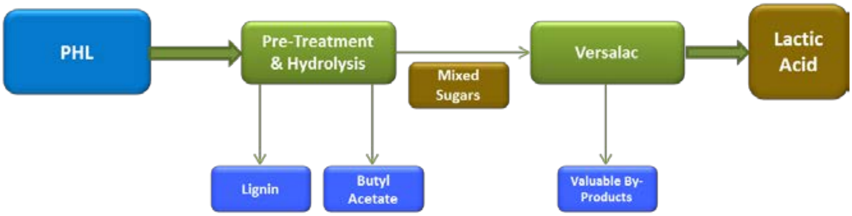

Figure 1. Summary Versalac Flowsheet.

Integration with the Mill

Plaxica's Versalac® process takes PHL from the mill and converts it into valuable chemical products. The PHL is no longer sent to the recovery boiler – this may allow an increase in pulp capacity where the recovery boiler is the mill's bottleneck. Modelling the impact on the mill's overall energy balance is also an important consideration.

Versalac uses sodium hydroxide as the main reagent – a chemical the mill operator is used to handling. The sodium hydroxide is fully recycled in the Verslac process. The few remaining organic by-products of the production process are incinerated in the recovery boiler.

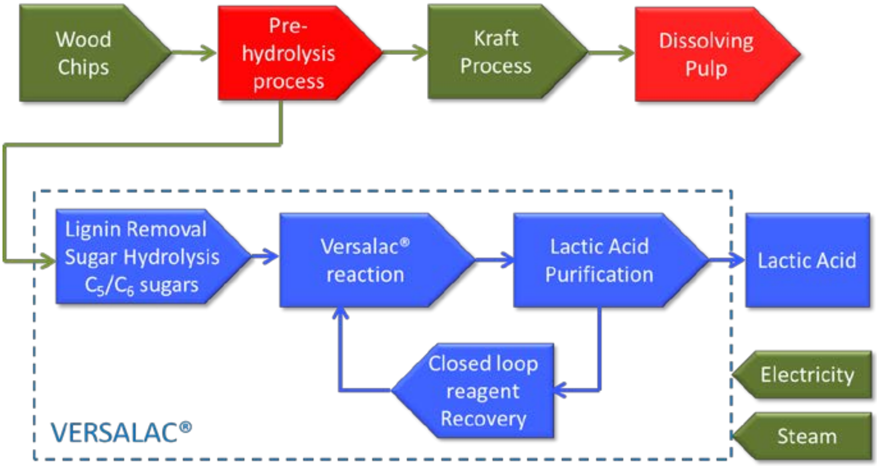

Figure 2. Mill Integration Concept.

Demonstration

Plaxica's Pilot Plant in Wilton, UK

Plaxica has successfully demonstrated the process at laboratory scale (up to 20L) using “real world” PHL feedstock. Parts of the process have successfully operated at the 500L scale.

We have partnerships with a number of dissolving pulp plants globally and are working with them to validate both the feedstock suitability and prepare robust project proposals. The technology will be ready to license in 2016.

Conclusion

Plaxica’s Versalac® process offers operators of dissolving pulp mills to convert their PHL by-product to high volume chemicals with existing proven markets. Up to 80% of the carbon in the PHL is converted into saleable products – a true bio-refinery strategy which can transform the profitability of a mill.

Sustainable and Economic Separation of Complex Biomass Streams Through Membrane Technology

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Abstract

The depletion of fossil fuels as a source for fuels, chemicals, and energy is driving the transition of our economic model towards a more sustainable bio-based economy. Following this strategy, the use of renewable resources and the production of industrial (bio)chemicals in a biorefinery approach contribute to a large extent to climate change mitigation and environmental protection. Since a few years, the scientific community has been initiating this transition through, among others, the development of new and/or optimized process technologies for biomass conversion; including the conversion of wood biomass, agro-residues, bio-based waste streams, plants, algae…

In this framework, cost-effective separation processes are of utmost importance to enable the separation of biomass components on an industrial scale. As most chemicals in petroleum refineries are volatile, separation schemes are dominated by distillation. By contrast, most compounds derived from biomass are non-volatile and process streams are typically dilute, which implies that large volumes of water need to be evaporated. Whereas research techniques such as size-exclusion chromatography are excellent tools for producing small quantities of pure biomass substances, these processes are difficult to scale up and production levels remain limited. Energy-efficient separation and purification of bio-based chemicals at the industrial scale remains, therefore, a challenge.

Within this context, VITO's research activities are mainly focused on the development and demonstration of membranes and membrane processes for the fractionation and the purification of bio-based derivatives. An example lies in the valorization of biomass through transformation of lignocellulose towards bio-aromatics as building blocks for the chemical industry. VITO is participating to various running actions, concerned with depolymerization of lignin and adequate conversion to monomeric/oligomeric derivatives. In these different projects, VITO is principally focused on the fractionation and purification of the obtained lignol fragments through membrane separation to enable the use of these molecules in chemical and materials applications.

Membrane Separation Technology

To enable the development of a viable industrial scale process related to biomass valorization, cost-effective separation processes are essential. In mature chemical processes, separation usually accounts for 60 to 80% of the total costs [1,2]. Membrane processes appear as a "natural" technology for separations in biorefineries. The energy requirements for water removal by ultrafiltration (UF) and reverse osmosis (RO) are < 5 kWh.m^{-3} and < 10 kWh.m^{-3}, respectively, whereas evaporation typically requires 30-40 kWh per m³ of water removed.

In recent years, membrane separations are receiving enhanced attention in the context of future biorefineries [3,4] not only because of their low energy requirements, but also owing to their mild processing conditions, straightforward operation, moderate cost to performance ratio, compactness and flexibility in equipment design, making it overall a highly attractive technology for use at industrial scale.

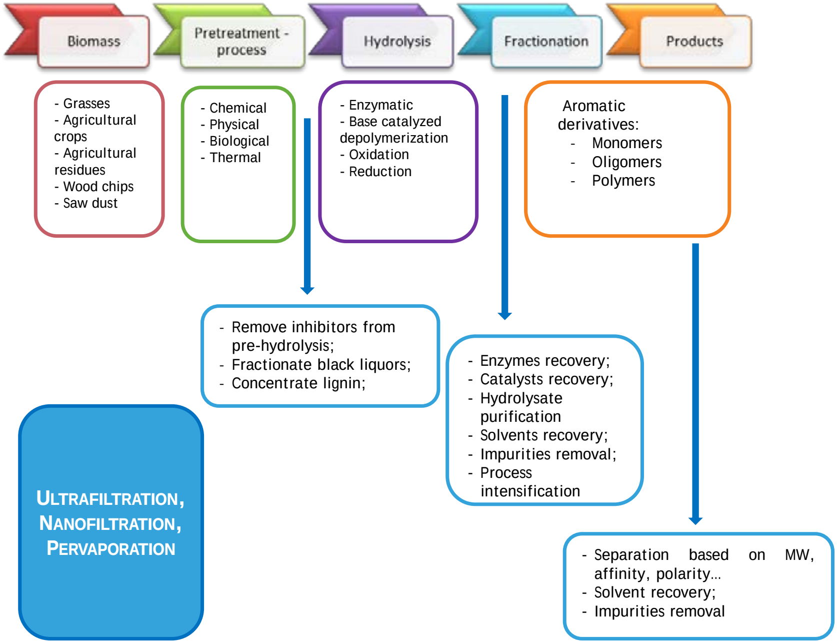

Figure 1. Potential implementation of membrane separation along the biomass valorization value chain (adapted from [5]).

Membrane processes are promising methods to recover lignin and hemicellulose by providing high rejection of lignin and hemicellulose, low rejection of impurities (e.g. inorganic salts) without the addition of chemicals, resulting in high purity final products.

However, despite their clear benefits and huge application potential, membrane separations of complex (biomass-derived) fluids remain poorly understood. The inherent complexity of this kind of membrane processes, especially in case of separations at the molecular level, stems from the subtle interplay between the permeating species (solutes and solvent) and the membrane material.

Fractionation of lignin derivatives through nanofiltration

Materials and methods

Organosolv lignin, received from the Fraunhofer Center for Chemical and Biotechnological Processes (CBP) in Leuna (Germany) has been derivatized according to the derivatization method followed by reductive cleavage (DFRC) described by Nanayakkara *et al.* [6].

The DFRC depolymerization mixture of the Organosolv lignin was characterized by means of GC-MS and LC-am-MS screening (Figure 2). Many different monomers and oligomers derivatives, mainly issued from the guaiacol and syringol units, as well as residual lignin were observed.

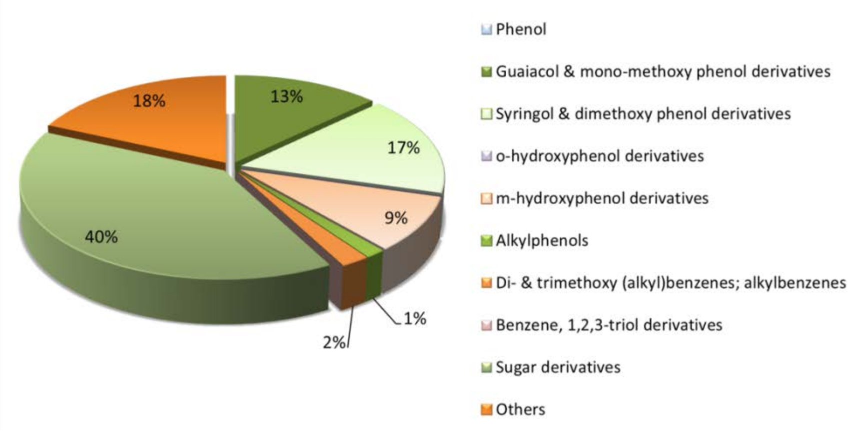

Figure *2*. Composition of the DFRC derivatized lignin as determined by LC-am-MS and GC-MS screening.

Nanofiltration experiments

Screening trials were performed to evaluate the applicability of nanofiltration (NF) to isolate/purify monomeric/oligomeric fractions or individual compounds from the depolymerization mixture. Thereto, both commercial polymeric and in-house functionalized ceramic membranes (FunMem®) [7] were used; the influence of the process parameters was investigated.

An example is given in Figure 3 where the rejection coefficient is indicated for three commercial membranes, as a function of the molecular weight ranges of the lignin derivatives. The rejection coefficient (R%) is defined as:

$$R\% = \left(1 - \frac{C_p}{C_f}\right) \times 100$$

where C_p and C_f are the concentrations of the compound or molecular weight class under consideration in the permeate and feed, respectively.

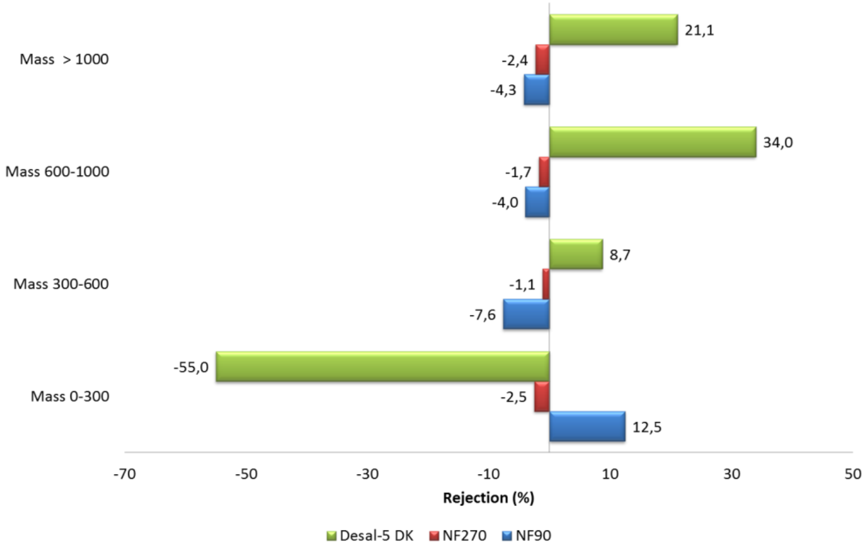

Figure 3. Rejection of different mass (m/z) fractions by the polymeric NF membranes NF90 (MWCO 200 g/mol), NF270 (400 g/mol) and Desal-5 DK (MWCO 150 g/mol) at 30 °C, 15 bar.

While the NF270 and NF90 are not suited for the separation of the lignols under these process conditions, the Desal-5DK membrane shows a higher separation capacity with a rejection of the phenol derivatives with a higher molecular weight and a preferential permeation of the components with a molecular weight inferior to 300 g/mol through the membrane.

A further improvement in the separation capacity can be obtained with tailored functionalized ceramic membranes (FunMem®) developed at VITO [7], allowing a separation mainly focused on the affinity of the membrane with the feed components (Table 1), as previously reported for water treatment [8] and separations in organic solvents [9]. In that case, a same component is separated as a function of the affinity of the component with the ceramic top-layer.

Table 1. Differences in separation efficiency of lignin derivatives using FunMem® 1 and FunMem® 2 membranes as a result of affinity of either the solute or the solvent for the membrane

	Rejection		
	tri-ethyl benzene (162 g/mol)	2,6-dimethoxy-4-(2-propenyl) phenol (194 g/mol)	2-acetoxy-3-hydroxy-acetophenone (194 g/mol)
FunMem® 1	- 46.8%	- 2.8%	+ 5.4%
FunMem® 2	+ 59.2%	+ 2.7%	- 55.4%

Tri-ethyl benzene can be either preferentially permeated trhough FunMem® 1, while it is significantly rejected by FunMem® 2. Additionally, if we consider two components with the same molecular weight (194 g/mol): 2,6-dimethoxy-4-(2-propenyl) phenol and 2-acetoxy-3-hydroxyacetophenone respectively, we observe a difference in separation according to the type membrane. This opens new possibilities in the separation of components through affinity of either the solute or the solvent for the membrane.

Conclusions

Depolymerization of lignin usually results in complex phenolic-based mixtures with a broad range of molecular weight and oxygen-based functionalities. Valorization of these lignols can only be pursued for well-defined purified components or mixtures. Well-defined mixtures, which can find for instance applications in the field of phenolic resins, can be obtained through the use of (nanofiltration) membranes with sufficiently sharp MWCO operated under adequate process parameters. When further purification is required (as for the obtaining of a single component), standard membrane separation processes might fail, and the appeal for affinity separation is then necessary. While affinity-based separation is still in its infancy, the premises are encouraging. Components with a similar molecular weight, but different functionalities can be separated from each other.

Acknowledgments

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Chromatographic Separation as Enabling Technology for Concentrated Acid Hydrolysis of Lignocellulose

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Abstract

Monosaccharides are valuable platform chemicals that can be produced with high yield from lignocellulose via concentrated sulfuric acid hydrolysis. However, implementation of this hydrolysis method requires the recycling and reuse of the hydrolysis acid. In this work, it is shown that chromatographic separation can be used for the recovery and recycling of sulfuric acid from concentrated acid hydrolysates, thus, enabling the monosaccharide production from lignocellulose via concentrated acid hydrolysis.

Introduction

Monosaccharides are valuable platform chemicals that can be converted into a wide variety of products either by bio- or thermochemical means [[1-[7]. Celluloses and hemicelluloses in lignocellulosic biomasses can be hydrolyzed to monosaccharides with mineral acids or enzymes as catalysts [[8]. Hydrolysis with concentrated sulfuric acid results in high monosaccharide yield (≥ 80 %) and generates only low amounts of by-products (acetic acid, furans). It is also a fast process when compared to enzymatic hydrolysis [[8]. The challenge is that the resulting hydrolysates contain large amounts of H_2SO_4 that must be removed prior to the monosaccharide processing. To avoid high costs, H_2SO_4 should be removed in a way that enables recycling and reuse of the acid.

In this work, it is shown that concentrated acid hydrolysis coupled with electrolyte exclusion chromatography (EEC) is a viable option for producing monosaccharides from lignocellulosic biomasses. EEC can be used to fractionate the concentrated acid hydrolysates of lignocellulose into sulfuric acid, monosaccharide, and by-product fractions [9,10].

Hydrolysis of lignocellulosic biomasses is studied experimentally and modelled. The chromatographic fractionation is investigated experimentally and models are derived to describe the separation process. Industrially relevant process schemes for hydrolysate fractionation (batch process, Japan Organo (JO) process, and Multi-Column Recycling Chromatography (MCRC) process) are compared. In addition, a recycle-integrated process coupling hemicellulose hydrolysis with chromatographic fractionation is studied.

Concentrated acid hydrolysis

Two step concentrated acid hydrolysis of softwood and hardwood chips was investigated experimentally. In the first step, the wood chips were added to 70 wt. % sulfuric acid at 50 °C temperature in order to break down the crystalline structure of the cellulose. In the second step, the actual hydrolysis was carried out at 80 °C temperature with 30 wt. % H_2SO_4. Detailed description of the experiments is given in Ref. [11].

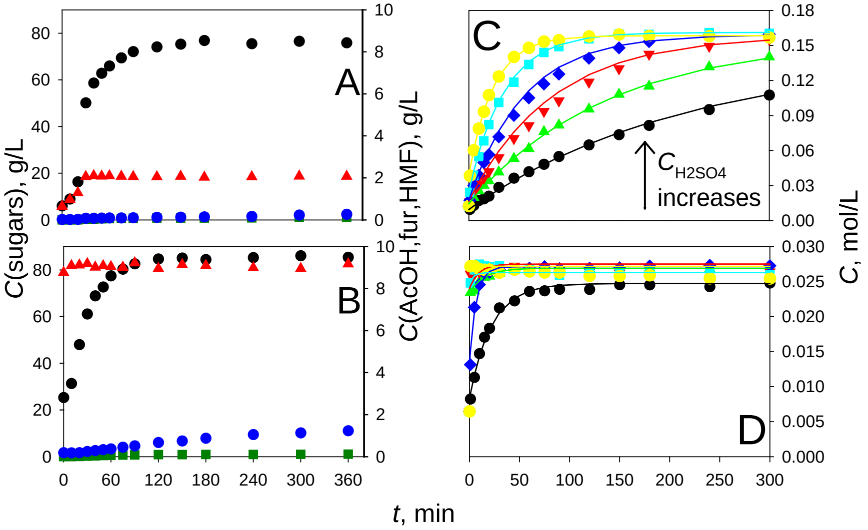

Figure 1. **A**-**B**: Concentrated acid hydrolysis of spruce (A) and birch (B) chips at 80 °C temperature. Symbols: black = monosaccharides; red = acetic acid; blue = furfural; green = HMF. **C**-**D**: Formation of monosaccharides (C) and acetic acid (D) in hydrolysis of hemicelluloses at 80 °C temperature. Experimental data from Ref. [12].Symbols: experimental results. Lines: model predictions. Colors: H_2SO_4 concentration; black = 5 wt. %; green = 7 wt. %; red = 10 wt. %, blue = 13 wt. %; cyan = 17 wt. %; yellow = 21 wt. %.

The kinetics of concentrated acid hydrolysis of spruce and birch chips is shown in **Figure 1A-B**. Only the second hydrolysis step is shown. All monosaccharides are shown as a single pseudocomponent. The differences in the monosaccharide concentrations with the spruce and birch hydrolysis at the beginning of the hydrolysis result from the different particle sizes of the wood chips (larger for spruce). The actual hydrolysis occurs relatively fast and the monosaccharide concentrations level off in approximately two hours. The monosaccharide yields with both materials were approximately 70 %.

Acetic acid is formed from the acetyl groups in hemicellulose sugars. These are cleaved off quite easily and, thus, the acetic acid concentration levels off quite fast.

In addition to acetic acid, the only by-products detected in the hydrolysates were hydroxymethyl furfural (HMF) and furfural. The furan formation rates and concentrations were low in the case of both hydrolysates (**Figure 1A-B**).

Hydrolysis of hemicelluloses with 5-21 wt. % H_2SO_4 was modelled with a pseudo-first order model in which the rate constant depended on proton and bisulfate ion concentrations (**Figure 1C-D**). Detailed description of the model is given in Ref. [13].

Hydrolysis data was taken from Ref. [12]. In the hydrolysis experiments, acetic acid was the only notable by-product formed. Thus, furans were omitted from the model.

The rate constants (given in Ref. [13]) were obtained by fitting the model predictions to experimental hydrolysis data. The correlation between the experimental results and the model predictions is very good.

Chromatographic fractionation of acidic hydrolysates

Chromatographic fractionation of authentic concentrated acid hydrolysates was investigated with gel type sulfonated PS–DVB cation exchange resins in H^+ form with different crosslinking densities (see Ref. [9]). Of these, CS16GC (8 wt. % crosslinking density; Finex Oy, Finland) was chosen for this work.

Detailed discussion of the phase equilibria, modelling, and model validation can be found from Ref. [10]. Sorption of the main components in the concentrated acid hydrolysates (H_2SO_4, monosaccharides, acetic acid) on CS16GC resin in H^+ form were investigated experimentally with synthetic solutions. Modelling of the sorption was carried out using accurate empirical models.

H_2SO_4 was found to have a significant co-operative effect on the sorption of the other solutes in the concentrated acid hydrolysates due to a salting out effect (**Figure 2A**). This effect could be modelled accurately using simple empirical sorption models. The sorption of H_2SO_4 was not affected by the other solutes present.

The models were validated with column experiments with a synthetic solution representing acidic hydrolysates (20 wt. % H_2SO_4). A typical elution profile is shown in **Figure 2B**. The models describe accurately the behavior of the studied system.

Sulfuric acid elutes first due to electrolyte exclusion. Monosaccharides elute after H_2SO_4. The co-operative effect of H_2SO_4 on the monosaccharide sorption is seen in the elongated fronts of the monosaccharides and in the focusing of these at the rear of the H_2SO_4 profile. Focusing is beneficial for the separation performance. Effect of H_2SO_4 on acetic acid is not very strong due to rapid separation of the acids.

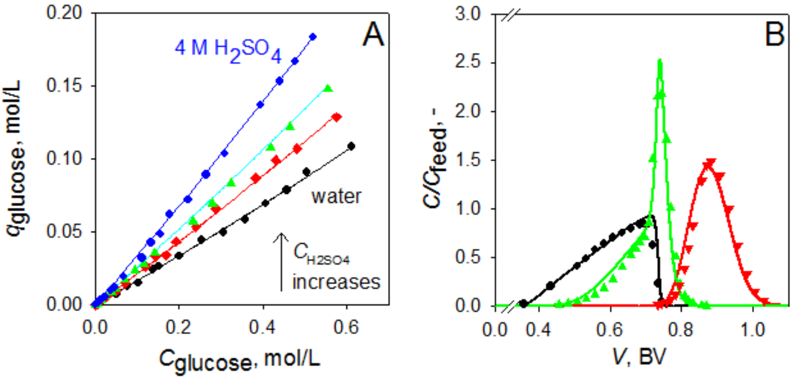

Figure 2. A: Sorption of glucose on CS16GC resin in H^+ form in pure water and in presence of H_2SO_4 (1-4 mol/L). Symbols: experimental results. Lines: model predictions. Colors: black = pure water; red = 1.0 M H_2SO_4; green = 1.8 M H_2SO_4; blue = 3.5 M H_2SO_4. **B**: Typical elution profile obtained in fractionation of acidic hydrolysates of lignocellulose. Symbols: experimental results. Lines: model predictions. Colors: black = H_2SO_4; green = monosaccharides; red = acetic acid.

Process schemes and process evaluation

A four-column MCRC process was developed for the fractionation of the concentrated acid hydrolysates and compared with single-column batchwise process (four columns parallel) and four-column JO process by simulations (**Figure 3**). Detailed description of the comparison and the results is given in Ref. [14].

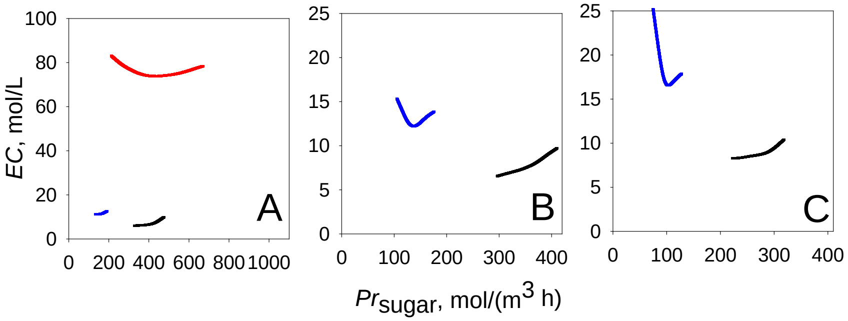

Figure 3. Process comparison. Relation between eluent consumption *EC* and monosaccharide productivity *Pr* at constant monosaccharide yield *Y* levels of 70 % (A), 80 % (B), and 90 % (C) in the fractionation of concentrated acid hydrolysates. Colors: blue = MCRC process; black = JO process; red = batch process.

Of the studied processes, the MCRC process was found to be most efficient mainly due to very low eluent consumption (*EC*). The single-column process had the highest monosaccharide productivity (*Pr*), but also highest *EC*. The JO process was not as efficient as the MCRC with respect to *Pr* and *EC* but had still a very low *EC*. The multi-column processes could reach over 90 % monosaccharide yield (*Y*) whereas approximately 70 % yield was maximum for the single-column process. Each of the processes could recover over 95 % of H_2SO_4 in the hydrolysates.

Investigation of the sole separation unit in cases in which one or more product streams are recycled to the preceding process steps gives a conservative impression of the process performance. The process steps coupled with the separation unit should be taken into account in order to obtain a more realistic picture of the performance. Here, a recycle-integrated process coupling the hydrolysis of hemicelluloses with a chromatographic fractionation of the resulting hydrolysates via sulfuric acid recycle stream was investigated (**Figure 4**). The hydrolysis was carried out in a plug-flow reactor and single-column batchwise process was used in the fractionation. The effect of H_2SO_4 concentration on the performance was investigated. For details, see Ref. [13].

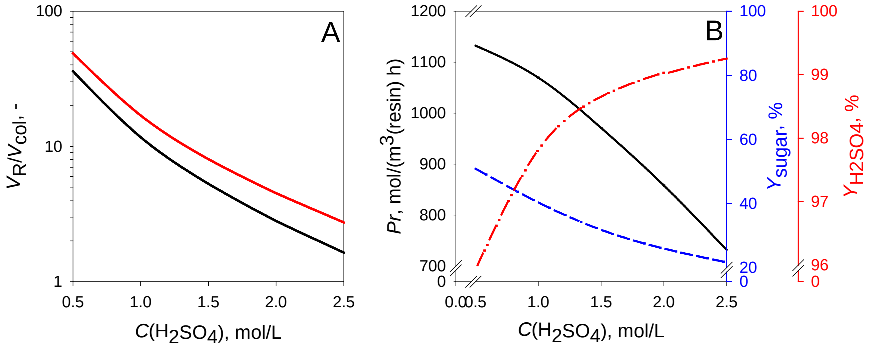

Figure 4. Recycle-integrated process. **A**: Ratio of the hydrolysis reactor volume V_R and chromatographic column volume V_{col} at various H_2SO_4 concentrations with target *PR* of 1 kmol/h (black) and 3 kmol/h (grey). **B**: Effect of H_2SO_4 concentration on the separation performance at operating points giving the maximum *Pr*.

H_2SO_4 was found to have a significant effect on the volumes of the hydrolysis reactor and separation column when the monosaccharide production rate (*PR*) was kept constant (**Figure 4A**). Decrease in H_2SO_4 concentration decreases the hydrolysis rate and leads to an increase in the reactor volume (V_R). The opposite is true when H_2SO_4 concentration is increased. Reasonable values for V_R were obtained for 1 and 3 kmol/h *PR* with H_2SO_4 concentrations higher than 1.0 and 1.5 mol/L, respectively.

In the separation step, increase in the sulfuric acid concentration leads to larger overlapping of the sulfuric acid and monosaccharide profiles and decrease in the separation performance (**Figure 4B**). Thus, to obtain the required level of *PR*, a larger separation column must be used with higher H_2SO_4 concentrations.

Conclusions

It was shown that chromatographic separation is a versatile method for the fractionation of concentrated acid lignocellulosic hydrolysates into sulfuric acid, monosaccharide, and by-product fractions in industrial scale. Moreover, this can be done without addition of chemicals. It was shown that advanced chromatographic process schemes (e.g., MCRC) offer very significant improvement in productivity over classical batch operation. This should considered when assessing profitability of sugar platform biorefinery concepts.

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Filtration in Bio-refineries May Imply Challenges: Methodology to Understand and Overcome these Challenges

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Abstract

Today filtration is one of the most common unit operations in the process industry, but in tomorrows bio-refineries (in particular wood based) it will be even more central. However, the various solid organic materials (different forms of cellulose, hemicellulose or lignin based particles) have very different filtration properties and generally form compressible filter cakes. These materials may also contain charged functional groups that influence particle-particle and particle-filtration medium interactions. The filtration behavior of these types of materials is often difficult to predict. In this paper a methodology for measurement of relevant filtration properties for materials forming compressible filter cakes will be presented. The data obtained with this methodology may be used for scale-up and design of filters. Furthermore, filtration of different types of lignin and cellulose based materials and how some challenges can be overcome will be discussed.

Introduction

Presently the filtration operation can be found in almost all process industries, but is of particular importance for e.g. the pulp and paper industry, the mineral industry and in water and effluent treatment. It is therefore not surprising that it is a unit operation that has been studied for a long period of time. Darcy’s famous work from 1856 is often referred as the starting point of the more structured research on filtration [1]. This work has been followed by early works of e.g. Kozeny [2] and Ruth [3]. These works forms the theoretical basis for studying average properties of filter cakes, which has been the, by far, most common method for evaluation of filtration experiments. In many cases (particular in the mineral industry) knowledge regarding average properties has been good enough. The reason for this is that filter cakes formed from inorganic materials tend to be only slightly or at most moderately compressible. Under these circumstances it is often possible to use average laboratory results in the design of industrial scale filters.

In future bio-refineries filtration will be a very common method for separation and dewatering of solid materials, both in various intermediate process steps as well as in formation of various devices. However, organic material often form rather compressible filter cakes and in these cases it will be very helpful to have knowledge of local filtration properties in order to use laboratory data in the design of an industrial filter. Relatively few investigations regarding local data can be found in the literature. However, some pioneering work was done by the research groups led by Shirato [4] and Tiller [5]. Later also e.g. Chase and Willis [6], La Heij et.al [7], Fathi-Najafi and Theliander [8], Bergström [9], and Johansson and Theliander [10] have presented methodologies for measuring local properties. In most of these cases the local hydrostatic pressure was measured. Furthermore, in order to measure the local solidosity (i.e. local volume fraction of solids) several different methods have been employed, the most common are γ- or x-ray, NMR or conductivity, but also other methods have been used.

The aim of the work performed at Chalmers University of Technology during the past 30 years regarding filtration has been to find improved methods to determine filtration properties. The work started with conventional measurements of average filtration properties, continued with the first attempts to determine local properties (local hydrostatic pressure was determined) and led to an experimental methodology where it is possible to simultaneously determine both local hydrostatic pressures and local solidosities during the build up as well as expression of the filter cake. Having both local hydrostatic pressures and local solidosities makes it possible to determine local filtration resistances. The developed experimental equipment may also be used to determine local “break though” curves during the washing operation.

Experimental equipment

Figure 1 shows the basic features of the test filter unit used today at Chalmers University of Technology. The filtration cell consists of a plexiglas cylinder and a pneumatically driven piston. 8 capillary tubes have been mounted from underneath, through the filter medium, these tubes are of different heights, water filled and have a small opening (0.6 mm) perpendicular to the flow direction. Hydrostatic pressure measurements through these tubes can be used to determine the local solid compressive pressure profile throughout the filter cake. The solidosity is determined using a γ-ray methodology (241 Am).

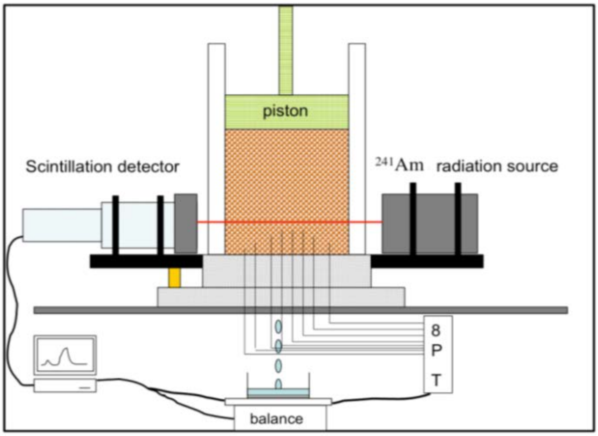

Figure 1. A sketch of the filtration equipment used at Chalmers.

A γ-ray with the dimension of 30 times 1 mm is formed and the amount of radiation passing the filter cake (and cell walls) are measured by a scintillation detector. The position of the measuring device can be changed (i.e. measurements can be made at different heights). From these data the local solidosity can be calculated. In addition the flow rate of filtrate and the position of the piston are recorded. During a filtration test all the data is collected using a data acquisition system.

Data evaluation

A comprehensive description of the evaluation of the experimental data can be found in e.g. the work by Johansson and Theliander [10]. Here only some basic information is given.

Since the flow rate is very low and the height of the filter cake is small a very simple relationship between the hydrostatic pressure (p_l) and the solid compressive pressure (p_s) can be used:

$$dp_s = -dp_l \tag{1}$$

This means that the pressure on the particles is increasing in the flow direction. Thus from these measurements both the hydrostatic and solid compressive pressure can be determined. The local specific filtration resistance can be calculated using Darcy's equation:

$$\frac{1}{A}\frac{dV}{dt} = -\frac{1}{\alpha \cdot \phi \cdot \rho_s \cdot \mu}\frac{dp_l}{dz} \tag{2}$$

where A is the filtration area, V is the filtrate volume, t is the time, α is the local specific filtration resistance, ϕ is the local solidosity, ρ_s is the density of the solid material, μ is the dynamic viscosity and z is the position in the filter cake in the flow direction.

Examples of results

The equipment has been used in several different applications during the last almost 15 years. One early finding was that it was much easier to determine if a test was successful or not compared with conventional filtration experiments. The reason for this is that the pressure measurements are very sensitive and allow detection of very small disturbances (e.g. small local collapses of the filter cake). These disturbances are not possible to identify either with visual inspection or the traditional way of evaluating a filter test. Consequently, when using this type of equipment the quality of the results from the filtration tests becomes higher: unsuccessful experiments results are more easily identified and excluded.

Below some examples of results from filtration tests of different lignin and cellulosic materials will be discussed.

Depending on the type of “bio-refinery”, lignin will have very different properties. We have extensively studied both so called hydrolysate lignin (from acidic and enzymatic hydrolysis of wood) and lignin precipitated from black liquor, referred to as “LignoBoost lignin” in this paper. Figure 2 shows one example where the local filtration resistance is plotted versus the solid compressive pressure for LignoBoost lignin (softwood lignin). The figure shows a summary from several tests, each having different solid concentration of lignin in the suspension (6.7–17 vol %) and different applied pressures (0.2–2.6 MPa). First of all it can be concluded that the filtration behavior is independent of the concentration in the suspension. Secondly, it can be concluded that this type of lignin forms filter cakes that is only slightly compressible. It should be kept in mind that most lignin tested have a lower filtration resistance compared to the results in Figure 2, thus most LignoBoost lignins form even less compressible filter cakes.

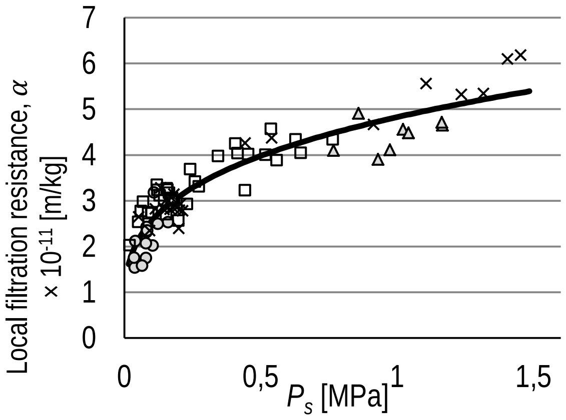

Figure 2. One example of local filtration resistances for LignoBoost lignin.

The results in Figure 2 could be compared with similar tests made on "hydolysate lignin", see Figure 3. The tested lignin is from experiments where the hydrolysis of the carbohydrates was driven far towards complete hydrolysis, thus the content of carbohydrates in the lignin is quite low. If the results in Figure 3 is compared with the ones in Figure 2, it can be concluded that hydrolysate lignin has a much higher filtration resistance and forms filter cakes which are much more compressible compared to LignoBoost lignin (N.B the logarithmic scale in Figure 3).

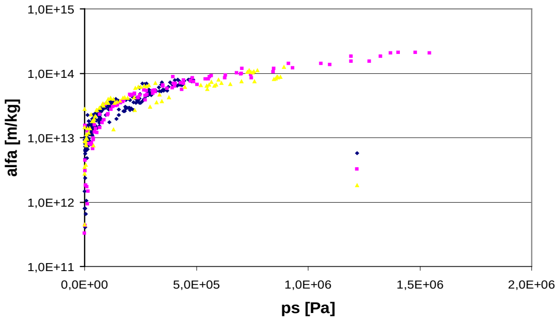

Figure 3. Three filtration tests with "hydrolysate lignin" at three different applied pressures (0.5, 1 and 2MPa).

A number of investigations have also been made on micro crystalline cellulose (MCC). In one of these studies we investigated how the filter cake formation was influenced by different pH of the suspension (different degree of protonation of carboxylic groups of MCC) and different materials in the filter media. Figures 4 and 5 (hydrostatic pressure at different positions plotted versus the time) show some of the results. The experimental conditions were the same in the two cases except from the fact that the material in the filter medium was different. The behavior shown in Figure 4 is as expected: the hydrostatic pressure at the different positions in the filter cake decreases with time. In Figure 5 a very different result can be observed: here the hydrostatic pressures at the different positions are more or less constant. The interpretation of this is that the major part of the pressure drop is below the lowest pressure measuring point (in this case 1 mm above the filter medium). Also note that the filtration time is one order of magnitude longer in Figure 5 compared to Figure 4. After additional test where the possibility of clogging of the filter medium was investigated and excluded, our interpretation of this is that a thin filter cake with a very high filtration resistance has been formed at the top of the filter medium: a so-called "skin layer". To our knowledge this was the first time a skin-effect could be demonstrated during the build up of the filter cake (in earlier studies one has suggested this effect after dissection of the filter cake, once the filtration experiment was terminated).

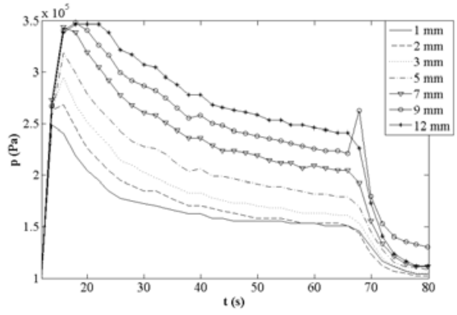

Figure 4. Local hydrostatic pressure at different positions from the filter media plotted versus time.

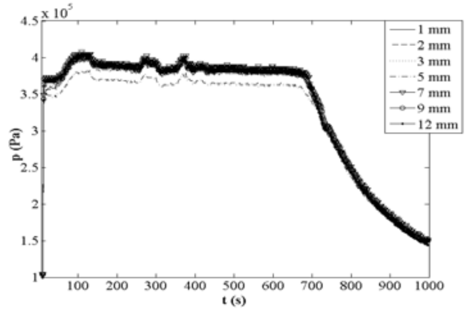

Figure 5. Local hydrostatic pressure at different positions from the filter media plotted versus time for experiments with formation of a "skin layer".

Furthermore if the pH was lowered, no skin effect was observed for any of the two filter media. When lowering the pH the surface charge of the MCC particles as well as the material in the filter medium will be changed. This indicates that the skin-effect was a result of the interaction between the MCC and the material in the filter medium. This demonstrates how our experimental methodology may be used in troubleshooting.

Conclusions

Measuring local filtration properties gives many advantages compared to traditional methodologies for studying filtration properties. First of all the measurements of local filtration properties gives a good measure on if the filter cake has been stable during the filtration of if it has collapse to some degree. Furthermore, the measurements provides local filtration data that gives a more accurate result in calculation of necessary filtration area of industrial filters. Finally, local data are very useful in for example troubleshooting, the example shown in this paper is on the findings regarding skin formation, but there are other cases.

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DES & IL

Fundamental Studies on Natural Deep Eutectic Solvents: Physico-Chemical, Thermal and Rheological Properties

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Abstract/Introduction

When combined at particular molar fractions, sugars, aminoacids or organic acids a present a high melting point depression, becoming liquids at room temperature. These are called Natural Deep Eutectic Solvents – NADES and are envisaged to play a major role on the chemical engineering processes of the future. Nonetheless, there is a significant lack of knowledge of its fundamental and basic properties, which is hindering their industrial applications. For this reason it is important to extend the knowledge on these systems, boosting their application development [1].

In this work, we have developed and characterized NADES based on choline chloride, organic acids, amino acids and sugars. Their density, thermal behavior, conductivity and polarity were assessed for different compositions. The conductivity was measured from 0 to 40 °C and the temperature effect was well described by the Vogel-Fulcher-Tammann equation. The morphological characterization of the crystallizable materials was done by polarized optical microscopy that provided also evidence of homogeneity/phase separation. Additionally, the rheological and thermodynamic properties of the NADES and the effect of water content were also studied. The results show these systems have Newtonian behavior and present significant viscosity decrease with temperature and water content, due to increase on the molecular mobility. The anhydrous systems present viscosities that range from higher than 1000Pa.s at 20 °C to less than 1Pa.s at 70 °C. DSC characterization confirms that for water content as high as 1:1:1 molar ratio, the mixture retains its single phase behavior.

The results obtained demonstrate that the NADES properties can be finely tunned by careful selection of its constituents. NADES present the necessary properties for use as extraction solvents. They can be prepared from inexpensive raw materials and tailored for the selective extraction of target molecules. The

data produced in this work is hereafter importance for the selection of the most promising candidates avoiding a time consuming and expensive trial and error phase providing also data for the development of models able to predict their properties and the mechanisms that allow the formation of the deep eutectic mixtures.

Experimental

Preparation of NADES mixtures

The mixtures were prepared by mixing choline chloride or betaine with xylose, glucose, sucrose, citric acid and tartaric acid. The combinations of the different molecules were mixed, in the required amounts, to obtain molar ratios of 4:1, 3:1, 2:1, 1:1, 1:2, 1:3 and 1:4. Table 1 presents the NADES combinations which resulted in a liquid mixture at room temperature. For each mixture, the constituents were transferred to a tightly closed glass flask and heated to 90 °C with constant stirring, for the time required until the formation of a clear liquid. For the mixtures which did not form a liquid, the process was considered concluded after 16 hours.

Rheological measurements

Rheological measurements were performed on a Malvern rheometer, model kinexus Prot, equipped with a cone-plate geometry (diameter of 4 cm) and a protective hood. During measurement, a stream of N_2 gas was maintained in order to avoid water absorption.

Results and Discussion

NADES preparation

The different mixtures were obtained by direct mixing of the solid components. The formation of liquid mixtures was assessed by differential scanning calorimetry (DSC) and polarized optical microscopy (POM) (Table 1).

The preparation of Bet based NADES was found to be more difficult than those based on CC, requiring the inclusion of water to promote the formation of the liquid mixture. Therefore, the mixtures between Bet and CA or Tart were prepared as three component systems, of equal molarity, with water as the third component.

Table 1. Nomenclature and molar ratios of the NADES that are liquid at room temperature.

NADES designation	Component 1, molar ratio X1	Component 2, molar ratio X2	Molar ratios found to be liquids*
[CC:Xyl; X1:X2]	Choline Chloride (CC)	Xylose (Xyl)	1:1
[CC:Glu; X1:X2]	CC	Glucose (Glu)	1:1
[CC:Suc; X1:X2]	CC	Sucrose (Suc)	1:1
[CC:CA; X1:X2]	CC	Citric acid (CA)	2:1; 1:1; 1:2
[CC:Tart; X1:X2]	CC	Tartaric acid (Tart)	2:1; 1:1; 1:2
[Bet:CA:H_2O; X1:X2:X3]**	Betaine (Bet)	CA	1:1:1
[Bet:Tart:H_2O; X1:X2:X3]**	Bet	Tart	1:1:1

*classified after POM and DSC characterization results. ** Betaine based mixtures were prepared as three component mixtures of equal molarity, with water (X3) as the third component.

Rheological Properties

The rheological properties were assessed by obtaining flow curves. The effect of temperature and water content on the NADES viscosity was determined. The characterization of the CC based NADES was performed for the mixtures of molar ratio 1:1. The mixtures with glucose, xylose and sucrose were characterized in the presence of diferent water contents, namely of 0, 1, 3 and 5 % wt. %.Citric acid and tartaric acid NADES were characterized in the presence of 0, 1 and 5 % wt. % water content. Betaine based NADES were characterized for the mixtures [Bet:CA:H_2O; 1:1:1] and [Bet:Tart:H_2O; 1:1:1].

The rheological characterization results have shown that these liquids behave as Newtonian fluids. For a given system, temperature and water content, the viscosity is constant and independent of the shear rate applied.

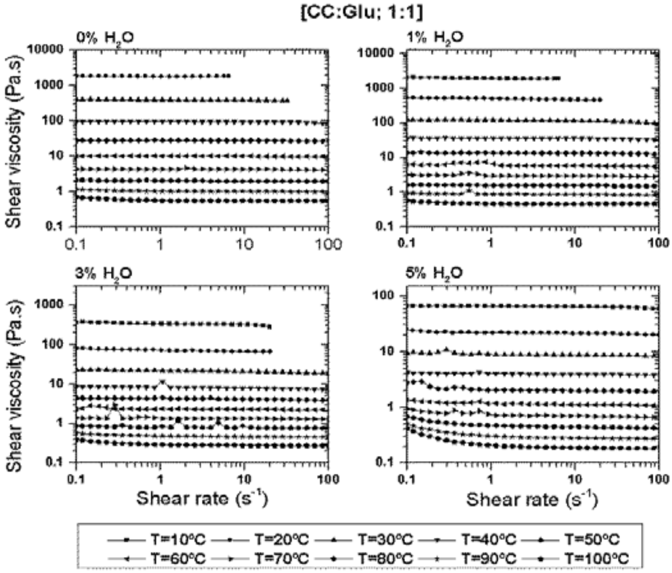

Figure 1. Viscosity-shear rate curves for [CC:Glu; 1:1] with water content of 0, 1, 3 and 5% wt.%.

The NADES viscosities vary greatly with the nature of the constituting components, the temperature and the water content. In general, these are highly viscous liquids, with typical viscosities higher than 1000Pa.s at 20 °C. The viscosity decreases significantly with both temperature and water content, as it can be observed in figure 1 for the system CC:Glu; 1:1.

Considering the choline based NADES, the viscosity is higher for [CC:Suc; 1:1], followed by [CC:CA; 1:1], [CCTtart; 1:1], [CC:Glu; 1:1] and [CC:Xyl; 1:1]. This trend is maintained for the range of temperatures considered and for the mixtures with different water contents. The bet based nades present similar viscosity.

The variation of viscosity with temperature can be represented by the Arrhenius equation:

$$\eta_0 = Ae^{E_\eta/RT} \quad (1)$$

and by representing the ln of shear viscosity as function of the reciprocal of temperature (T), it is possible to determine the flow activation energy, E_η, which represent the energy necessary to provide to the system to achieve the desired flow, respectively (where R is the ideal gas constant and A a constant for each system).

Representing the logaritm of shear viscosity as function of the reciprocal of temperature, it is possible to determine the flow activation energy, E_η, which represents the energy necessary to provide to the system to achieve the desired flow respectively. The calculated values for **E_η** are presented on Table 2.

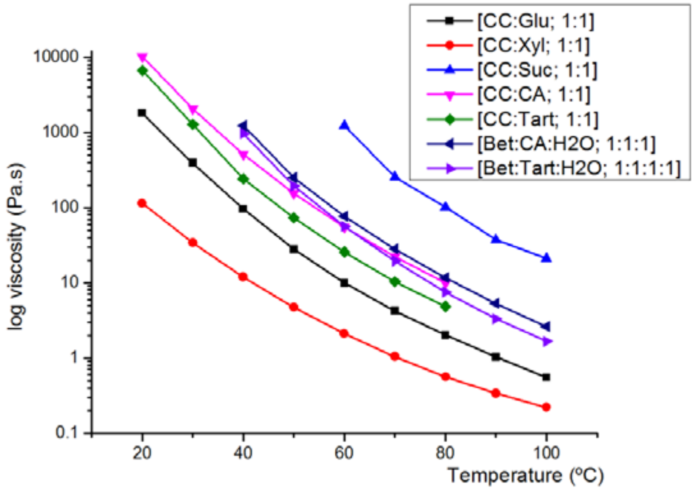

Figure 2. Variation of viscosity with temperature, for selected NADES.

Table 2. Flow activation energy, E_η, calculated from the Arrhenius plots.

NADES	Water content			
	0%	**1%**	**3%**	**5%**
	E_η, kJ/mol			
[CC:Glu; 1:1]	91.7	77.0	61.0	50.1
[CC:Xyl; 1:1]	71.0	68.5	56.3	47.9
[CC:Suc; 1:1]	104.5	85.2	42.1	32.2
[CC:CA; 1:1]	96.1	89.4	---	70.6
[CC:Tart; 1:1]	103.6	93.7	---	74.4
[Bet:CA;H_2O; 1:1:1]	101.9			
[Bet:Tart;H_2O; 1:1:1]	97.8			

Conclusions

The formation of liquid mixtures only occurs for specific components molar ratios. The NADES are highly viscous liquids, following a Newtonian behavior. Furthermore, the viscosity decreases significantly with temperature and water content. The finding of this work contribute to the enhancement of the state of the art and to the future design of processing technologies based on NADES.

Acknowledgments

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Conversion of Wood Biomass into Valuable Components Using a Novel Deep Eutectic Solvent Mixture

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Abstract

Deep eutectic solvents (DESs) are generally regarded as a sub-class of ionic liquids prepared from low-cost, biodegradable and non-toxic substances by mixing of them at room or lightly elevated temperatures. From a physicochemical point of view, DESs are low-volatile eutectic mixtures of two or more components with significantly decreased freezing points than that of each individual component. The large decline in freezing point is usually explained through non-symmetric complexation of substances via hydrogen bond interactions. Recently DESs have emerged as a new potential breakthrough technology for the conversion of biomass into valuable platform chemicals and polysaccharide components. Here we present a new DES composition based on a specific hydrogen bond donating species and choline chloride, a common quaternary component in DESs, and demonstrate its efficiency in the fractionation of wood-based biomass. The resulting DES mixture is able to fractionate lignin directly from wood in high purity while simultaneously preventing degradation and condensation reactions of lignin. Furthermore, dissolved hemicellulose can be efficiently converted to valuable biochemical such as 5-hydroxymethyl furfural (5-HMF), furfural and levulinic acid. Conventional methods for biomass deconstruction into cellulose, hemicelluloses and lignin often require high pressures and temperatures causing undesired side reactions for lignin and polysaccharides. DESs seem to be a promising future alternative that may be able to surpass the defects of ionic liquids. We anticipate that the development of new DES compositions will continue to bring new alternatives and enhance the use for those wood components that have previously been used only for production of energy.

Introduction

The use of non-edible lignocellulosic biomass as a source of chemicals and fuels has been a subject of interest recently due to the need to find an alternative to fossil resources. Currently, the main transport biofuel products on the market are bioethanol, biodiesel, and biogas. Biomass valorization concentrates mainly on cellulose, but an economically viable production necessitates the exploitation of hemicelluloses and lignin too. Wood-based hemicelluloses can be applied in coatings, while lignin has significant potential as an aromatic resource for bulk chemical and fuel production.

The development of the next generation industrial processes are increasingly based on green chemistry, sustainability and eco-efficiency. The goal of modern biorefineries is the entire valorization of lignocellulosic biomasses to compensate processing costs by providing a wide range of products of both high and low value. Pretreatment is one of the most critical steps in converting lignocellulosic materials into biofuel or other chemicals. An efficient pretreatment process decomposes the cell wall and separates the material into its components, partly degrading the biopolymers into smaller fragments. Efficient pretreatment also reduces the cellulose crystallinity and increases the porosity of the material; however, fractionation should not cause remarkable carbohydrate yield losses by Sun and Cheng. Several pretreatments have been studied in degradation purposes. Among these are steam explosion, organosolv pulping, acidic pretreatments, and wet oxidation. These kinds of pretreatments are usually carried out under acidic conditions, while wet oxidation performed under neutral environment.

During past years novel chemical techniques for wood fractionation have been emerge. Ionic liquids (IL) and deep-eutectic solvents (DES) have become topic of interest. ILs are generally defined as nonvolatile salts that melt around 100 °C. Typically, they consist of organic based cation with delocalized charge and inorganic anion. IL have been studied in dissolution of various lignocellulosic materials, such as softwoods, hardwoods and grasses.

Another type of solvent with similar physical properties and phase behavior to ILs are deep eutectic solvents (DES), also known as low transition temperature mixtures (LTTM) were first presented by Abbott et al. Generally, DES is a mixture of high melting temperature solids, typically quaternary ammonium halide salt and carboxylic acids, amino acids, alcohols, amines or carbohydrates in different molar ratios. Carboxylic acid serves as hydrogen-bond donor and halide of quaternary ammonium salt act as hydrogen-bond acceptor. It is suggested that hydrogen bonding interactions cause the deep freezing point depression of the mixture. A classic example is the combination of choline chloride (m.p. 302 °C) with urea (m.p. 132 °C), forming a DES with a melting point of 12 °C. DES has lower toxicity than imidazolium- based IL and they are cheaper and biodegradable, which makes them more attractive as green solvents than ionic liquids. Also, DESs are more chemically inert to water. Deep eutectic solvents have been applied in various chemical processes, such as organic synthesis, catalysis, electrochemistry, and dissolution and extraction processes. DESs have been applied in various biopolymer pretreatment. Choline chloride – thiourea has been used for the production of chitin nanofibres from crab shells, while choline acetate – tributylammonium chloride was used to dissolve and decrystallize pure cellulose. Production of 5-hydroxymethyl furfural and furfural from cellulose and xylan have been reported. Choline chloride-lysine-water – DES was used to sugar cane bagasse pretreatment prior to enzymatic hydrolysis by Hou et al. The authors reported that 61.5% of lignin was extracted with this DES and 44.9-63.3% removal of lignin with other choline chloride –amino acid DESs.

Experimental

Raw materials

Softwood saw dust and thermo mechanical pulp (TMP) were used in fractionation experiments. Softwood saw dust was collected from a Finnish saw mill and had an average particle size of 1–2 mm. A portion of the coarse material (SW Coarse) was ground using Wiley-mill equipped with a 1.0 mm sieve as sawdust fine (SW Fine). TMP was also ground with Wiley-mill using 0.25 mm sieve.

All the used chemicals to form deep eutectic solvents were purchased from Sigma (St. Louis, MO, USA). Sodium hydroxide and hydrochloric acid were purchased from Merck.

DES preparation and fractionation

The experiments were carried out using Tornado Plus Overhead Stirring System with six seat reactor carousel made by Radleys (Radleys Discovery Technologies, UK). DESs consisting of choline chloride and hydrogen bond donor (HBD) in molar ratio of 5:3 were first prepared by mixing components at 60 °C.

DES extractions for lignicellulosic materials were carried for 16 hours out at 95 °C. The amount of lignocellulosic material was 5 wt% of the total DES weight. Wood material was added slowly under mechanical stirring to ensure good mixing of DES solution and wood.

After extractions the mixtures were diluted with excess of boiling water and immediately conducted through metallic sieves (1 mm, 0.3 mm and 0.15 mm) under vacuum suction. The obtained fractions (insolved and precipited ones) were carefully washed with water and oven-dried (60 °C, 24 hours).

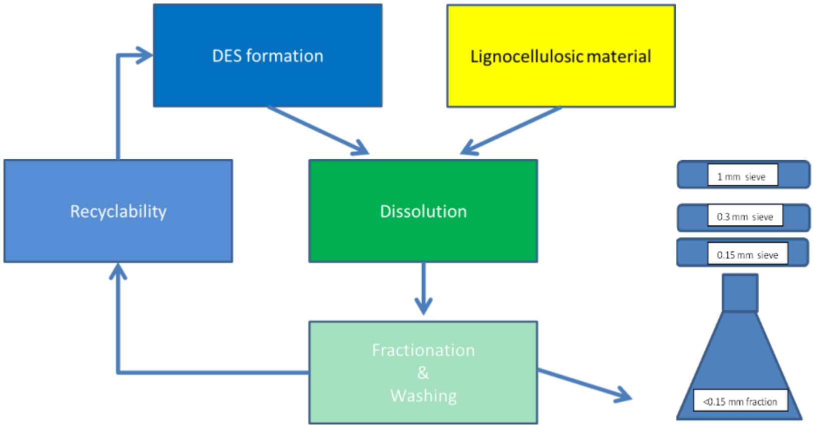

Figure 1. Extraction and fractionation procedures.

Analyses

Lignin and saccharide compositions of fractions: samples were hydrolyzed with sulphuric acid and monosaccharides were analysed with HPAEC/PAD with pulse amperometric detection (Dionex ICS 3000LC) equipped with CarboPac PA1 column. Unsolubilized lignin concentration was determined gravimetrically and solubilized lignin was quantized by UV-visible spectrophotometry.

UV-VIS spectrophotometer (Perkin Elmer UV/VIS/NIR Spectrometer Lambda 900) equipped with a 1 cm path length cell was used for the qualitative analysis of acidic DES liquors. Absorbance within 190-600 nm was measured using 1 nm spectral resolution. Liquid samples were diluted 1:100 v/v with ultra pure water. Samples were referenced to ultra pure water.

The 5-hydroxymethyl furfural (5-HMF) and furfural as well as formic acid, acetic acid and levulinic acid contents in DES solutions were analyzed with a P/ACE MDQ capillary electrophoresis instrument equipped with a photodiode array UV/Vis detector (PDA) (Beckman-Coulter, Inc., Fullerton, CA, USA). Prior to the acid analyses, chloride was removed with OnGuard II Ba/Ag/H cartridges (Dionex Ltd.)

^{31}P NMR was used to determine the functional groups of lignin in “lignin fraction”. ^{31}P NMR measurement is based on the method developed by Granata et al.

Results

Fractionation of softwood with eutectic solvent

Gravimetric fraction distribution in percentage of the fractionated wood samples is presented in Figure 1 at 95 °C is presented. The better the fractionation ability, the better the wood meal settle to smaller fractions. The influence of refining the samples can be seen in case of TMP at 95 °C. Comparison of the samples SW coarse and SW fine shows clearly the effect of the particle size, while finer particle size fractionate more easily to smaller cuts.

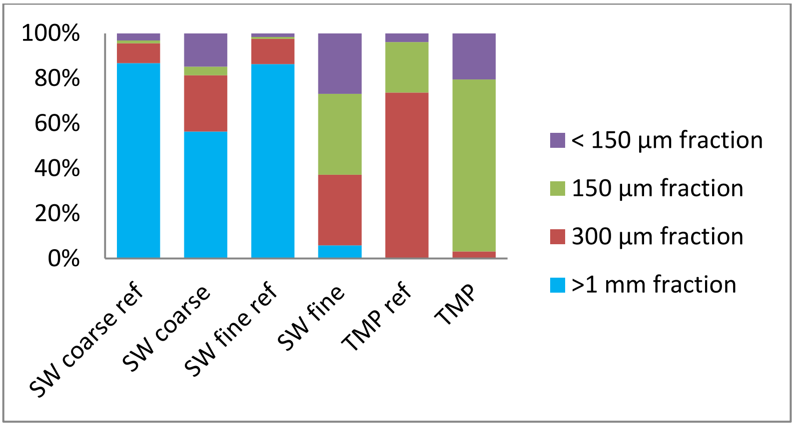

Figure 2. Percentage distribution of fractions at 95 °C.

UV-VIS measurements of the DES solutions revealed the presence of the 5-HMF and furfural (Figure 3). VTT's DES mixture promotes the formation of 5-HMF from hexoses and in smaller extent the formation of furfural from pentoses of hemicelluloses. Production of organic acids is also possible. Capillary electrophoresis (CE) was used for the quantitative analysis of these compounds. The overall yield of furans and organic acids corresponded to 27% of the theoretical maximum yield achievable from the total hemicellulose content. Temperature and the amount of water can be used to optimize the DES treatment in order to prepare 5-HMF and furfural in high quantities.

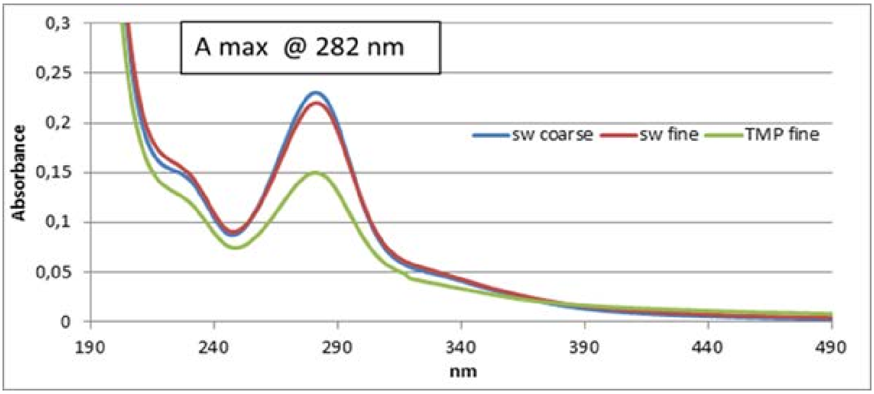

Figure 3. UV-VIS measurements revealed the presence of the 5-HMF and furfural.

VTT's DES mixture seems to fractionate lignin very effectively from wood chips. The smallest fractions contained 35–60% of lignin, corresponding to 20–50% from the total content of lignin in softwood sawdust. ^{31}P NMR reveals that the amount of condensed OH units is very low, which means non-condensed lignin structure. Polysaccharide particles may contribute to the amount of aliphatic hydroxyls. Mw of the samples between 2500–3500 measured by GPC.

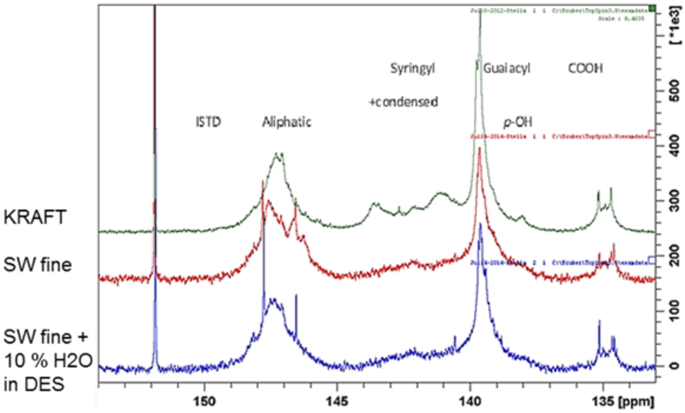

Figure 4. ^{31}P NMR measurements.

Molecular modelling (quantum mechanics, molecular dynamics) was utilized in order to receive deeper understanding of the formation of eutectic mixtures like information about good mixture ratio (phase separation), existence of hydrogen-bonding between solvent components or effect of water for mixture.

Conclusions

VTT's deep eutectic solvent mixture was successfully used for the fractionation of sawdust samples utilizing standard laboratory stirrers. Non-condensed lignin can be produced in good purity and yield without mechanical or chemical pretreatment methods. Hemicelluloses can be converted into valuable platform chemicals in high yields. Instead of ”trial and error” and endless laboratory tests, VTT uses molecular modelling as a tool to predict the formation and the properties of DES mixtures

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Processing of Lignin and the Removal of Detrimental with Deep Eutectic Solvents

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Abstract/Introduction

Lignocellulosic biomass, the primary building block of plant cell walls, consists of three main components, i.e. cellulose, hemicellulose and lignin. A rather important, but in current processes inefficiently used substance of this biomass is lignin. Lignin is a natural occurring complex biopolymer found in the cell walls of higher plants and woody tissue. It consists of a complex network of phenylpropanoids connected mainly by ether bonds and condensed C-C linkages. In the paper industry, lignin prohibits the production of high quality cellulose pulp directly from biomass and efficient delignification is required. It is favored for this lignin to be removed without altering its structure for further valorization.

For this development Deep Eutectic Solvents (DESs) show promising characteristics. DESs are low transition temperature mixtures (LTTMs) consisting of at least one hydrogen bond donor (HBD) and one hydrogen bond acceptor (HBA) that result in a liquid mixture showing an unusual low melting point.[1] Due to the high hydrogen bonding interaction, some of the promising characteristics of ionic liquids are shared by DESs.[2] For example, DESs show a wide liquid range and good solvation properties. Additionally, they can easily be prepared upon mixing at moderate temperatures without the need of purification. Generally, DESs are considered as environmentally benign solvents.[3]

Currently in industry delignification takes place by cooking with chemicals at high temperatures and pressure followed by multiple bleaching steps. A ‘greener’ and more efficient method for wood would be highly beneficial for both environment and business. Previously, ionic liquids (ILs) have shown their ability to selectively extract lignin from biomass without disrupting the cellulose.

Delignification using Deep Eutectic Solvents

Previous research in our group has shown DESs which possess properties suitable for delignification. These DESs show a lignin solubilty up to 25 wt% while the maximum solubility for cellulose remains below 1 wt%. (Table 1) What we present today, are new found DESs with lignin solubilities all above 30 wt% with 37 wt% the maximum found so far. (Table 2)

Table 1. Lignin Solubilty in various DESs.

DES	Lignin solubilty [wt%]	Cellulose Solubility [wt%]
Malic A:Proline 1:3	15	<1
Glycolic Acid:ChCl 1:1	22	-
Glycolic Acid:ChCl 3:1	25	-
Glycolic Acid:Proline 3:1	20	-
Glycolic Acid:Betaine 3:1	16	-

Table 2. Lignin Solubilty in new DESs.

DES	Lignin solubilty [wt%]
DES1	35
DES2	33
DES3	37
DES4	31

Lignin extractability with DESs

Next to lignin solubilty in DES, which were measured using commercially available alkali lignin, the DESs were also tested for lignin extractability from actual pulp. Delignification was monitored with kappa number determination, which is a measure for all oxidizables in the pulp, mainly lignin. The pulp used had an initial kappa number of 25.5. In all cases the kappa number decreased and for DES1 it even reduced to 8.2 Table 3).

Table 3. Effect of new DESs treatment on kappa number pulp.

	Kappa number
Untreated ground pulp	25.5
DES1 treated ground pulp	8.2
DES2 treated ground pulp	13.2
DES3 treated ground pulp	15.7
DES4 treated ground pulp	18.4

DESs effect on pulp

Figure 1 shows the different effects the DESs have on pulp. It becomes clear that the more delignified the pulp becomes, the more the fibers are affected. Although it seems like a compromise between fiber quality and delignification must be reached, it could also mean that a whole new pulping process is next.

Figure 1. Effect of different DESs on pulp. Left: DES1 right DES3.

Hydrophobic Deep Eutectic Solvents for removal of Detrimental

Abstract/Introduction

Deep eutectic solvents (DESs) have emerged in literature at the start of 2003 when the combination of urea and choline chloride, in a 2:1 ratio, was published.[4] Up until now, all the published DESs have been hydrophilic, and thus dissolve in water. However, recently we have shown that hydrophobic DESs can also be prepared by the combination of a fatty acid, decanoic acid (DecA), and quaternary ammonium salts, tetrabutylammonium chloride (N_{4444}-Cl), methyltrioctylammonium chloride (N_{8881}-Cl), tetraheptylammonium chloride (N_{7777}-Cl), tetraoctylammonium chloride (N_{8888}-Cl), methyltrioctylammonium bromide (N_{8881}-Br) and tetraoctylammonium bromide (N_{8888}-Br).[5] All DESs were prepared in a 2:1 ratio. Here, our results regarding the hydrophobicity are summarized and we will show the extraction of volatile fatty acids (VFAs) from the water phase.

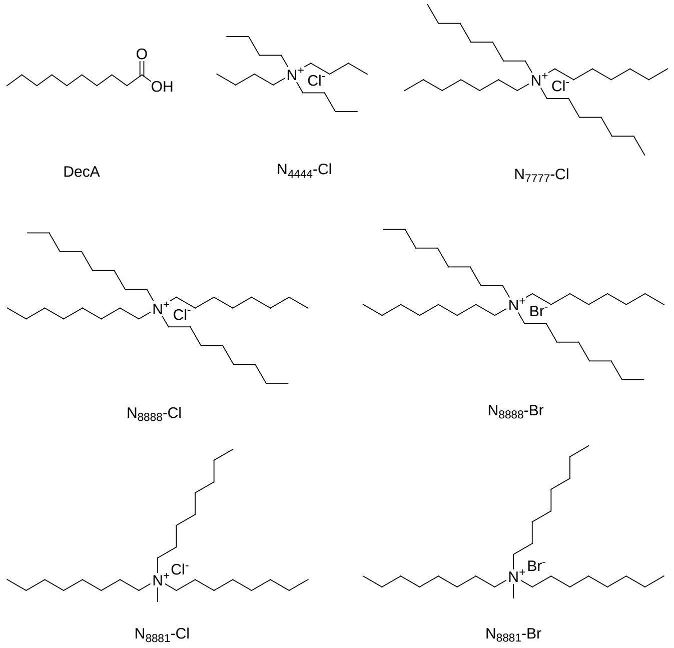

Figure 2. Structural formulas used for the preparation of the hydrophobic DESs.

Results and discussion

Regarding the hydrophobicity of the DESs, the leaching of the constituents was investigated. Since DecA showed a rather low water solubility, 0.15 mg·g^{-1} at 20 °C,[6] the leaching of this component was not further investigated. The leaching of the salts showed that the DES consisting of DecA and N_{4444}-Cl had the biggest leaching with an approximate value of 34.8% ($m_{salt,leached}/m_{salt,DES}$). This amount of leaching was too high for further use, so it was decided to continue the investigation with longer quaternary ammonium salts such as N_{8881}-Cl and N_{8881}-Br, which showed leaching of respectively 3.0% and 2.3%. From these results it was hypothesized that symmetrical quaternary ammonium salts would even decrease the leaching more. The results of the leaching indicated that for the chloride anion indeed the leaching became less with a change to the symmetrical quaternary ammonium salts. The salt N_{7777}-Cl leached approximately 2.32%, while this was 1.93% for the N_{8888}-Cl. For the N_{8888}-Br, the results showed that the leaching increased to 5.23%. A summary of the results can be found in Table 4.

Table 4. Leaching of the quaternary ammonium salts to the water phase.

DESs	C_{salt} *[mg_{salt}/g_{water}]*	$m_{salt,leached}/m_{salt,DES}$ *[$g \cdot g^{-1}$]*
DecA:N_{4444}-Cl (2:1)	155.21	0.3475
DecA:N_{8881}-Cl (2:1)	16.19	0.0300
DecA:N_{7777}-Cl (2:1)	13.09	0.0232
DecA:N_{8888}-Cl (2:1)	11.44	0.0193
DecA:N_{8881}-Br (2:1)	13.08	0.0231
DecA:N_{8888}-Br (2:1)	14.23	0.0523

The newly developed hydrophobic DESs were evaluated for the extraction of the VFAs acetic, propionic and butyric acids. The extraction efficiencies showed that all the newly developed hydrophobic DESs performed better than the conventionally used solvent trioctylamine (TOA). Regarding the comparison of the DESs it can be concluded that the DES DecA: N_{8881}-Cl, in a 2 to 1, ratio has the highest extraction efficiency. This can be explained by the the fact that the salt of this DES has the highest ability to undergo hydrogen bonding of all the reported DESs due to the lowest hydrogen bonding ability. In general, it can be concluded that an increase of the alkyl chain length of the VFA's leads to an increase of the extraction efficiency. An overview is given in Table 5.

Table 5. Extraction efficiencies of the VFAs with the hydrophobic DESs and TOA.

	E [%]		
DESs [a]	Acetic Acid	Propionic Acid	Butyric Acid
DecA:N_{8881}-Cl (2:1)	38.0	70.5	89.8
DecA:N_{7777}-Cl (2:1)	32.0	76.5 [b]	91.5 [b]
DecA:N_{8888}-Cl (2:1)	25.0 [b]	52.7	81.3
DecA:N_{8881}-Br (2:1)	29.7	63.4	83.1
DecA:N_{8888}-Br (2:1)	30.6	65.9	87.4
TOA	18.6	45.9	73.5

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Textiles

Wood Based Textiles Fibres – Sustainable Solution for Future

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Abstract

Regenerated cellulose fibres have been considered as materials from past, but sustainability issues related to cotton as well synthetic textiles are creating a renaissance of wood based materials. Issue is markedly on the renewable raw material base not interfering food-chain having low water foot print, but also the possibility to create textile ecosystem for future circular economy.

Introduction

Reborn of the Ryon requires development both in qualities and environmentally friendly production methods, which are competitive on the tight and far developed markets. Innovation is definitely much more than just a simple change of raw material base, as can be learned e.g. from bamboo viscose case.

There are several new technologies developing and some of them entering the market place. In the water based regenerated technologies main drivers are to get rid of carbon sulphide used with viscose and reduce the overall cost with improved processes and more affordable raw materials. On the other hand the technical performance of the fibres is to be improved especially in solvent processes from that of NMMO to totally a new level with ionic liquids.

Even more challenging ideas have been introduced, like recently applying cellulose pulp or nano-cellulose for yarn production. However the later items are yet in development phase, even though they open revolutionary concepts for future textile and composite industry. One example is the idea of markedly reduced length of delivery chain and complete production near consumer.

Novel alkaline dissolving systems

Consequently, derivatisation with carbon disulphide is used in the viscose process to dissolve and convert them into variously shaped articles. However, carbon disulphide is a highly toxic chemical, which requires special care in handling and recovery. [1]Therefore, an ecological method to dissolve cellulose in an aqueous environment is still being sought. One alternative is the invention that relates to a method for producing cellulose carbamate [2] and method for preparing a cellulose carbamate solution in sodium hydroxide reaching 9 wt% cellulose solution. [3] Another is enzyme assisted route. Enzymes have proved to be powerful biocatalysts that modify the cellulosic material into an alkaline soluble form. [4] The cellulose concentration of the spinning solution can be raised from 6 wt% up to 7.2 wt% by decreasing the molecular weight of cellulose. [5] The limited solubility of cellulose effects on the highest reachable strength of fibre.

Ionic liquids (ILs)

The ability of ionic liquids (ILs) to dissolve cellulose and the precipitation of the cellulose, upon addition of water or other antisolvents, has been subject of much recent interest. Because cellulose cannot be melt-processed, processing of cellulose requires either derivatization into cellulose xanthate (viscose) or dissolution into a direct solvent. [6] Currently, the only commercialized direct solvent process uses the monohydrate of *N*-methylmorpholine *N*-oxide (NMMO), [7] which is problematic because the cyclic ether bears a redox-active moiety and is prone to dangerous runaway decomposition. [8] ILs are generally thermally stable and thus less hazardous, suitable ILs could potentially replace $NMMO \cdot H_2O$ as a direct solvent. However, the behavior of cellulose-IL solutions needs to be properly characterized prior to establishing a process in larger scale.

Recently, King et al. published a class of distillable ILs based on the *N*,*N*,*N*,*N*-tetramethylguanidium cation ($[TMGH]^+$). [9] Their cellulose solvation capabilities are similar to that of imidazolium-based ILs when dry, but, in addition, they can be recycled via distillation.The distinct difference between dissolution and regeneration is clearly demonstrated by [TMGH]OAc and $[TMGH]EtCO_2$. Although they are very sensitive toward water when dissolving cellulose, they tolerate more water when regenerating the cellulose from solution. Due to the hydrotropic nature of the more bulky cations, cellulose regeneration may require more hydrophobic mixtures (e.g., water–alcohols) for more efficient regeneration of pure cellulose. [10] The chemical inertness and ability to dissolve a wide spectrum of substances are probably the biggest advantages of ILs as solvents for biopolymer processing. [11]

Cellulose (I) nano fibrillated yarns

Total another way of producing (composite) textile yarn of cellulose is that, where TEMPO-nanofiber suspension in water spun up to 100 m/min into an acetone coagulation bath aligned the nanofibers to the spun fibers had a Young's modulus of 23.6 GPa, tensile strength of 321 MPa, and elongation at break of 2.2%. [12] In theory these yarns could reach modulus better than aramid 140-220 GPa, but in practice yet closer to that of polypropylene.[13] Recent development of spinning technologies have however improved performance markedly up to tensile strength 600 Mpa (appr. 4,6 cN/dtex). [14,15]

Experimental

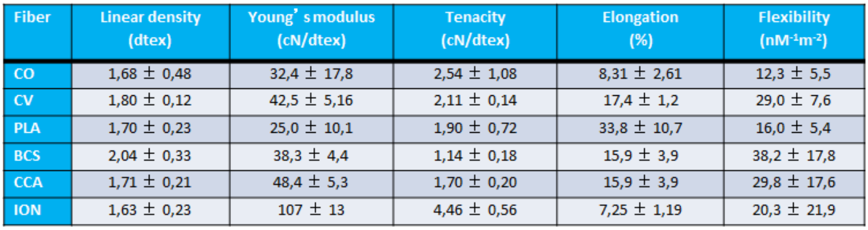
There has been made several test runs in recent years of the different processes e.g. in Fibic ltd project Fubio Cellulose and Large Technology Opening called Design Driven World of Cellulose. In the following are collected highlights of the information of those and earlier experiments.

Results and discussion

Based on those we have compared different fibre types CO cotton, CV viscose, PLA poly lactic acid, BCS biocelsol, CCA and ION Ioncel fibers. From the table 1. can be simply observed that the strength of experimental alkali dissolved cellulose fibres and viscose follow simply the cellulose content in the dope, having 1,14, 1,70 and 2,10 cN/dtex for biocelsol, cellulose carbamate and viscose respectively when the dope concentrations were 7,2, 9 and 10 wt% respectively.

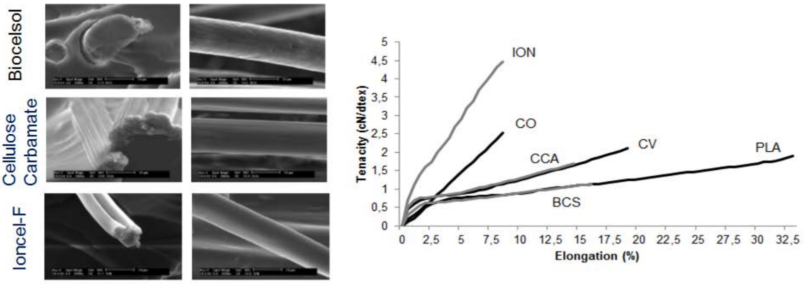
However, in the case of cellulose carbamate earlier development Celca, was reached 2,4 cN/dtex with 1,67 dtex fibre. Celca differentiated that from CCA in that it was regenerated back to cellulose with sodium hydroxide after spinning.[16] When elongation was up to 10%, the fibre was closer to Modal and markedly better than viscose.

Table 1. Comparision of CO cotton, CV viscose, PLA poly lactic acid, BCS biocelsol, CCA and ION Ioncel fibers.



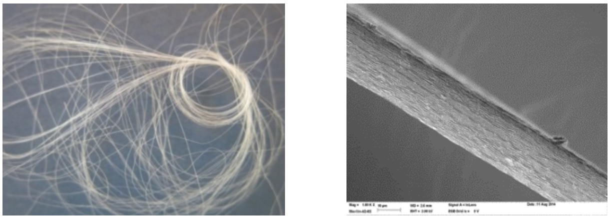
Fiber	Linear density (dtex)	Young’ s modulus (cN/dtex)	Tenacity (cN/dtex)	Elongation (%)	Flexibility ($nM^{-1}m^{-2}$)
CO	1,68 ± 0,48	32,4 ± 17,8	2,54 ± 1,08	8,31 ± 2,61	12,3 ± 5,5
CV	1,80 ± 0,12	42,5 ± 5,16	2,11 ± 0,14	17,4 ± 1,2	29,0 ± 7,6
PLA	1,70 ± 0,23	25,0 ± 10,1	1,90 ± 0,72	33,8 ± 10,7	16,0 ± 5,4
BCS	2,04 ± 0,33	38,3 ± 4,4	1,14 ± 0,18	15,9 ± 3,9	38,2 ± 17,8
CCA	1,71 ± 0,21	48,4 ± 5,3	1,70 ± 0,20	15,9 ± 3,9	29,8 ± 17,6
ION	1,63 ± 0,23	107 ± 13	4,46 ± 0,56	7,25 ± 1,19	20,3 ± 21,9

Even further is reaching the fibres produced with novel Ioncel-F process in totally new spinning process, it is possible to reach regenerated cellulose fibres which are even better than those produced with NMMO process. Reason for the improvement is simply the superior dissolving capacity of ionic liquids, which may also open totally new avenues like recycled pulps [17] or lignin containing cellulose applied as raw-material for textile fibre production. Recycled materials have been applied earlier also with alkaline process,[18] but never as strong as now with ionic liquids.



Picture 1. Fibre structure of biocelsol, cellulose carbamate and Ioncell-F.

In the attached **picture 1** on left can be seen the actual fibre structure of biocelsol, cellulose carbamate and Ioncell-F and on the right the actual properties of the fibres. It can be observed that most crystalline fibre is most strong one. Comparing that to CNF yarn in **picture 2** can be observed totally different morphology produced in continuous process. Even if tensile strength is 250 MPa (appr. 2 cN/dtex) the main difference is, however, in the markedly worse water stability of the cellulose I yarn.



Picture 2. CNF yarns produced in continuous process by VTT.

In the **picture 3** are shown examples of lignin containing cellulose fibres manufacture with Ioncel-F process. The fibers have improved water stability and their mechanical properties are yet among the best fibres. Lignin may also improve their compatibility and increase usefulness as composite fibers.

Picture 3. Lignin containing cellulose fibres manufacture with Ioncel-F process by Sixta et.al. (left) and cloths of those by Kääriäinen P., Tanttu M., et.al. Aalto 2014.

Conclusions

Regenerated cellulose fibres have been considered as materials from past, but sustainability issues related to cotton as well synthetic textiles are creating a renaissance of wood based materials. Issue is markedly on the renewable raw material base not interfering food-chain having low water foot print, but also the possibility to create textile ecosystem for future circular economy.

Customer acceptance takes not only adaptation of the message of sustainability but also improved customer experience through textile properties combined with competitive presence on market. Brand owners are adopting and developing offering based on consumer opinion, and it seems that we are facing an era where new solutions are well come. Emerging markets are to be found prior to garments in the home-, technical-, automotive-, hygienic- and several other special textiles as well novel composite materials.

Acknowledgements

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Design Driven Development of Novel Biomaterials from Wood Based Cellulose

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Wood based cellulose has a remarkable role in Finnish industry, however, it has been mainly utilized in bulk products with no design involved. The unique properties of cellulose together with high quality research and technological development offer a great potential to develop new products for forest based industry. In this paper we are exploring possibilities of utilizing wood cellulose based materials in textiles and 3D printing.

Consumption of textiles is constantly increasing in the world. The textile industry has taken initiatives to reduce its environmental impact and improve social conditions. Currently dominating cellulosic yarns, man-made and cotton, have several downsides. Man-made cellulosic yarns are presently produced using methods which require heavy modification of cellulose or use of environmentally unfriendly chemicals. Production of cotton, on the other hand, is environmentally burdening due to its requirements for water, artificial fertilizers and pesticides. This opens markets for new types of textile materials from wood cellulose. In this project we have developed several methods to produce filaments utilizing native crystalline structure of cellulose.

3D printing is a group of manufacturing methods that enable production of customized structures for personal and commercial use. As most of the materials used in 3D printing currently are oil based and nonbiodegradable, cellulosic materials have a competitive advantage over these materials with regards to sustainability. Versatility of 3D printing techniques enables utilization of cellulosic materials for variety of applications. Cellulosic materials were used to print 3D structures using several different commercially available printers. 3D printing techniques were also used to print structures on textiles to modify their properties, for example, folding and haptic properties.

Lignin

Successful Start-up of Lignin Extraction at Stora Enso Sunila Mill

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Abstract

Utilizing a greater part of the raw material (wood) and producing other marketable products than pulp has become a focus recently for the pulp and paper industry. Doing this in a sustainable way is often referred to as “The Biorefinery Concept”. Lignin is one of the non-traditional products produced today on a commercially viable scale.

Recently, the world’s first integrated lignin extraction plant to produce dry kraft lignin with the possibility of firing lignin directly into the lime kiln has been started up at the Stora Enso Sunila Mill in Finland. This paper will describe learnings from the two first commercial LignoBoost installations, the Sunila plant and the Domtar Plymouth plant in North America. Included in this review are design of the systems for lignin precipitation, safety related issues including gas handling along with experiences from the start-up and ramping up of production. Initial effects of lignin extraction on pulp mill operations will also be presented.

Introduction

A decreasing supply of raw material e.g. oil, has pushed the development of processes to be more environmentally friendly. R&D projects in recent years have been focused on finding alternative “green” raw materials or sources of energy that can replace the ones from the fossil supply chain. Bio-based markets are expected to grow significantly in the coming years. One example of that is the market for bio-based plastics which is expected to rise to 2.65 Mt by 2018 from 1.29 Mt in 2013 (Pöyry report “Biosight up to 2025”). Despite rapid growth this is estimated to be less than 1% of the total plastic demand in 2018. A similar trend can be seen in the bio-based chemical market. Even though the oil based platform is still the largest in terms of volume the bio-based platforms, including sugar and lignin, have a higher degree of diversity.

Utilizing a greater part of the raw material and produce other marketable products than pulp has been in focus the latest years for the pulp and paper industry. Doing this in a sustainable way is often referred to as “The Biorefinery

Concept". Lignin is one of the non-traditional products produced today on a commercially viable scale. Lignin is a heterogeneous macromolecule that can be found in most vascular plants. Lignin is degraded and solubilized by the chemical reactions in the digestion plant in the pulp mills by help of chemicals, high temperature and pressure. Solubilized lignin follows the spent cooking liquor and ends up in the recovery cycle in the mill. Through this a huge amount of lignin is produced yearly in the pulp and paper mills worldwide. The kraft pulping process is the most dominating process, comprising 95% of all chemical pulping and alone producing about 130Mt of pulp annually (Gellersted et. al 2013). Black liquor from softwood kraft pulping, e.g. pine or spruce, contains about 490 kg lignin/ton of pulp (~25%-weight) while black liquor from hardwood pulping contains slightly less, about 330 kg/ton pulp (~17%-weight), due to a lower lignin content in the wood. Consequently, the total yearly production of lignin globally in the pulp and paper industry is about 54Mt. The maximum removal rate is certainly dependent on mill energy situation but generally 75% could be considered as the maximum. This would give a total yearly kraft lignin market size of roughly 40 Mt and is well in line with what others haves presented (Wimby 2014; Gellerstedt et al 2013).

Lignin is the main energy carrier in the black liquor and is burnt in the recovery boiler in order to produce steam and electricity. Recent development of equipment found in a pulp and paper mill has been driven towards energy efficiency. Hence, many mills have an energy surplus that could be transformed into a new bio based product revenue stream, e.g. by lignin extraction. By extracting lignin from black liquor the recovery boiler will be off loaded in terms of energy and more black liquor could be fed to the boiler. Depending on if there are other bottle necks in the mill more pulp could be produced.

With the start-up of lignin production sites at Domtar's Plymouth NC Mill in the USA and Stora Enso's Sunila Mill in Finland the existing kraft lignin market has grown significantly. Lignin extraction could be one of the door openers in transforming the pulp and paper industry towards the biorefinery concept among other fractionating technologies. Refined lignin can be used for producing e.g. bioplastics, adhesives and chemicals such as phenol or BTX or replacing fossil based fuel. Other interesting areas where it could be utilized are in carbon fibre production (low cost Carbon fibre) and as precursor to "green carbon" products such as reinforcement filler or activated carbon.

The LignoBoost process

LignoBoost is a stand-alone process that extracts lignin from black liquor. Lignin is extracted by well-known unit operations like gas absorption, precipitation, solid liquid separation and displacement washing. This process is connected to the evaporation plant and sends all processed streams back to the mill for recovery of cooking chemicals (see Figure 1 below).

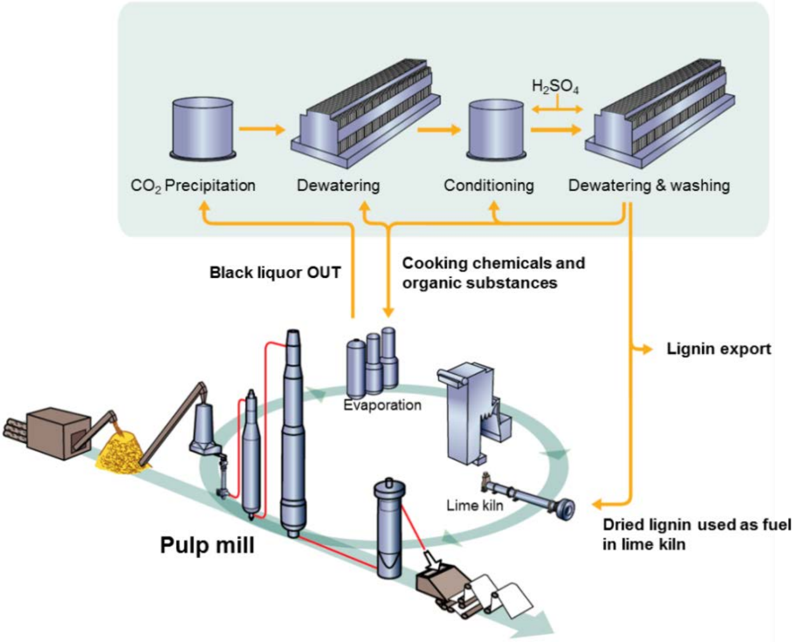

Figure 1. Flow of black liquors from and to the host mil and possible lignin revenues.

Black liquor is fed to the plant from the evaporation train at approximately 40% dry solids content. After fine tuning of temperature, the pH of the black liquor is lowered by absorption of CO_2 gas. When pH is lowered, the phenolic groups of the dissolved lignin become “protonized” and the solubility decreases i.e. the lignin precipitates. After precipitation, the slurry is conditioned in order to create larger agglomerates before the solid lignin is separated from the liquor in a filtration step. This is done by pressure filtration in a batch operated chamber filter. Filtrate from the filtration process is lean black liquor that is sent back to the mill downstream of the black liquor extraction point. Lignin cake from the filtration process is dropped to a belt conveyor that transports it to a re-suspension step where it is mixed with spent wash water from the downstream displacement washing. Pure sulphuric acid is also charged in this step to lower the pH to 2.5. When lowering the pH to 2.5 all carbonate and sulphide ions, that originate from the entrapped black liquor in the first stage cake, forms CO_2(g) and H_2S(g). This off-gas is re-circulated back and used as precipitation gas in order to decrease the use of fresh CO_2(g) in the precipitation step. After acidification down to pH 2.5 the slurry is left in some tanks for maturing and de-gassing before it once again is dewatered using a second chamber pressure filter. This second filtration stage is a combined filtration washing stage. After cake formation, low pH water (pH adjusted to 2.5 using fresh sulphuric acid) is pressed through the cake to wash away impurities. This washing lowers the ash content and improves the lignin quality.

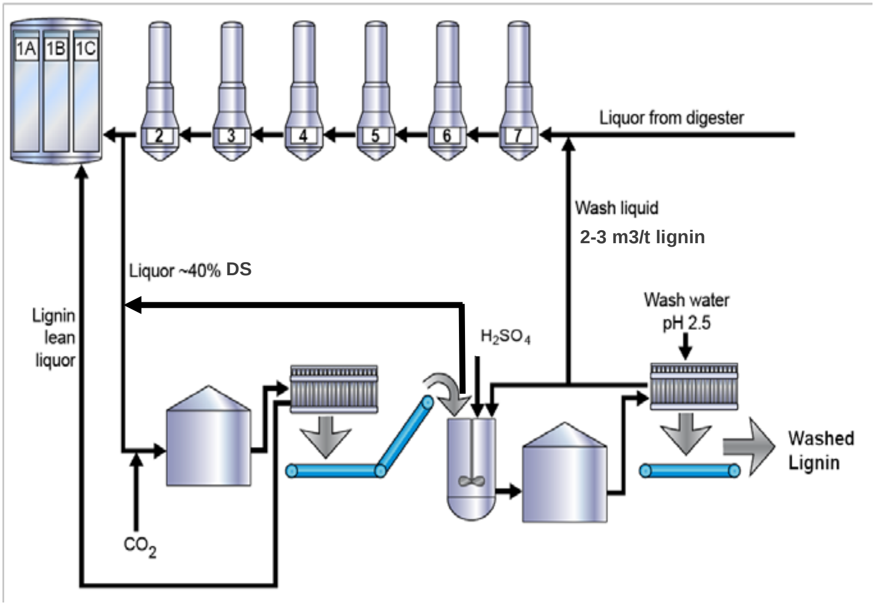

Figure 2. Schematic figure of the LignoBoost process.

One of the key requirements the LignoBoost process is to quickly lower the pH in the re-suspension step and to keep the pH and ionic strength gradients between the formed cake and the applied wash water as small as possible. This helps controlling the lignin solubility (Öhman et al 2007). By doing this a smaller amount of wash water can be used in the washing step and the impact on the evaporation plant in the mill is kept to a minimum. Washing at high pH would lead to high lignin losses and a lignin product with a higher amount of impurities or a significantly higher amount of washing water consumption. Figure 2 above shows a simplified schematic figure of the process.

Sunila LignoBoost plant

The second commercial LignoBoost plant started up in 2015 at Stora Enso’s Sunila Mill in Finland. Sunila produces 370.000 ADMT of bleached softwood kraft pulp from pine and spruce and the annual capacity of the lignin plant is 50.000 MT. The aim of this installation was not to de-bottleneck the recovery boiler or to increase pulp production but to replace fossil fuels in the mill’s lime kilns and start exploring the external markets for new products based on renewable solutions out of raw materials that do not compete with food production.

The investment decision was taken by Stora Enso in July 2013 and contract written in October 2013. The plant erection started in April 2014 and the first lignin was produced on December 7, 2014. The overall project duration was 18 months. A close cooperation between Stora Enso and Valmet has characterized the project. Focus has been on safety and the LignoBoost plant has been developed jointly throughout the project.

The installation in Sunila also includes storage for moist lignin, a dryer, lignin dust burners in the lime kilns and a packaging line. Moist lignin that has a dry solids content of about 65% is dried in a ring dryer utilizing flue-gases from the lime kilns as drying media. During drying lignin particles break down into a fine powder with dry solids content above 95%. Dried lignin is thereafter pneumatically conveyed to the lime kilns and/or the packaging plant.

Safety has been a main concern in the project considering both management of gases formed during lignin precipitation and the dust explosion risks connected to handling of the fine, dry lignin powder. Large amounts of hydrogen sulfide (H_2S) are released when the pH of the black liquor is lowered. Since main part of the equipment for lignin precipitation has been placed in an existing building it has been of outmost importance with a proper design of the gas collection system. The dry lignin powder is not explosive by itself but may cause a dust explosion if it is suspended in air at sufficient concentrations and in proximity to an ignition source. The atmosphere in the dryer area is kept inert and non-explosive by utilizing flue gases from the lime kiln with low oxygen content together with nitrogen as purge gas.

Experiences from start-ups

The first commercial LignoBoost plant in Plymouth, North Carolina in the USA next to the Domtar fluff pulp mill that started up early 2013 was followed by the plant in Sunila less than two years later. Naturally there is a great potential for learning during a plant start-up and for a novel technology the potential is even larger. Before these start-ups there were a number of equipment tests as well as laboratory and pilot trials.

During the early stages of the Plymouth plant start up time was spent on tuning controlling parameters and to get the process parts to work optimally. The first washed lignin cake was produced 17 days after start up, on February 15 2013. Production during this period was basically only on-and-off production during the day shift. One important lesson learned during this period included the importance of having stable conditions for lignin precipitation. Unstable operation during CO_2(g) absorption, i.e. large swings in pressure and flow, will lead to variable alkaline slurry quality.

Slurry produced during precipitation also puts demands on the downstream equipment design and type, such as heat exchangers. In all positions where slurry is heated or cooled there’s a need for using heat exchangers that can handle suspended particles without major plugging issues.

Foam formation in different positions was an issue during the start-up in Plymouth plant and it was necessary to re-design both process and equipment to handle or try to minimize foam formation. This led to the introduction of a foam tank, which can handle any excess foam created in the re-suspension stage, and a new design of a carbonation absorption unit.

When pH of the black liquor is lowered H_2S gas is formed. All the gases from venting of tanks must be properly collected and treated, both from an environmental and safety point of view. Both filters needs to be inside a ventilated enclosure and should be isolated during operation. In Plymouth all tanks and pumps are situated outdoors but in Sunila most equipment has been located inside an existing building. Naturally, all H_2S releases inside a building can create a potentially dangerous situation. Hence, the gas system and tanks in Sunila have been designed to eliminate hazardous gas release. It has been proven during the first half year of operation in Sunila that the LignoBoost gas collection system works as intended.

During start-up and ramping up period in Plymouth all experiences where thoroughly noted and followed up in a separate lessons learned project. All changes in design from this process were implemented in the Sunila plant. During the Sunila start-up it took about 10 days from first day until all process parts had been tested and the first washed lignin cake was produced from the second pressure filter. Almost from the first day the alkaline part of the plant was operated continuously which naturally facilitated the tuning and ramping up period.

Influences on pulp mill operation

A lignin extraction plant is closely integrated with the pulp mill since lignin lean black liquor as well as added water and chemicals are circulated back to the liquor cycle.

There is an impact to the energy balance of the mill, since lignin is the main energy carrier in the black liquor. Extracting lignin corresponding to 50 000 MT per year corresponds to an average reduction in steam production from the recovery boiler with almost 10 kg/s. In Sunila the energy balance is managed by a combination of utilizing an energy surplus, increased steam generation in the bark boiler and energy savings in the mill.

One key parameter within each mill is management of the Na/S-balance. The balance is seriously affected by the sulphuric acid that is used to precipitate the lignin. roper management of sodium-sulphur balances is essential at all kraft pulp mills, as increased sulphur amounts would result in high cooking liquor sulphidity, corrosion problems and other undesired effects. Most softwood mills have an excess of sulphur in the liquor system and the traditional approach to manage the Na/S-balance is disposal of recovery boiler ESP (electrostatic precipitator) ash, as that contains up to 90-95% of sodium sulphate. However, when extracting larger lignin volumes it would be impossible to compensate the sulphur intake to lignin extraction with traditional ash purging. The ash volumes would be too large from an environmental point of view and the compensation for the sodium lost with the ash will be high. Hence, other solutions must be considered e.g. production of sulphur containing chemicals from strong gases or split the sodium from the sulphur using techniques such as electrochemical cell with ion selective membrane or sulphur split from green liquor [5, 6]. At Sunila the sulphur balance is managed by increased internal production of sodium bisulphite that allow purging of a pure sulphur stream.

Integration of a lignin extraction plant will also change the composition and the combustion properties of the black liquor. Carbon dioxide and sulphuric acid used for lignin precipitation will be recirculated to the evaporation plant in the form of carbonate and sulphate. By increasing the concentration of inorganic elements in the black liquor the solubility and formation of scaling salts such as burkeite and dicarbonate are affected. Wallmo et al 2014 reported that the meta solubility point, the dry solids level at which crystal particles starts to precipitate, was pushed towards lower dry solids when lignin was removed. Extracting a part of the lignin decreases the viscosity of the black liquor especially at higher dry solids. In Sunila, that has a final black liquor dry solid content of 80%, this means that it is necessary to lower the temperature of as-fired black liquor to maintain the same viscosity with the lignin lean black liquor as earlier.

Black liquor gross calorific value will decrease slightly from the addition of lignin lean black liquor from the lignin separation plant. This will have a minor impact on the recovery boiler operations and tuning of the air systems may be required.

Conclusions

Commercial production of kraft lignin has started and the market has almost been doubled due to the start-ups of lignin extraction plants during the last few years. Valmets LignoBoost technology works as expected. The first and second LignoBoost plants are commercial, and several other projects are being developed.

Experiences from the start-ups have and will be successfully transferred to the next project. This has shortened the start-up time and increased the knowledge in how to operate the plant efficiently and ramp up the capacity. The gas collection system in Sunila is designed to eliminate hazardous gas release. It has been proven during the first half year of operation that the LignoBoost gas collection system works as intended.

A lignin extraction plant is closely integrated with the pulp mill since lignin lean black liquor as well as added water and chemicals are circulated back to the liquor cycle. The most immediate effect can be seen on the energy balance and the reduction in steam production from the recovery boiler. In Sunila the energy balance is managed by a combination of utilizing an energy surplus, increased steam generation in the bark boiler and energy savings in the mill.

Another key parameter is management of the Na/S balance which is affected by the use of sulphuric acid during lignin precipitation. At Sunila the balance is managed by increased internal production of sodium bisulphite that allow purging of a pure sulphur stream.

LignoBoost is an innovative bioenergy technology that takes a low value stream and converts it into potential value-added revenue streams by separating the lignin from the black liquor.

Acknowledgements

Thanks to all those pioneers of lignin separation development over the years prior to lignin separation becoming commercial.

The mill staff from both Stora Enso and Domtar start-ups that were involved during the period are greatly acknowledged.

All the members of the project teams, technology teams and process teams from both projects are also acknowledged for their hard work both in the project and start-up phases.

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Sulphur Profile of the LignoForce System™ as Compared to Conventional Lignin Recovery Processes

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Abstract

In most of the lignin precipitation processes from kraft black liquor that are using acid addition, acidification is predominantly performed by using either carbon dioxide or a mineral acid or a combination of the two to drop the pH of the black liquor from about 13-14 to about 9-10, followed by lignin particle coagulation, lignin slurry filtration and lignin cake washing with sulfuric acid and water. At pH values of less than 11, the potential exists for the generation of significant quantities of totally reduced sulphur (TRS) compounds and other volatile sulphur species. Such compounds which include hydrogen sulphide, methyl mercaptan, dimethyl sulphide, and dimethyl disulphide are strongly odorous compounds with well-known negative effects on human health and other forms of life. To address this problem, as well as other problems associated with existing lignin recovery processes, FPInnovations and Noram recently developed a new process called the LignoForce System™ (US Pat. 8,771,464). This process employs a black liquor oxidation step to convert TRS compounds present in kraft black liquor to non-volatile species. In this paper, the sulfur profile of the LignoForce System™ will be discussed and compared to a base case consisting of the same process but without black liquor oxidation.

Introduction

In the kraft pulping process, white liquor (a mixture of sodium hydroxide and sodium hydrosulphide) is used to delignify wood chips at high temperatures and pressures. During this process as well as other kraft pulp mill operations, significant amounts of Totally Reduced Sulfur (TRS) compounds can be generated, namely: hydrogen sulfide (H_2S), methyl mercaptan (MM), dimethyl sulfide (DMS), and dimethyl disulfide (DMDS). MM and DMS are formed through the reaction of hydrosulfide ions (HS^-) and mercaptide ions (CH_3S^-), respectively, with lignin methoxyl groups ($-OCH_3$), while DMDS is formed through the reaction of mercaptan with oxygen [1-4]. It is well known that these compounds produce unpleasant odours at concentrations as low as a few parts per billion in air and might lead to serious environmental, health and safety issues if not properly collected and disposed of [5].

Most of the TRS compounds generated during the kraft pulping process end up in the digester condensates and the residual pulping liquor (black liquor). Since most black liquors are highly alkaline (pH>13), TRS compounds such as hydrogen sulphide and mercaptan, which possess ionisable sulphur groups, are totally in the sodium form, and, therefore, can not be easily volatilized. However, when such black liquors are acidified below pH 11, as is the case in most lignin recovery processes, emissions of these two TRS compounds can become a significant problem. Since the obnoxious odour, health and safety issues of sulfur compounds found at kraft pulp mills are characteristic of mostly those which contain sulphur atoms in the (-2) oxidation state, oxidation of the sulfur present in these compounds to a higher valence state can substantially reduce or eliminate the odour problem [4-5]. Consistent with this approach, FPInnovations and NORAM have recently developed a new process for the recovery of lignin from kraft black liquors (US Patent No. 8,771,464; July 8, 2014) in which the BL is oxidized with oxygen, under controlled conditions, before the acid precipitation step. This process is currently being commercialized by NORAM under the trade name «LignoForce System™» [6-7].

The main objective of this paper is to investigate the sources and fate of several sulphur compounds, including TRS and sulphur dioxide, during the main steps of the LignoForce System™ as compared to conventional lignin recovery processes.

Experimental

Black liquor was obtained from a Member Company kraft pulp mill (Mill A) and was used with or without oxidation. Three levels of black liquor oxidation were employed: a) no oxidation (conventional process), b) oxidation until a residual sulphide concentration of 0.5 g/L was reached, and c) oxidation until no residual sulfide was detected. The precipitation was conducted by blowing CO_2 into the oxidized or non-oxidized black liquors through a sparger. Acidification was stopped when the black liquor reached a pH of 9.5. The lignin slurry was, subsequently, agitated gently, in the same tank, in order to allow the lignin particles to grow. After 45 to 60 minutes of coagulation, the lignin slurry was filtered and washed. A small filter press from LAROX was used to filter and wash the lignin. Without any re-slurrying step, the lignin was then washed with two dilute sulphuric acid solutions and then with water. The lignin was, subsequently, dewatered by pressing and air drying to remove excess water. In total, four filtrate samples per experiment were collected in 0.5L Nalgene bottles. Samples were collected during the following steps: a) 1F: the filtration of the acidified BL (lignin slurry), b) 1AW: the first lignin cake acid wash, c) 2AW: the second lignin cake acid wash, and d) WW: the lignin cake water wash and air blow. Each Nalgene bottle was tightly connected to a 1-L Tedlar bag in order to collect the corresponding sulphur compound-containing gas samples. Therefore, four sulphur compound-containing gas samples were collected during each one of the four lignin processing steps and these were analyzed using an SRI 8610 gas chromatograph (GC) with a sulphur-specific detector.

At the end of each filtration/washing step, the gas bag was filled to its 1-L full capacity by blowing nitrogen, as needed, through the lignin cake. Hence, some stripping of sulphur compounds is expected to have taken place due to the blowing of nitrogen through the cake – this practice, is expected to have increased the amount of sulphur-containing compounds collected in each case. Consequently, the results obtained in this study represent the worst-case scenario since no sulphur compound stripping would occur in commercial lignin plants except for the last step in which the lignin cake is air dried.

Results and discussion

Table 1 shows the pH of the filtrates produced from the four different stages of the lignin recovery process at the three different black liquor oxidation levels evaluated in this work.

Table 1. pH of the filtrates produced, at the three different oxidation levels, from the four different stages of the lignin recovery process.

Filtrates	Unoxidized BL	BL oxidized to 0.5 g/L S^{2-}	Fully oxidized BL
First lignin cake filtrate	9.8	9.6	9.5
1st lignin cake acid wash filtrate	9.45	9.1	8.9
2nd lignin cake acid wash filtrate	1.3	1.5	1.5
Lignin cake water wash filtrate	1.8	2	1.6

The pH values of the 1st lignin cake filtrate (pressate) and the 1st lignin cake acid wash filtrate ranged from 9.5 to 9.8 and 8.9 to 9.45, respectively, while the pH values of the 2nd lignin cake acid wash filtrate and the water wash filtrate ranged from 1.3 to 1.5 and from 1.6 to 2, respectively. It must be clarified here that the pH values presented in Table 1 are the values obtained for the total volume of filtrate collected in each experiment. However, in the two lignin cake acid wash steps, it is expected that the pH of the later fractions would be lower than the earlier ones thereby being more likely to liberate pH-sensitive TRS compounds such as hydrogen sulphide and mercaptan. In contrast, in the lignin cake water wash step, the pH of the later fractions is expected to be higher than the earlier ones, levelling off to a steady level once most of the residual acid is removed from the lignin cake.

Figure 1 shows the amounts of H_2S, MeSH, DMS, and DMDS generated during the lignin cake filtration (pressing), first acid wash, second acid wash and water wash steps.

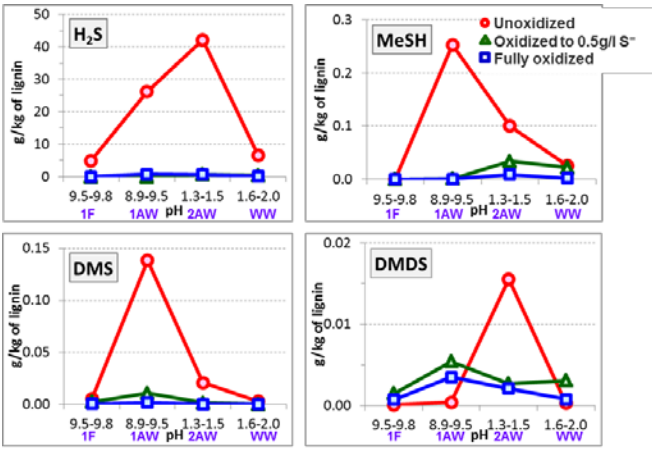

Figure 1. H_2S, MeSH, DMS, and DMDS emissions based on lignin final product from the four main lignin production steps: 1F – lignin cake filtration (pressing); 1AW – 1st lignin cake acid washing; 2AW – 2nd lignin cake acid washing and WW – water washing of the lignin cake.

As seen in this figure, in the case of unoxidized BL, H_2S is produced in all processing steps. About 5g of H_2S/kg of lignin was generated during the first filtration step (pH = 9.8) while about 26g of H_2S/kg of lignin was produced during the 1st acid wash step (pH = 9.45). The maximum amount of H_2S (about 42.10 g of H_2S/kg of lignin) was detected during the 2nd acid wash step (pH = 1.3). In addition, about 6.6g of H_2S/kg of lignin was detected in the last water wash step indicating possible contamination of the lignin cake with H_2S - this could limit the range of applications in which such lignins could be used. In contrast, negligible amounts of H_2S were produced from all processing steps when the BL was oxidized to either 0.5g/L residual sulphide or no residual sulfide. This is likely to be due to the oxidation of NaHS to non-volatile compounds in the latter two cases which are typical of LignoForce System™ black liquor oxidation conditions. The amounts of the organic TRS compounds (MM, DMS and DMDS) generated during these experiments (with and without BL oxidation) were quite low compared to H_2S (below 0.3g of organic TRS/kg of lignin). However, the amounts of these gases were negligible in the case of the two LignoForce™ cases as compared to the conventional process where no BL oxidation was applied. As expected, in the case of unoxidized or oxidized black liquor, the emission of DMS and DMDS did not demonstrate any clear dependence on pH. For unoxidized black liquor, DMS emission peaked during the first acid wash while DMDS emission peaked during the second acid wash.

The results shown in Figure 1 are consistent with the main sulphur species that are expected to be present in solution at any given pH in consideration of the pK_a of hydrogen sulphide which is around 7.04 and that of mercaptan which is about 10.33 [8]. This means that at pH 7.04, 50% of hydrogen sulphide molecules are in the non-volatile sodium form (sodium hydrosulphide, NaHS) while the remaining 50% are in the easily volatilized acid form (hydrogen sulphide, H_2S). Similarly, in the case of mercaptan, at pH 10.33, 50% of mercaptan molecules are in the non-volatile sodium form (sodium mercaptide, CH_3SNa) while the remaining 50% are in the easily volatilized acid form (mercaptan, CH_3SH). As it was mentioned above, the pH values presented in Table 2 are the values obtained for the total volume of filtrate collected in each experiment. Therefore, since during the lignin cake acid washing steps, the pH of the later fractions was lower than the earlier ones, pH-sensitive TRS compounds such as hydrogen sulphide and mercaptan were liberated when the conventional process was used. The generation of TRS compounds in the case of the two oxidized black liquors was rather limited because these compounds were oxidized to non-volatile sulphur species. The LignoForce benefits will be particularly relevant when lignin does not undergo an extensive washing process. For a conventional process, less washing would result in an odorous lignin containing large quantities of reduced sulfur components. Oxidation will minimize LignoForce product odor even if less extensive washing is performed.

Figure 2 shows the amount of SO_2 generated during the lignin cake filtration (pressing), first acid wash, second acid wash and water wash steps.

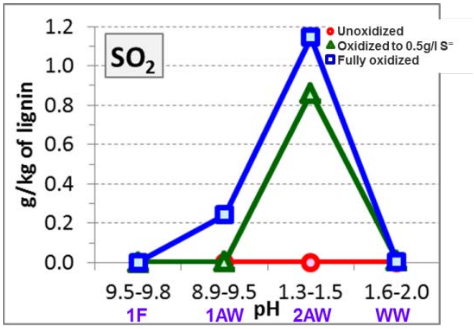

Figure 2. SO_2 emission based on lignin final product from the four main lignin production steps: 1F – lignin cake filtration (pressing); 1AW – 1^{st} lignin cake acid washing; 2AW – 2^{nd} lignin cake acid washing and WW – water washing of the lignin cake.

As seen in this figure, small amounts of sulphur dioxide were detected in the samples that were collected during the filtration and washing of lignin recovered from the two oxidized black liquor samples (LignoForce System™) while no SO_2 was detected in the case of unoxidized BL.

The emission of sulphur dioxide in the case of the two oxidized black liquors is due to the relatively mild oxidation conditions (low temperature, low degree of oxidation, etc…) used in these two experiments. Under these conditions, not all hydrosulphide ions were fully oxidized to sulphate. Instead, some other partially oxidized sulphur species such as thiosulfate were generated. It is well known in the literature that when thiosulphate is exposed to pH levels below 4 (e.g. during lignin sulphuric acid washing step), sulfur dioxide (SO_2) can be generated according to the following reaction:

$S_2O_3^{2-}$ (aq) + $2H^+$ (aq) → H_2O + SO_2 (g) + S (s)

Since significant amounts of sulfuric acid were used during the lignin cake acid washing steps, the pH of the acid filtrates was reduced to levels close to the pK_a of bisulphite (HSO_3^-), which is about 1.8, leading to the generation of sulfur dioxide (SO_2) during these two steps.

As seen in Figure 2, the levels of SO_2 emission from the cases representing the LignoForce System™ are very low as compared to the amount of H_2S produced in the conventional process where no BL oxidation was used (1.14 g of SO_2/kg of lignin produced from the LignoForce System™ vs. 42.10 g H_2S/kg of lignin produced from the conventional process). The low SO_2 emissions from the LignoForce System™ are expected to be easily vented away from the lignin plant to the mill NCG system. In addition, when the NORAM proprietary modified washing cycle is used, the SO_2 emission levels will be further reduced. In addition, as mentioned before, a high acid concentration was used in the lignin acid washing step and a significant amount of nitrogen was used in each step to fill up the gas bags to their 1-L full capacity in order to make sure that all the volatile sulphur-containing compounds produced in the system are captured in the sample bags. Therefore, higher amounts of sulfur-containing compounds are likely to have been stripped from the lignin cake and to a lesser extent from the filtrates, during each step compared to the industrially realistic cases in which no such stripping is part of the process. This was verified in our LignoForce™ Demo plant in Thunder Bay, Ontario.

Based on the results obtained in this investigation as well as prior work, all reactions that are likely to occur in conventional lignin recovery processes as well as in the case of the LignoForce System™ are summarized in Table 2 of Appendix 1.

Conclusions

The sulfur profile of the LignoForce System™ was studied at three different levels of black liquor oxidation. The main findings of this investigation can be summarized as follows:

a) High levels of TRS compounds, and especially H_2S, can be generated at most steps of conventional lignin recovery processes while the BL oxidation step employed by the LignoForce System™ reduces dramatically TRS emissions from all steps of the process.

b) During the second acid wash step of the LignoForce System™, small amounts of SO_2 can be generated. However, this level of emission remains negligible compared to the amount of H_2S produced under the conditions of the conventional process where no BL oxidation is used.

c) About 75.5g vs. 2.2g of volatile sulphur compounds (expressed on a S basis) per kg of lignin was produced from the reference conventional process vs. the LignoForce System™, respectively.

d) Under industrially-realistic conditions, TRS emissions from the conventional process are expected to be lower than the values obtained in this work but still high enough to be of concern in relation to the health and safety of workers in the vicinity of the lignin plant and/or those involved in the processing of the lignin product - this could limit the range of applications in which such lignins could be used.

e) Under industrially-realistic conditions, the TRS and/or SO_2 emissions from the LignoForce System™ are expected to be sufficiently low not to pose any concerns with respect to the health and safety of workers involved in lignin production or processing of the lignin product. This was verified in our LignoForce™ demo plant in Thunder Bay, Ontario.

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Appendix 1

Table 1. Possible chemical reactions during the recovery of lignin from conventional processes and the LignoForce System™.

Conventional process	LignoForce System™
No black liquor oxidation	**Black liquor oxidation (pH: 12-13)**
	$2NaHS + 2O_2 \rightarrow \mathbf{Na_2S_2O_3} + H_2O$ $Na_2S_2O_3 + 2\,O_2 + 2NaOH \rightarrow 2Na_2SO_4 + H_2O$ Organic TRS compounds + O_2 → non-volatile sulphur compounds Sugars → Sugar acids
Black liquor acidification to pH 9-10	**Black liquor acidification to pH 9-10**
$2NaOH + CO_2 \rightarrow Na_2CO_3 + H_2O$ $3Na\text{-}L + CO_2 + H_2O \rightarrow NaHL + Na_2CO_3$ $2CH_3SNa + CO_2 + H_2O \rightarrow Na_2CO_3 + 2\mathbf{CH_3SH}\uparrow$ $2NaHS + CO_2 + H_2O \rightarrow Na_2CO_3 + 2\mathbf{H_2S}\uparrow$	$2NaOH + CO_2 \rightarrow Na_2CO_3 + H_2O$ $3Na\text{-}L + CO_2 + H_2O \rightarrow NaHL + Na_2CO_3$ $2CH_3SNa + CO_2 + H_2O \rightarrow Na_2CO_3 + 2CH_3SH\uparrow$ $2NaHS + CO_2 + H_2O \rightarrow Na_2CO_3 + 2H_2S\uparrow$
Acid washing of lignin (pH: 1.3 – 4)	**Acid washing of lignin (pH: 1.3 – 4)**
$Na_2CO_3 + H_2SO_4 \rightarrow Na_2SO_4 + CO_2\uparrow + H_2O$ $NaHL + H_2SO_4 \rightarrow HL + NaHSO_4$ $CH_3SNa + H_2SO_4 \rightarrow NaHSO_4 + \mathbf{CH_3SH}\uparrow$ $NaHS + H_2SO_4 \rightarrow NaHSO_4 + \mathbf{H_2S}\uparrow$	$Na_2CO_3 + H_2SO_4 \rightarrow Na_2SO_4 + CO_2\uparrow + H_2O$ $NaHL + H_2SO_4 \rightarrow HL + NaHSO_4$ $CH_3SNa + H_2SO_4 \rightarrow NaHSO_4 + CH_3SH\uparrow$ $NaHS + H_2SO_4 \rightarrow NaHSO_4 + H_2S\uparrow$ $\mathbf{Na_2S_2O_3} + \mathbf{H_2SO_4} \rightarrow Na_2SO_4 + \mathbf{SO_2}\uparrow + S + H_2O$

Lignin Firing in Lime Recovery Kilns

KFS: Martin Beddows, Richard Manning, Cliff Rennie

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Abstract/Introduction

Pulp mill operations worldwide have been pushing capacity over recent years. As pulp production increases other parts of the mill, particularly in recaust at the recovery boiler, can become the bottle neck. Lignin extraction technology has been developed to lower the hydrocarbon load in the black liquor to the recovery boiler. Uses for the lignin have been explored including use as a fuel to supplement traditional fossil fuels. The world’s first integrated lignin extraction process to produce lignin which is dried and stored before firing directly into the lime kiln has been started up at the Stora Enso mill at Sunila, Finland. This paper describes the equipment packages used in the process of drying, storing and firing lignin for safe and reliable operation in the kiln. The impact on kiln operation from continued use of the new fuel together with the key lessons learned will be described.

Paper Content

Background

The paper outlines the history of development of lignin extraction from black liquor through to installation of the world’s first commercial integrated dry lignin production/lime kiln combustion system at the Stora Enso Sunila Mill in Finland. The main equipment provided by Kiln Flame Systems (KFS) is summarised as part of the Stora Enso Sunila Mill Selix Project.

Conventional Fossil Fuels vs Lignin

The typical combustion properties of different fuels are evaluated in comparison to traditional fossil fuels used in lime kiln i.e. natural gas and oil.

Lignin System Design

The paper considers the design requirements related to the use of dry lignin as a fuel within the storage, transportation and combustion systems including moisture content, low melting point of the material, low minimum explosion energy, static build-up. Some of the practical issues related to the design, manufacture and commissioning of the equipment are discussed.

Comparison of Combustion Performance Before and After Start-up

Data collected during the commissioning of the lime kiln is analysed in detail.

Summary

Dry lignin has been proven to be a viable option for substitution of conventional fossil fuels in lime kilns as part of the Kraft recovery process. While this has provided some challenges due to its physical properties and characteristics of the lignin, safe and reliable operating system have been demonstrated. Additional work is planned to increase the % lignin substitution rates over time.

Lignin Properties for the Biorefinery, and Their Analytical Challenges

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Background

Utilization of lignin for high-value applications requires processing to achieve certain chemical and molecular properties. This in turn requires robust and precise chemical analysis methods. Without reliable analytical methods, systematic improvement of process and product becomes very difficult or even impossible.

Most of the currently used methods for characterization of lignin structure were developed for wood and pulp samples, often aiming at understanding wood structure and delignification. In order to apply these methods for improved production of high-value lignin, further method development or method adaption is needed. Furthermore, no official standardized methods for lignin are available. As a consequence, the results from analysis of lignin properties largely depend on which method or laboratory that is used. Harmonized methods are essential to facilitate communication between manufacturers and purchasers. In the past years these questions have been addressed for example within the framework of the EuroLignin network [1-3]. A number of draft analytical protocols are available for ILI members on [http://www.ili-lignin.com/projects/norms.php]. However, still, much remains to be done. Finally, development of new value-added lignin products will most likely generate a need for new, more detailed analyses compared to those developed for pulping applications.

The most important lignin characteristics that need to be addressed are purity, molecular structure and thermal properties. The challenges for analysis of these parameters will be discussed in the present paper.

Purity

Analysis of lignin purity includes determination of:

- Lignin content
- Carbohydrates
- Extractives
- Volatile compounds
- Ash
- Metals
- Sulphur, etc.

In connection with lignin purity, specifications concerning the requirements for different applications are lacking, and harmonized and more sensitive methods are needed.

Molecular properties

Important lignin molecular properties include molecular mass, molecular mass distribution, molecular size, as well as content and distribution of functional groups. Attempts to harmonization of methods have indeed been made, but still no standard method is available. As a consequence, the results from analysis of these properties largely depend on which method, or which method parameters, are used.

Thermal properties

Thermal properties of interest for lignin product development are for example glass transition temperature (T_g), decomposition temperature (T_d), curves from differential scanning calorimetry and thermogravimetric analysis, viscosity, etc. As in the case of molecular properties, attempts towards harmonization have been made but no standard methods are available [2-4].

Summary

In order to allow producers of biorefinery products to prepare specifications for their products, and to improve the possibilities for systematic development of process and product, relevant and harmonized analytical methods are needed. This demands evaluation of the current status of the most important methods for lignin characterization, as well as method development or method adaption in order to meet the requirements for high-value lignin products.

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Thermochemical biorefinery & products

High Quality Renewable Diesel Fuel from Forest Industry Residues

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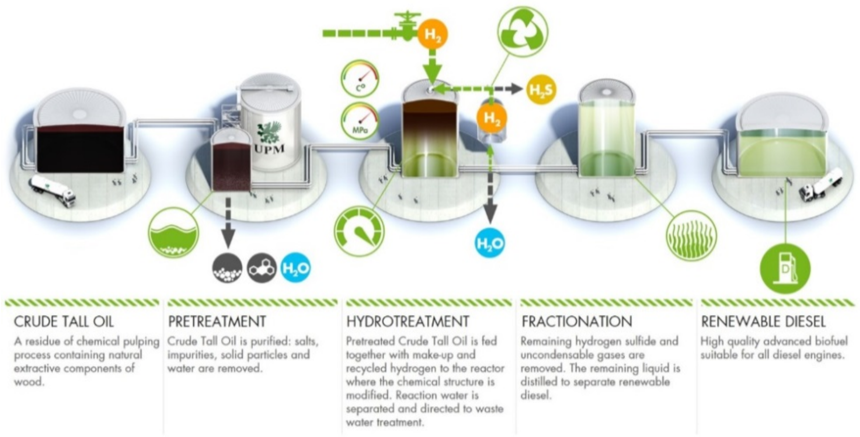
Introduction

The Finnish bio and forest company, UPM, has built a first of a kind biorefinery producing wood-based advanced biofuels to Lappeenranta, Finland. The commercial production started in January 2015, and the annual capacity is 100.000 tonnes of pure renewable diesel. UPM uses its own wood-based residue of pulp making process, crude tall oil (CTO), as raw material of the biorefinery. Majority of the raw material comes from UPM´s own pulp mills in Finland.

The biorefinery is based on hydrogenation process (Figure 1.) and the product has fuel properties comparable to EN590 diesel fuel with significant improvement in other properties, such as cetane number. It can be used as such or as a blending component in all diesel engines without modification, and it reduces greenhouse gas (GHG) emissions by 80% compared to traditional diesel. Moreover, it does not compete with food production like first generation biofuels.



CRUDE TALL OIL
A residue of chemical pulping process containing natural extractive components of wood.

PRETREATMENT
Crude Tall Oil is purified: salts, impurities, solid particles and water are removed.

HYDROTREATMENT
Pretreated Crude Tall Oil is fed together with make-up and recycled hydrogen to the reactor where the chemical structure is modified. Reaction water is separated and directed to waste water treatment.

FRACTIONATION
Remaining hydrogen sulfide and uncondensable gases are removed. The remaining liquid is distilled to separate renewable diesel.

RENEWABLE DIESEL
High quality advanced biofuel suitable for all diesel engines.

Experimental

The biorefinery product has been tested in various test facilities in Europe, as a blending component with regular EN590 diesel fuels. Also 100% UPM BioVerno diesel has been tested against fossil EN590 diesel. These laboratory tests proved that the CTO-based renewable diesel can be used as a blending component or as a 100% product, without compromising the engine functionality or increasing the fuel consumption. The fuel properties, such as high cetane and low aromatic content had a decreasing effect to the overall emissions.

UPM BioVerno diesel has also been tested previously in passenger car field tests. The aim of the field test was to evaluate the functionality and performance of four passenger cars (Figure 2.) by taking into account fuel consumption and exhaust emissions when compared to fossil reference fuel. The field test included 80.000 km on-road driving, 20.000 km with each car by experienced drivers from VTT with variable trip lengths, traffic and climate conditions. Initial, mid-term and final in-laboratory tests were run for performance and emissions. Four other make/model cars were subjected to similar tests with UPM BioVerno test blend and reference diesel. Apart from regulated exhaust emissions, a list of non-regulated species were also measured.

Figure 2. Bioverno fleet vehicles.

Discussion

In the passenger car field tests, UPM´s renewable diesel proved to be a high quality blending component that did not change the functionality nor the emission characteristics of the tested diesel passenger cars. These results, together with other engine and vehicle tests, prove the functionality and usability of crude tall oil based renewable diesel in modern diesel engines. In addition, one of the BioVerno test cars is still on test drive, and the results are the same as initial findings.

The Role of Intermediate Products in Biorefinery Development

- Kraft Lignin and Pyrolysis Oil as Intermediates for Production of Naphtha Cracker Feed from Forest-Based Raw Materials

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Abstract

Replacement of fossil fuels and raw materials with renewable equivalents with low CO_2 footprint is a topic high on the agenda today. This study investigates the implications of replacing fossil naphtha cracker feed to a petro chemical plant with feed products produced from forest biomass, assuming value chains with production of intermediate products integrated with regional pulp mill industry. Pyrolysis oil and kraft lignin are the investigated intermediates. Yield, cost and CO_2 footprint from full value chain calculations are reported and compared to direct production of bio naphtha from forest residues at the petrochemical plant and fossil naphtha.

Introduction

One important aspect when replacing fossil raw materials with biomass is the low energy density of biomass as harvested. Raw material transportation costs can thus rapidly become prohibitive in establishing a large scale biorefinery. It is thus of great interest to develop processes that densify biomass and turn it into a so-called intermediate product that can be transported more easily with lower specific transportation emissions and less cost. Examples of intermediate products are pyrolysis oil, wood pellets, purified lignin, and alcohols. Another important aspect is the heterogeneous nature of biomass raw materials, which makes it complicated to use for direct replacement of conventional fossil feed. Conversion to an intermediate product can be a benefit here, as the intermediate is processed to be more uniform in quality. However, one negative aspect introduced when considering dividing the conversion into final product into several steps is the risk of reduced overall conversion yield, and increased investment in process equipment. This potential disadvantage can be counteracted by savings in infrastructure and costs for build-up of know-how, if the conversion to intermediate product is integrated with another industry that already processes biomass.

Combined with the possibility to utilise by-products, excess energy and efficient integrations, substantial cost savings can potentially be made.

The goal of this study is to estimate key performance factors important for development of biomass value chains with intermediate products. This is accomplished by studying specified value chains with production of intermediates in a large kraft pulp mill. Biomass raw material available for export, either in the form of by-products from pulp production or from collection and transportation of forestry residues (forestry residues, stumps) from the nearby area are used. The selected intermediates are kraft lignin and pyrolysis oil. The intermediates are transported to a large petrochemical industry for final conversion to the end product. In the selected case, the end-product should be suitable as feed product to a naphtha cracker. The results are put into relation with direct conversion of forest residues to naphtha cracker feed at a petrochemical plant and the use of fossil naphtha.

Value chain evaluation

The three bio-based value chains evaluated in this study to produce a bio-based feed to a naphtha cracker are illustrated in **Figure 1** - **Figure 3** below, including the reference chain with direct transport followed by conversion of the biomass at the naphtha cracker site, **Figure 1**.

In the cases with production of intermediates at a pulp mill, (Figure 2 - Figure 3), it is assumed that three hypothetical nearby pulp mills of the same size support one centrally located petrochemical site with a naphtha cracker with the bio-based intermediate product based on locally sourced raw material. In the reference case, all the raw material is sourced around the refinery site and transported to the centrally located biomass conversion plant at the refinery. The same total amount of biomass raw material are utilised in all cases.

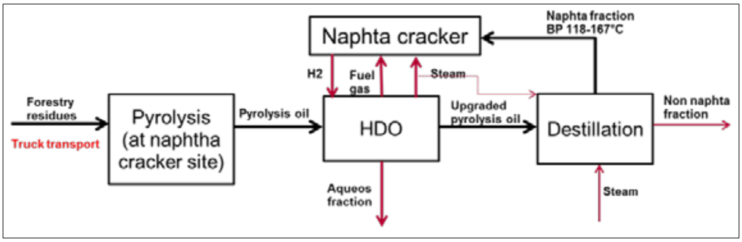

Figure 1. Biomass based value chain without intermediate. Forest residues are transported directly to the naphtha cracker. *(Yellow bars in following figures)*

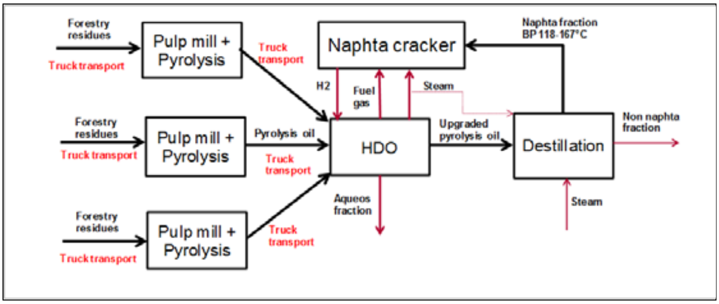

Figure 2. Biomass based value chain with pyrolysis oil as intermediate. The pyrolysis of forest residues is located at the pulp mill. *(Green bars in following figures)*

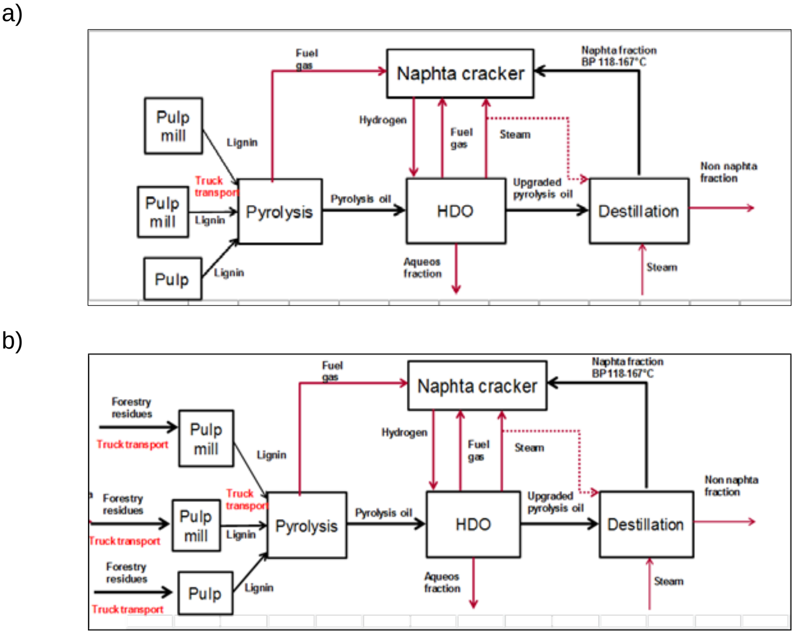

Figure 3. a and b. Value chain with kraft lignin separated from black liquor as intermediate. The lignin is transformed to pyrolysis oil, hydro deoxygenated and distilled at the site of the cracker. In option a, the electricity production at the mill is reduced as a consequence of lignin removal, leading to less electricity export. This is compensated by externally generated electricity. In b additional forest residues is instead used in a biomass boiler to compensates for the reduced steam production due to lignin removal. *(a) light blue bars, (b) dark blue bars) in Figures.*

The reference point for description and comparison of the identified value chains is the end product delivered at user location, in this case naphtha cracker feed product delivered at the gate. The entire value chain from forest to end-product is evaluated, including production of intermediate and end-product as well as collection, preparation and transportation of the forestry by-product and intermediate. All changes in mass and energy flows, investments and fossil CO_2 emissions are calculated and compared to the base case with normal pulp mill operation (without integration with lignin removal and pyrolysis) as well as naphtha cracker operation without integration of bi-products or need of utilities as a result of upgrading of the bio-based material at the refinery site. The same approach is applied to the reference value chains where the forest by-product will be transported directly to the end-user site (naphtha cracker) without conversion to intermediate for direct conversion to the end product. It should be noted that external costs related to changes in NO_x, SO_x, and particle emissions as well as revenues and costs from policy instruments, with the exception of renewable electricity certificates (16 €/MWh), have not been included.

The following *main* assumptions have been used in the example evaluation presented in this paper, see **Table 1**. Further details about the assumptions can be found in [1].

Table 1. Main assumptions used for evaluation of biomass value chains.

Assumption	**Description**
Total raw forest biomass feed	213 MW, LHV 8 MJ/kg wet, 14 €/MWh
Outtake of forest residues, case with intermediates	Outtake around 3 pulp mills. Average truck transport distance 50 km from an area 70 km in diameter.
Outtake of forest residues, case without intermediates	Average outtake is 50% of case with intermediate due to location and expected forest growth density. Average transport 122 km from an area with a radius of 173 km.
Pulp mill for integration	2010 BAT Scandinavian softwood pulp mill [2]. 700 000 ADt/y. Condensing turbine.
Kraft lignin production	76 200 t DS/y, i.e. about 20% removal. Dried to 3-6% moisture before transport, 26-28 MJ/kg tot. LignoBoost technology.
Transport distance, pulp mill to refinery	150 km
Truck transport cost and fossil CO_2 emissions, forest residues	3140 + 79.9 x €/GWh[1] 29.4 g CO_2/MWh, km
Truck transport cost and fossil CO_2 emissions, dried lignin	600 + 14.4 x €/GWh 9.28 g CO_2/MWh, km
Truck transport of pyrolysis oil	1013 + 24.3 x €/GWh 15.7 g CO_2/MWh, km
Pyrolysis of forest residues	64 % wt., dry feed, 40% wt. O, 25% H_2O, 16 MJ/kg tot,
Pyrolysis of lignin	60% energy, dry feed, 16% O, 20% H_2O, 16 MJ/kg tot.
CO_2 footprint, electricity	102 kg/MWh (Sw. mix)
Oxygen after HDO	5% wt.
Distillation yield	70% MWh/MWh (lignin and forest residues)
CO_2 footprint, crude oil assumed to be replaced by char and gases from pyrolysis and heavy fraction	309 kg/MWh
CO_2 footprint, H_2	10 t/t H_2
Operating hours	7800 h/y
Annuity factor	0.1
Electricity	40 €/MWh
Steam	18 €/MWh (HP), 12 €/MWh (LP)
Natural gas/fuel gas	35 €/MWh
Oil	Fuel oil 40 €/MWh, Crude oil 85 $/barrel
Maintenance	2% of investment
Investment, forest residue reference	191 (pyro) + 100 (HDO) + 25 (dist.) = 316 M€ [2]
Investment, pyro oil intermediate	53*3 (pyro) + 100 (HDO) + 25 (dist.) = 284 M€
Investment, lignin intermediate	29*3 (LB) + 186 (pyro.) + 95 (HDO) + 23 (dist.) = 391 M€ [2]
Investment, lignin intermediate, electricity from forest residues	29*3 (LB) + 49*3 (bio boiler) + 186 (pyro.) + 95 (HDO) + 23 (dist.) = 520 M€ [2]

Innventia's simulation model in WinGEMS is used to simulate the hypothetical reference pulp mill and effects of integration with the lignin removal (LignoBoost) and pyrolysis equipment.

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[1] x is the distance in km

[2] Cost of pyrolysis plant has been estimated to be higher in close proximity to refinery, 20% additional cost has been estimated on equipment and engineering, construction and start-up costs are estimated to be 3 times higher.

Results and discussion

About 700-750 GWh/y of naphtha cracker feed can be replaced with a feed product produced from the forest material in each of the cases according to the calculations. This represents about 10-15% of the total feed to a large petrochemical site like the one in Stenugnsund, Sweden. The overall yield from the 1 660 GWh/y forest based biomass to naphtha cracker feed is 43-46% on energy basis. The yield in the cases with lignin is in the lower end due the assumed slightly lower pyrolysis yield, 60% vs. 64% for forest residues. The yield for lignin is very uncertain, as very few experimental results are available.

Another major difference between the cases based on pyrolysis of lignin and forest residues is the demand of hydrogen to reach the targeted 5% oxygen content in the pyrolysis oil, 3 ktonne/y vs. 12 ktonne/y. This is a result of the lower oxygen content in lignin compared to forest residues and the estimated lower oxygen content in the resulting pyrolysis oil, 16% vs. 40%. However, experimental verification data on elemental composition of pyrolysis oil from lignin is lacking.

One of the main items investigated is the impact on energy demand, cost and emissions as a result of transportation of the forest raw material and the intermediates. Figure 4 shows the direct diesel consumption for the different cases. Lower diesel consumption is found for all cases with intermediates under the specific assumptions used.

The resulting specific CO_2 emissions per MWh naphtha cracker feed produced is shown in Figure 5 and range between (-80) – 44 kg/MWh or (– 1000) – 550 kg/tonne naphtha feed. The main processes influencing the CO_2 emissions are use of hydrogen from methane steam reforming in the HDO process, use of remaining fractions from the distillation of the upgraded pyrolysis oil to replace petroleum products in the petro-chemical plant and the emissions from the replacing electricity production in the case where lignin removal is not compensate with steam production in a new biomass boiler. Use of diesel for transportation of raw material or intermediates has a minor influence on the overall CO_2 emissions.

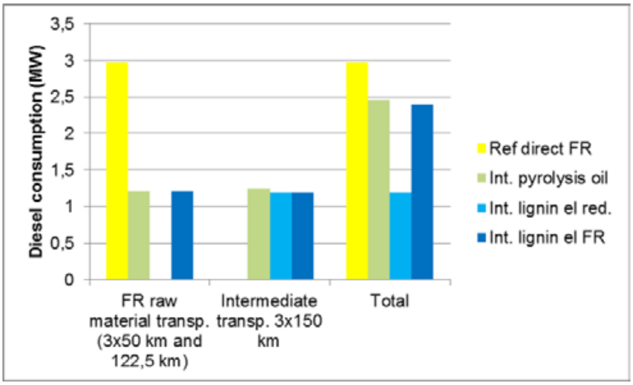

Figure 4. Diesel consumption for transport of forest residues and intermediates, assuming a forest residue and lignin input of 212 MW in all cases.

As a comparison, the reported CO_2 footprint of fossil naphtha is in the range of 336-520 kg/tonne naphtha, excluding the last step in the lifecycle where the product produced from naphtha is combusted releasing its carbon content as CO_2. If this final step is included, the footprint is increased to about 3 500 kg CO_2/tonne naphtha.

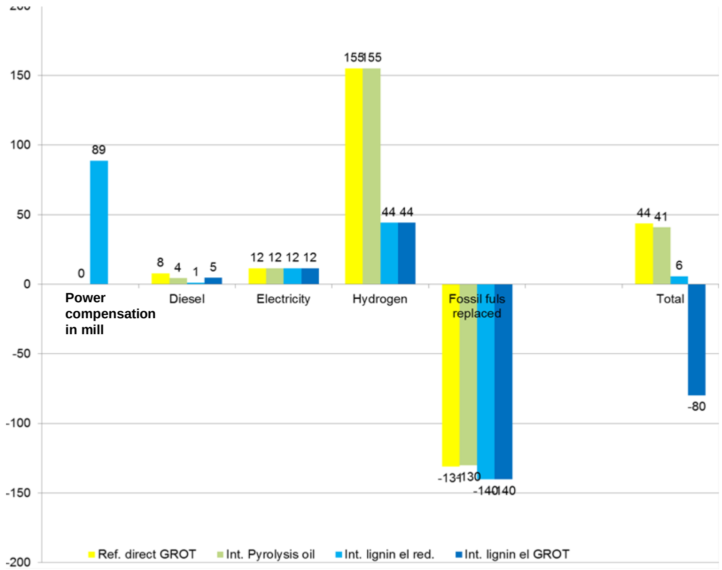

Figure 5. Specific CO_2 emissions from the described value chain to produce naphtha cracker feed. H_2 and electricity CO_2 footprint is estimated based on natural gas steam reforming respective Swedish electricity mix. Grot = forest residues.

The total (CAPEX and OPEX) naphtha cracker feed production cost broken down on the different main steps in the value chains is found in **Figure 6**. The total cost ranges from 116-160 €/MWh naphtha feed or 1 450-2 000 €/tonne. The value chain with pyrolysis oil produced directly from forest residues integrated with pulp mills as intermediate shows the lowest overall cost with the given assumptions, however the difference in total cost to the reference chain with total production at the petrochemical site and the lignin chain integrated with the pulp mill are still within the uncertainties of this study. A higher production cost is found in the case with lignin as intermediate where loss in power production at the pulp mill is compensated by steam production from a new biomass boiler at the pulp mill fuelled by forest residues (the combined cost of “outtake of forest residues”, “transportation of forest residues” and “power compensation…”).

The total cost of transportation of biomass (raw material and intermediate) is in the range of 7-28 €/MWh naphtha cracker feed with the given assumptions, i.e. in the range of 5-20% of the total cost.

As comparison, when this study was originally conducted in the fall of 2014 the fossil naphtha price fluctuated between 900 and 950 $/tonne. The current naphtha price is about 470 $/tonne (July, 2015). The cost of fossil naphtha varies with the oil price. However, also the electricity price is lower reducing especially the cost of the lignin case with compensating external power generation (light blue bars).

The current assessment of the lignin intermediate value chains has not taken into account the added value of increased pulp production through debottlenecking of the recovery boiler, which makes up a high potential but very site specific value, as the additional investments and potential to realise the increased production is dependent on the available over-capacity in the different parts of the pulp mill.

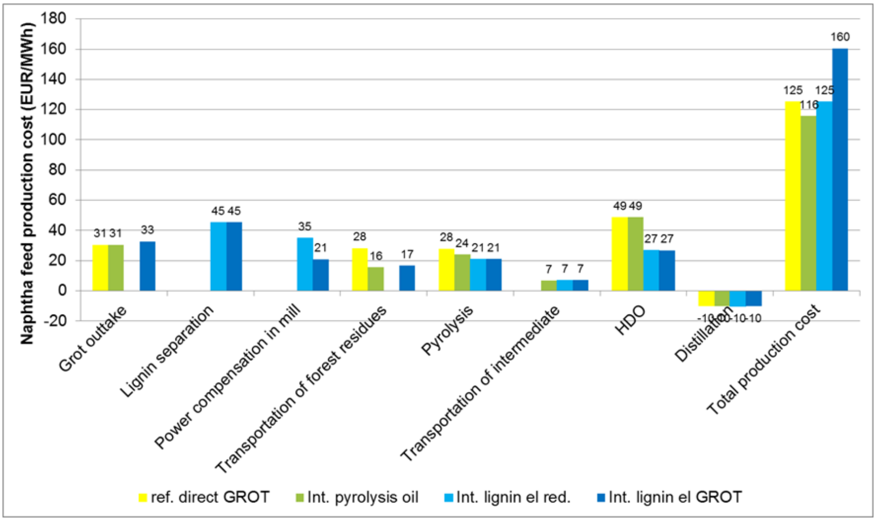

Figure 6. Naphtha cracker feed production cost (CAPEX + OPEX) (EUR/MWh naphtha cracker feed) broken down on the main process steps in the value chains and total. Use a factor of 12.5 MWh/tonne naphtha feed to convert to mass-basis.

Conclusions

- Use of intermediates produced integrated with decentralised local industrial plants has been shown to be a way to reduce total cost and CO_2 emissions of transporting forest based biomass to a centrally located conversion plant. This is valid in case the transport distances are long, the intermediate energy densification is high and the local availability of biomass around the central plant is low. However, the study has also revealed that the economic benefit is not very large in relation to the overall value chain cost to produce the final product. Other factors are more likely to promote introduction of value chains with intermediates. Examples of such factors are possibilities for efficient integration with existing industry, use of existing knowledge of handling and processing the raw material and utilisation of existing infrastructure, safety aspects, possibilities to handle large investment in new equipment and processes, demands on profitability and margins on production costs, business model and other specific market aspects.
- Bio-based naphtha cracker feed can be produced at a cost of about 1 500 €/tonne naphtha cracker feed (September 2014 costs), to be compared to the naphta price in September 2014 of 900-950 $/tonne, (which follows the crude oil price).
- The CO_2 footprint is estimated in the range of (– 1000) – 500 kg CO_2/tonne bio based naphtha feed, with the lower range valid for lignin as intermediate. The footprint is mainly dependent on the necessary amount and source of H_2,

possibilities to replace fossil raw material with the by-products from processing of the forest material, and how the reduction of power production in the mill is replaced with lignin as intermediate. These factors also have a significant effect on the overall cost. The CO_2 footprint of fossil naphtha is 336-520 kg/tonne naphtha, and about 3 500 kg CO_2/tonne if the final step in the lifecycle where the carbon content of the product produced from naphtha is released as CO_2.

- The cost of using fossil based raw materials and cost of resulting CO_2 emissions, including final destruction, when fossil based carbon is used in products need to be higher than what is the case today in order for bio-based materials to be competitive purely based on economic terms.
- Kraft lignin from pulp production is a very interesting intermediate especially in case the economic benefit of increased pulp production through lignin removal can be realised and the expected performance of pyrolysis of lignin can be demonstrated. The last requires more R&DD activities. Additionally, efforts to minimize H_2 consumption and cost and improve distillation yield are beneficial. There is then a good potential to reduce the economic gap to the fossil naphtha price.

Acknowledgements

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Fast Pyrolysis of Biomass into Fuels and Chemicals

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Extended abstract

Two first commercial size pyrolysis plants for renewable energy production in the world have been commissioned 2014-15: one in Joensuu, Finland, by Fortum and Valmet, and the other in Hengelo, the Netherlands by BTG-BTL/EMPYRO [1,2]. The aim of both of these installations is to produce high-quality renewable heating bio-oil from woody biomass, e.g. forest residues. Valmet has integrated the bio-oil demonstration plant to an existing 200 MWth Fortum combined heat and power (CHP) plant in Joensuu, Finland [13]. The nominal output of the pyrolysis plant is 30 MW of bio-oil with a planned annual output of 50,000 tons which equals to 210 GWh of energy. The demonstration plant will utilize 225,000 solid cubic meters of forest residue and sawdust annually. At the moment the main market for the fast pyrolysis oil is to replace heavy fuel oil (HFO). Standardisation towards boiler fuels under CEN is going-on [3].

The same technology may also be developed further for the production of transportation fuels and chemicals. One of the challenges in bio-oil storage and use is to avoid the phase-separation into aqueous and lignin-rich phases [4]. This phenomena could be applied as advantage for chemical production. If a wet feedstock is used for thermal fast pyrolysis, a spontaneous phase-separation of the aqueous and lignin-derived phases is obtained (Figure 1).

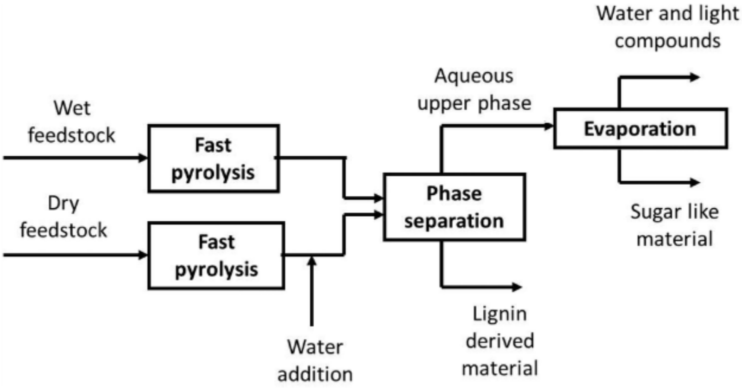

Figure 1. Fast pyrolysis as a fractionation process for fuels and chemicals. [15]

The aqueous phase organics can be converted for example into hydrogen by steam reforming [14], ethanol through fermentation, butanol via entsymatic treatment, or furfurals. Lignin-phase can be processed for example into oil refinery feed for fuels and chemicals [5], or hydrocarbons via catalytic hydrotreatment. Acids may be recoved as by-products. By substituting sand with catalyst heat as the energy source for pyrolysis, a more aromatic oil product (Figure 2) is obtained [6], which is potentially easier to convert further to transportation fuels due to e.g. its lower oxygen content. In order to better evaluate the viability of the various upgrading options that are being developed for fast pyrolysis bio-oil, detailed knowledge about the composition and the properties of the bio-oil is essential [7-12]. In-depth characterization of the bio-oil will also help to understand its behaviour and the challenges in the subsequent upgrading steps.

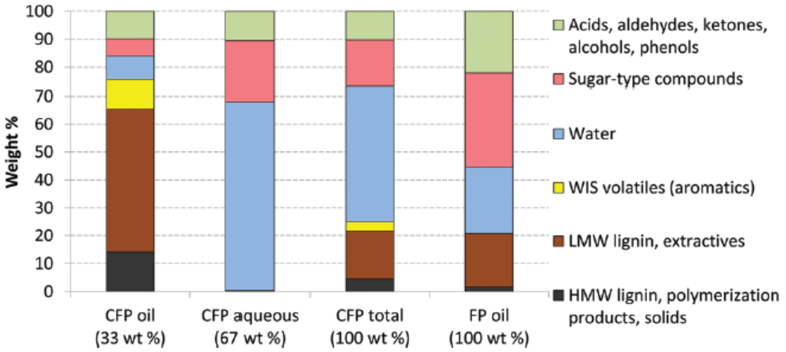

Figure 2. Solvent fractionation of CFP (catalytic fast pyrolysis) oil, CFP aqueous fraction and typical FP oil from pine. Relative amounts of product fractions are included for the two phase CFP product. [6]

This fractionation concept was developed in the EU Biocoup project in 2006–2011 [15]. A critical aspect of the biorefinery development program is industrially credible implementation. Phased implementation of the biorefining industry is considered to reduce risks for the investor. With phased construction, a realistic development path may be presented, in which new units are taken into operation at different times. The eventually complex biorefinery is built up in stages, allowing each new unit to evolve relatively independent of other new units. The procedure reduces risks in development and assures low development costs. Integration with existing mineral oil refinery infrastructure minimises overall costs. Figure 3 shows a chain of process steps, which integrate biomass conversion processes and equipment to produce transportation fuels, power, and chemicals from biomass in a phased industrial implementation mode. The bio-refinery concept is analogous to today's petroleum refineries, which produce multiple fuels and products from petroleum. Industrial bio-refineries are proposed as the most promising route to the creation of a new bio-based industry.

Based on Biocoup results extraction was the most suitable isolation technology for all target oxygenates [16]. The isolated oxygenates were fractionated (purified) by a multitude of techniques of which distillation appeared the most versatile for oxygenate recovery from the solvent as well as impurity/solvent removal. It appeared that the integrated isolation of acetic acid and glycoaldehyde offered much higher economical potential compared to their separate isolation, mainly due to increased yields and strongly reduced energy consumption. Aldehyde products and specially from the furanic family can be extracted from the wood oil pyrolysis process. After hydrogenation these aldehyds can be transformed into alcohol which have a potential interest alone or in mixture in bio solvent application.The work done toward this project consists in studying new solvent mixture of a fluorine product and furfurilic alcohol.

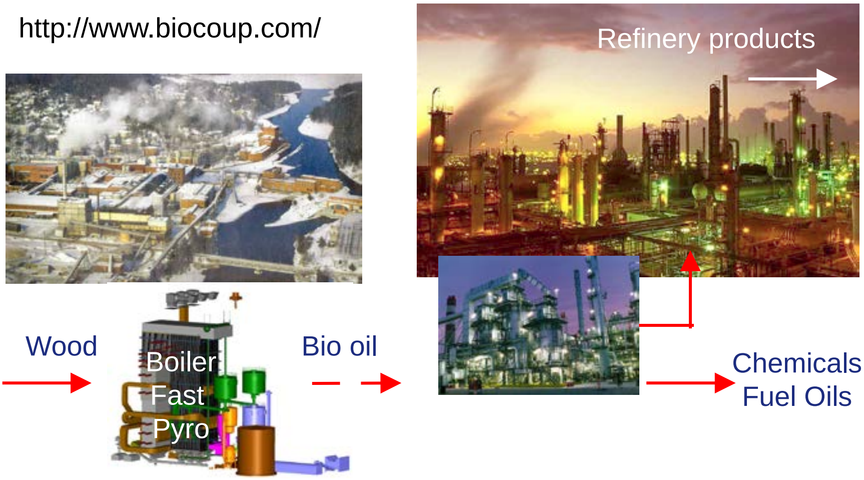

Figure 3. The biofuel chain is integrated to existing industries. [13]

Greenhouse gas (GHG) reduction potential for fast pyrolysis bio-oil concepts is high, especially when by-products are used efficiently. A GHG reduction of nearly 90 % has been reported, when mineral heating oil is produced. Recently VTT evaluated together with PNNL a GHG reduction of 63 %, when production of transportation fuels was considered. However, also higher GHG reductions have been reported in literature [17].

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Pressurized Entrained Flow Gasification of Pulverized Wood – Experimental Characterization of the Process Performance

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Abstract

One of the goals in the national energy strategy of Sweden is that the vehicle fleet should be independent of fossil fuels by 2030. Pressurized, oxygen blown, entrained flow gasification of forest residues followed by methanol production is one of the suggested routes for the production of synthetic motor fuels that could help reach this goal. One of the benefits with entrained flow gasification is that a syngas with high quality is generated. The high syngas quality is necessary for the subsequent synthesis to biofuels. Nevertheless, the efficiency of the process must be sufficient in order to make this technology economically viable and commercially attractive. In this context, a thorough process characterization was conducted with pulverized stem wood fuel in the 1 MW pilot plant at SP Energy Technology Center AB in Piteå, Sweden. Four of the most important process parameters (i.e. oxygen stoichiometric ratio (λ), fuel load, process pressure and fuel particle size distribution) were varied in order to study the effect on the process performance and the syngas quality. The experimental results of this work showed that the maximum cold gas efficiency (CGE) based on all combustible species of the syngas was 75% (at $\lambda = 0.30$), whereas the corresponding value based only on CO and H_2 was 70% (at $\lambda = 0.35$). To generate a high quality syngas, the gasifier should preferably be operated with a λ aiming for process temperatures above 1400 °C in order to keep the levels of CH_4 and other unwanted syngas species low. At this temperature (1400 °C), the experimental results suggest that a plug-flow residence time of 3 sec was sufficient to reduce the syngas concentrations of CH_4 and C_6H_6 below 1 mol-% and 100 ppm (on a dry and N_2 free basis), respectively. These results provide valuable information in the evaluation of the process from a system perspective, which subsequently can aid in decision making whether a specific installation is commercially viable.

Introduction

One of the goals in the national energy strategy of Sweden is that the vehicle fleet should be independent of fossil fuels by 2030 (Swedish Government, 2009). Pressurized, oxygen blown, entrained flow gasification of forest residues followed by methanol production is one of the suggested routes for the production of synthetic motor fuels that could help reach this goal (Börjesson & Ahlgren, 2012). One of the benefits with entrained flow gasification is that a syngas with high quality is generated (Higman & van der Burgt, 2008). The high syngas quality is necessary for the subsequent synthesis to biofuels, where impurities otherwise can cause problems (Woolcock & Brown, 2013). Nevertheless, the efficiency of the process must be sufficient in order to make this technology economically viable and commercially attractive. In this context, a thorough process characterization was conducted with pulverized stem wood fuel in the pilot plant at SP Energy Technology Center in Piteå, Sweden. Four of the most important process parameters (i.e. oxygen stoichiometric ratio (λ), fuel load, process pressure and fuel particle size distribution) were varied in order to study the effect on the process performance and the syngas quality.

Experimental

The gasifier and associated analytical equipment

The Pressurized Entrained flow Biomass Gasification (PEBG) pilot plant was designed for a maximum fuel load of 1 MW_{th}, 10 bar gasification pressure and to operate in slagging mode with process temperatures up to 1600 °C. A detailed description of the plant can be found elsewhere (Weiland, Hedman, Marklund, Wiinikka, Öhrman, & Gebart, 2013) and therefore only a brief description is given herein. The PEBG gasifier consists of a ceramic lined reactor (0.52 m inner diameter and approximately 2 m long) followed by a water sprayed quench for syngas cooling and smelt/particle separation. The burner where the pulverized fuel and oxidant (O_2) were injected was installed in the top of the reactor. Process temperatures were monitored by ceramic encapsulated type S thermocouples at different locations close to the reactor wall inside the gasifier. The raw syngas and other products from the reactor (i.e. gases, particulates and ash/char) were cooled to temperatures below 100 °C by water sprays in the quench. The process pressure was controlled by a regulating valve on the syngas outlet pipe. A small slip stream of the cooled syngas was continuously sampled and analyzed by a micro GC for the concentrations of the major syngas species (i.e. CO, H_2, CO_2) and CH_4. In addition, the syngas was sampled using 10 dm^3 foil gas sample bags for the analysis (on GC) of higher hydrocarbons such as benzene (C_6H_6). The gas sampling and analysis procedures are described in detail in previous publications (Weiland, Wiinikka, Hedman, Wennebro, Pettersson, & Gebart, 2015). Finally, the produced syngas was flared to eliminate any risks connected to the syngas.

Fuels and operating conditions

Table 1. Proximate and ultimate analysis of the stem wood fuels.

Proximate analysis	**GME**	**ST**
Moisture (%)	6.7	7.7
Volatiles (% ds[a])	82.4	84.4
Fixed carbon (% ds[a])	17.2	15.2
Ash (% ds[a])	0.36	0.37
Ultimate analysis		
C (% ds[a])	50.8	51.3
H (% ds[a])	6.2	6.4
O (% ds[a])	42.5	41.8
N (% ds[a])	<0.1	<0.1
S (% ds[a])	<0.012	0.024
LHV (MJ/kg ds[a])	19.6	19.5

[a] dry substance

Commercial stem wood pellet fuels were used in the characterization experiments due to its availability, its relatively uniform composition and its low ash content. The pellets were manufactured of stem wood from pine and spruce by two independent companies, Glommers MiljöEnergi AB (GME) and Stenvalls Trä AB (ST) and had similar compositions (**Table 1**).

The fuel pellets were milled in a hammer mill (MAFA EU-4B) before the fuel powder was filled into the fuel hoppers in the plant. Three different sieve sizes were used in the hammer mill (0.50 mm, 0.75 mm and 1.50 mm) to generate and test different fuel particle size distributions. The characteristic size distribution numbers d_{50}:d_{90}, representing the mass median particle size under which 50 % and 90 % of the distribution lies, were 125:230, 130:240 and 180:410 µm for the three resulting powders, respectively.

An extensive experimental set-up of gasification experiments were then executed where the operational parameters (1) O_2 stoichiometric ratio (λ), (2) fuel load and (3) gasification pressure were varied within the ranges: $0.25<\lambda<0.50$, 200 kW<fuel load<600 kW and 2 barA<pressure<7 barA, respectively. Each set-point was operated for at least 2 h, in order to reach thermal equilibrium of the gasifier, before the final samples were taken. Additionally, some of the set-points were repeated in order to estimate the robustness/repeatability of the process and thereby obtain important statistical measures for the process evaluation.

Results and discussion

Resulting process temperature and syngas yield

The process temperature is strongly affected by the stoichiometry (i.e. λ) during gasification. Increasing λ means increasing the proportion of O_2 fed to the gasifier.

This means that the exothermic combustion reactions are enhanced. Therefore, a λ increase results in increased process temperature. As an example, the measured process temperature at 600 kW fuel load and λ = 0.30 was approximately 1180 °C. Additional increase of λ in steps of 0.1 resulted in temperature increasing approximately 150-200 °C per step.

The experimental yields of the major syngas components (CO, H_2 and CO_2) and CH_4 are presented in **Figure 1**. The yields of CO and H_2 exhibited optima at λ~0.42 and λ~0.35, respectively. The syngas composition of H_2 and CO was such that the ratio H_2/CO was about 0.6. Therefore, the syngas requires shifting towards higher H_2 content prior to methanol synthesis (should be ~2). The yield of CO_2 was increasing with λ because of the increased proportion of combustion at higher λ. Furthermore, the yield of CH_4 was strongly correlated to process temperature, as will be discussed later, and reached up to 3.6 mol/kg fuel at λ = 0.25.

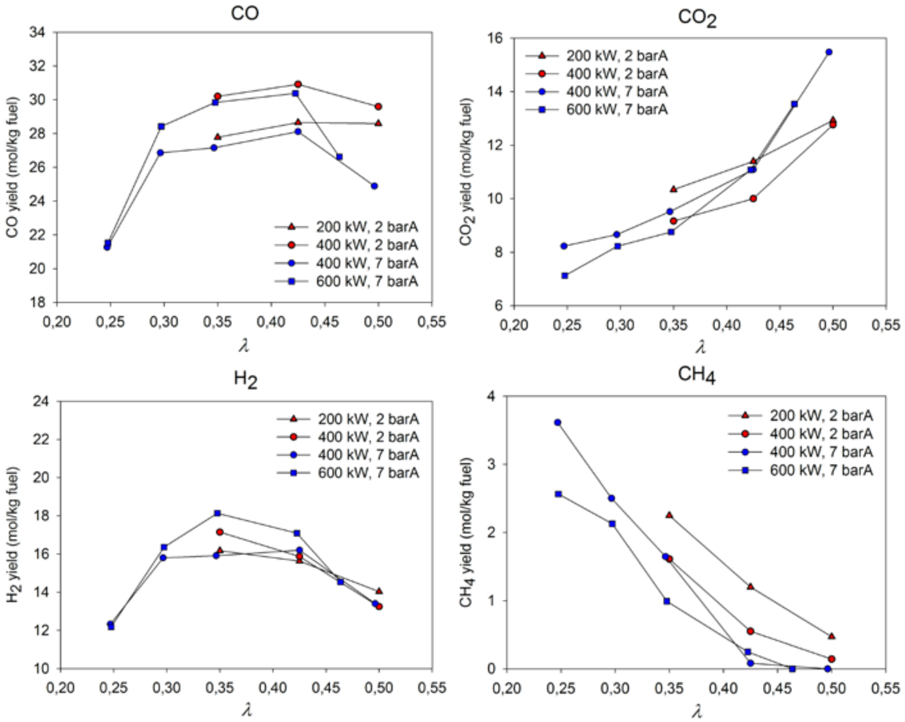

Figure 1. Syngas yields of CO, H_2, CO_2 and CH_4 at different operating contitions.

Carbon conversion and cold gas efficiency (CGE)

Fuel conversion is affected by several parameters during gasification, such as the fuel particle size, the residence time and temperature in the gasifier etc. It was found that the fuel conversion was complete within the range $0.35<\lambda<0.50$ for all the tested fuel particle size distributions of this work. However, the carbon conversion was reduced to 0.95 and 0.80 when the gasifier was operated at $\lambda = 0.30$ and 0.25, respectively. Depending on the purpose of the syngas generation, different measures of process efficiencies can be calculated. The most common efficiency measure is the cold gas efficiency (CGE), which is defined as the ratio between the chemical energy in the cold syngas and the energy input from the corresponding fuel (based on the lower heating value). The CGE_{power} is calculated from all combustible species in the syngas. This is a representative measure if the syngas is intended for combustion in e.g. a gas turbine for power production, where all combustible species of the syngas can be used. On the other hand, if the syngas is intended for catalytic synthesis of biofuels, only the yields of CO and H_2 in the syngas should be maximized, and thus, the need for an additional measure of efficiency, the CGE_{fuel}. The experimental CGEs can be found in **Figure 2**, where it can be seen that CGE_{power} reached a maximum of approximately 0.75 (at $\lambda = 0.30$). Lower λ resulted (as previously mentioned) in poor fuel conversion and thereby a reduction in efficiency. Excessive combustion of the energetic syngas species was responsible for the CGE_{power} reduction at higher λ (above 0.30). The correlation between CGE_{fuel} and λ had a less pronounced optimum being rather flat around the maximum, over a broad range of λ. This suggests that it is possible to operate the gasifier at an elevated λ without sacrificing too much of the CO and H_2 yields that constitutes the CGE_{fuel}. The benefit of operating the gasifier at an elevated λ is that it improves the syngas quality due to the conversion of CH_4 and other unwanted species (e.g. larger hydrocarbons and soot) because of the higher process temperature.

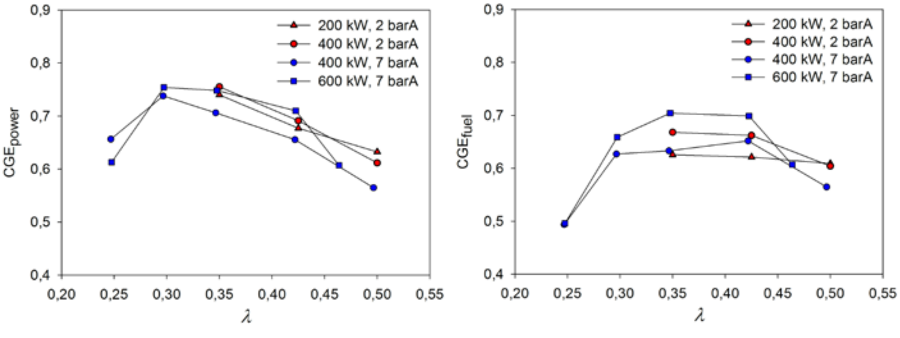

Figure 2. Cold gas efficiency at different operating conditions, CGE_{power} (left) and CGE_{fuel} (right).

Correlations against process temperature

The yield of CH_4 was strongly correlated to the process temperature as shown in **Figure 3**, not only for the stem wood pellets fuel, but also for other fuels tested in

PEBG (appended in the graph for comparison). These other fuels were (1) a spruce reference fuel and (2) the corresponding torrefied spruce fuel. They were gasified at different operating conditions at 7 barA. In addition to this, a beech wood fuel with two different fuel powder particle size distributions were also gasified at varying operating conditions (2-7 barA). Regardless of the fuel type or the fuel pretreatment the yield of CH_4 seems to be clearly correlated to the process temperature. Interestingly, two adjacent points in the graph can originate from different stoichiometric conditions during gasification. This graph, therefore, indicates that the CH_4 yield was mainly governed by the process temperature and that the operating conditions (e.g. λ and fuel load) only were control parameters for the temperature.

Conclusions

Syngas from pressurized entrained flow gasification of woody biomass can be produced in pilot scale with efficiencies CGE_{power} and CGE_{fuel} of 75 % and 70 %, respectively. The efficiency will certainly increase towards the theoretical maximums (89 % and 86 %, respectively) in large scale plants, where the relative heat losses are lower. Furthermore, the syngas requires shifting towards higher H_2 content prior to methanol synthesis. To generate a high quality syngas, the gasifier should preferably be operated with a λ aiming for process temperatures above 1400 °C in order to keep the levels of CH_4 and other unwanted syngas species low. These results provide unique information to system studies, which subsequently can tell whether the process is commercially profitable. Additionally, we have increased our knowledge in pressurized feeding of biomass powders.

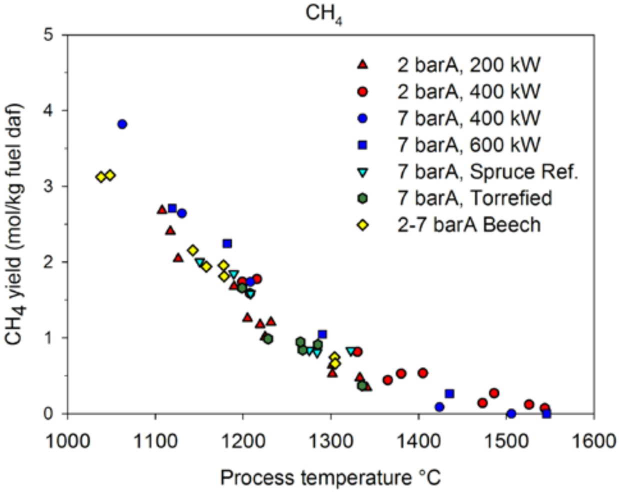

Figure 3. The yield of CH_4 (mol/kg fuel dry ash free) as a function of measured process temperature in the gasifier.

Acknowledgements

The PEBG project was financed by the Swedish Energy Agency. All personal at SP ETC are highly acknowledged for their commitment and skills. Our partners through fail and foul, IVAB/Biogreen/NIAB, are also acknowledged for their contribution to the project. Our collaborative partners from Umeå University (Bio4Energy/Bio4Gasification projects) as well as our partners from CEA Grenoble, France (Brisk project) are thanked for contributing to some of these results.

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Biorefinery products – carbon fibres

Carbon Fibres from Regenerated Cellulose Fibre Precursors

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Abstract

Bio-based polymeric materials are abundantly available in Finland, and forest industry is seeking new business opportunities for that raw material. Large business potential lay on many application fields utilizing macroscopic carbon, especially tailored carbons with added value and reduction of production price. We believe that bio-based, and more precisely wood-based polymers can be used to form precursors with various complicated shapes and sized in order to make tailored and functional carbon materials. In the recent project we surveyed technological possibilities to obtain bio-based carbon business in Finland applying biomass derived polymers and precursor structuring prior to carbonization. Work described here concentrates on cellulose based carbon fibre materials.

Introduction

The properties of carbon fibres, such as high stiffness, high tensile strength, low weight, high chemical resistance, high temperature tolerance and low thermal expansion, make them very popular in aerospace, civil engineering, military, and motorsports, along with other competition sports. Application fields with requirements of specific tailored carbon fibrous structure are also found in filter & membranes, capacitive desalination, catalyst carriers, gas storage as well electrodes for super-caps and batteries. In the recent years increasing interest has been paid towards affordable and sustainable sources for carbon fibres, especially from bio-based raw-materials like cellulose and lignin.

Carbon fibres based on viscose type regenerated cellulose precursor fibres have been available since 1920's [1]. Cellulose-based carbon fibres have been overtaken by polyacrylonitrile (PAN) and isotropic pitch in many applications, especially in high modulus composites. However, cellulose and more precisely viscose precursors, has still remained some markets due to beneficial properties including good thermal stability of resulted fibres, and lower prices of raw material as well as precursor fibre production compared to PAN based carbon fibres. [2] Cellulose comprises largely of crystalline regions to start with, and it does not melt down in high temperatures, and therefore does not require stabilization prior to carbonization like most used synthetic carbon precursor PAN [3]. Additional attractive feature is renewability and bio-based origin of precursor.

Due to environmental challenges of viscose process new type of cellulosic fibres also for carbon fibre precursors are actively studied at the moment [3, 4]. Other types of fibrous carbon materials from cellulose include activated carbon fibres [5] and nonwovens [6], carbon nanofiber structures from nanofibrillated cellulose [7, 8] and electrospun cellulosic fibres [9].

In this work we studied the use of non-viscose regenerated cellulosic fibres for production of carbon fibres and activated carbon fibres. We used impregnating agents to improve carbon yield, since without these treatments carbon, comprising 44.4 %, of cellulose structure, is partly removed. This is due to the formation of carbon containing volatiles during cellulose pyrolysis [10].

Experimental

Raw materials were enzymatically treated dissolved cellulose, so called Biocelsol fibres, and nitrogen containing cellulose carbamate, both materials produced from commercial dissolving pulp. These materials were wet-spun to viscose-like fibres and also carded and needle-punched into nonwovens. We studied the use of various chemical agents, $(NH_4)_2HPO_4$, H_2SO_4, and NH_4Cl, in order to increase low carbon yield and produced carbon yield.

Carbonization in fibres and nonwovens was carried out in high temperature furnace in N_2 atmosphere. Typical process had maximum temperature of 1500 °C for 30 min, with 5 °C/min heating. Fibres were tensioned with low loading during the carbonization process, but they were not subjected to high drawing. Drawing ratios upto 200 % is needed to form highly ordered structure and high strength [2]. Activation was carried out with CO_2 during carbonization.

Results and discussion

Properties of precursor fibres were similar to commercial viscose fibres. Appearance of enzyme treated fibres and properties of both precursor fibres compared to viscose are shown in Figure 1 and Table 1, respectively.

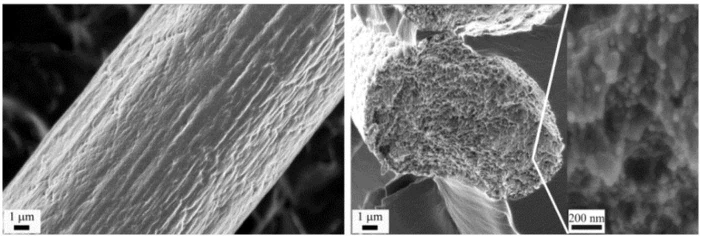

Figure 1. Surface and cross-section of precursor fibre (1.9 dtex → ~10 µm) imaged by scanning electron microscope (SEM).

Table 1. Properties of precursors and viscose reference.

Fibre	Titre [dtex]	Tenacity [cN/dtex]	Elongation [%]
Biocelsol	1.9	1.3	21
Cellulose carbamate	4.1	1.1-1.6	20-32
Viscose (ref)	2.8	2.1	19

In preliminary trials we studied the effect of different impregnation agents on carbon yield and mechanical properties of fibres (see Table 2). Obtained carbon yields in these un-optimized cases were 14-21 %, which was significantly higher than of non-treated reference (10-11 %). Best carbon yield was obtained with $(NH_4)_2HPO_4$, which was selected for sample preparation.

Table 2. Effect of impregnation agent to carbon yield and mechanical properties of fibres.

Agent	Carbon yield [5]	Mech. prop.
None (ref)	10-11	-
$(NH_4)_2HPO_4$	18-21	→
NH_4Cl	14-15	↓
H_2SO_4	14-18	↓↓

Carbonized fibre samples produced with tensioning had good appearance (see Figure 2) and fibres showed good conductivity (above 4000 S/m). With somewhat optimized carbonization process we were able to obtain carbon yield of above 30 % Strength of the obtained carbon fibre samples was not as good as needed for load-bearing composite applications, since we were not able to apply sufficient stretching. Fibres were still coherent and could be handled manually. Possible use of such material could be e.g. conductive filler in non-load-bearing composite applications or in various energy applications.

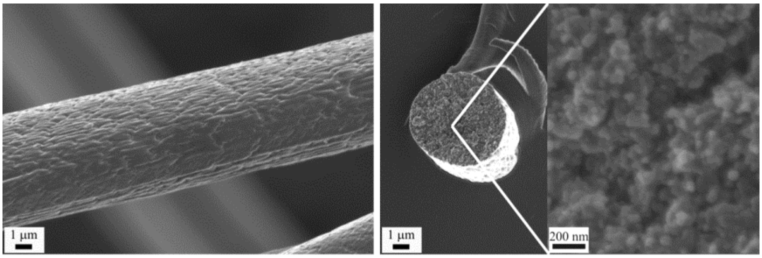

Figure 2. Surface and cross-section of carbonized cellulose fibre imaged by SEM.

Activated carbon fibres and nonwovens remained their structure within carbonization (see Figure 3). They had surface areas above 1000 m^2/g and single samples even above 2000 m^2/g. Carbon yields of activation process was lower than that of carbon fibres, but still around 15 % in best cases. Fibres and nonwovens were coherent and they could be used e.g. for water purification and removal of odours from gas flow.

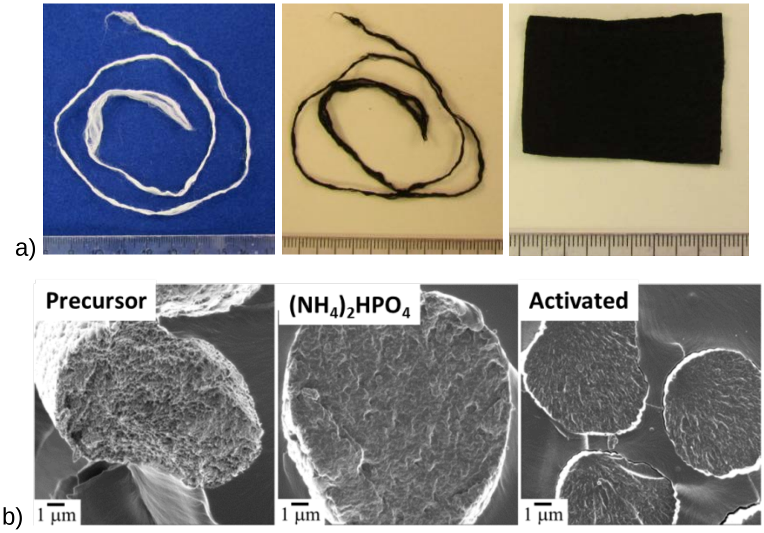

Figure 3. Appearance of (a) precursor and activated carbon fibres and nonwovens in photograph, and b) precursor, impregnated ($(NH_4)_2HPO_4$) and activated carbon fibres in SEM imaging.

Conclusions

Novel cellulosic fibre and nonwoven precursors has been studied, more environmentally friendly than viscose. Carbonized and activated materials have been produced using relatively simple process including:

1. Pre-treatment of cellulose
2. Dissolution
3. Wet-spinning
4. Impregnation
5. Carbonization (and optional activation).

Properties of carbon depended on raw materials and carbonization process. We showed that carbon yield can be increased into feasible level by adjusting chemistry, and yields are similar to those of viscose. Carbonization led to high electrical conductivity while activation led to high specific surface area. All fibres withstand manual handling, but were not strong due to lack of stretch, therefore applications of these fibres can be found in energy related applications requiring conductivity and high surface area, or in sorbent applications.

Acknowledgements

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Opportunities in Lignin Based Carbon Fibre

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Abstract

Carbon fibre is predominantly manufactured from polyacrylonitrile while small quantities are obtained from the conversion of petroleum pitches and regenerated celluloses. However, due to precursor fibre and conversion costs it remains a specialty product. One alternative precursor is lignin, which is attractive because it provides high carbon yields, is renewable, and is more cost efficient, even when additional preprocessing of the lignin to give a more suitable precursor is accounted for. Lignins are available in large quantities in the pulp and paper industry and are combusted in recovery boilers to recover inorganic chemicals and to provide facility energy. The capacity of the recovery boiler determines pulp mill capacity, and therefore innovative processes which could divert and utilize lignin streams, and potentially increase mill profitability are desirable.

Lignins with properties most suitable for carbon fibre manufacture have only been prepared at the laboratory or pilot scale, either by treatment of technical lignins or as a product of organosolv fractionations. Innventia have developed a process by which high purity lignins can be recovered from pulp mill liquors. This process, LignoBoost, has been demonstrated at the pilot scale in Bäckhammar, Sweden and deployed at the commercial scale in both Finland and the United States. Incremental changes to this process have led to the development of lignins that are more suitable for carbon fibre preparation. Innventia and Swerea SICOMP have therefore committed resources towards the Swedish commercial production of lignin based carbon fibres by 2025. Consequently, the development of a lignin carbon fibre test bed facility has been identified as a necessary component of this roadmap. Therefore, an overview of lignin carbon fibres, and the research, development, and infrastructure efforts of Innventia towards this will be presented.

Introduction

Carbon fibres consist of 92-100% wt. carbon, and depending on the precursor, process, and cost, commercial products have strengths from 2.5 GPa to 7 GPa (1). Their excellent properties make them attractive for use in composites for aerospace, military, industrial, sporting, and automotive applications. However, because of high manufacturing costs, wider utilization has not been enabled. The manufacturing cost typically consists of 51% precursor, 18% utilities, 12%

depreciation, 10% labor and 9% represented by other fixed costs; in 2010 the cost was well over US$30/kg when oil was at its highest price (2).

Several countries have enacted legislation to reduce fuel consumption in the transportation sector. For example, in 2012 the U.S. government legislated through updated Corporate Average Fuel Economy (3) standards that the average fuel economy of cars and light trucks sold in the U.S. for model year 2017 will be 35.5 mpg (6.63 l/100 km); increasing to 54.5 mpg (4.32 l/100 km); by 2025. The most effective way to increase fuel economy is to decrease vehicle weight through the use of smaller engines, smaller bodies, and so on. However, improved comfort, performance and safety have historically increased weight and therefore weight reduction is thought to be best achieved through the use of lighter weight materials. Studies have identified several materials that could be used to light-weight vehicles, one of the most effective are carbon fibre reinforced composites which could offer as much as 60% part-weight reduction (4,5). The U.S. automotive industry requires that carbon fibre cost be lower than $11-$15.40/kg, have a tensile strength of 1.72 GPa, and a modulus of 172 GPa for it to be attractive for utilization.

To reduce carbon fibre cost emphasis has been on lowering the cost of processing polyacrylonitrile through advanced oxidation techniques, the use of textile precursors (6,7), and the synthesis of new melt-spinable precursors (8). A process is also being developed by which polyolefin fibres can be converted to carbon fibre (9) with reported strengths of 0.758 GPa (8) to 1.39 GPa (10). Another program is directed towards cost reduction through use of renewable lignin precursors. The best lignin-based carbon fibre samples reported to date had an average strength of 1.07 GPa (11,12) and are projected to cost much less than other methods of carbon fibre production. Further details can be found elsewhere (5).

Lignin carbon fibre

Otani (13) described several methods of forming fibre from lignin. Consequently, lignin-based carbon fibre enjoyed a brief period of small-scale commercialization under the name of Kayacarbon (14). Sudo (15,16) suggested alternative preparations of lignin whereby infusible lignins were chemically modified to give thermoplastic lignins. Uraki (17,18) used an aqueous acetic acid pulping method which gave lignin that was suitable for melt-spinning due to a limited amount of acetylation which lowered T_g. Kadla & Kubo (19) later reported carbon fibre preparations giving fibres with strengths of up to 0.388 GPa from Alcell™, and 0.422 GPa from a hardwood kraft lignin. A method by which a kraft hardwood lignin could be plasticized by polyethylene oxide to improve fibre spinning performance was also reported. The patent literature also reveals a growing interest in carbon fibre from lignin/polymer blends.

The first successful pilot scale melt spinning of a kraft lignin was reported by Oak Ridge National Laboratory (20,21). However, owing to the low T_g of the solvent purified lignin, conversion of the fibres was slow with rates of oxidative thermostabilization as low as 0.01°C/min (14 days) being required before carbonization was possible. The carbon fibres were of low yield and tensile strength (33%; 0.517 GPa). The use of a thermal pretreatment (22,23) was used to increase T_g (and increase molecular weight) of the lignin starting material. This gave carbon fibres with tensile strengths of up to 1.07 GPa, carbon yields as high as 55%, and the time required for the conversion of some samples was less than one hour. Similarly, Alcell™ lignin was thermally pretreated giving carbon fibres with tensile strengths of up to 0.710 GPa and yield of 41%, compared with the original lignin which gave carbon fibres with strength of 0.338 GPa and yield of 31% (12). It is thought that differences in performance observed between the two lignins were due to their differing molecular mass and polydispersity, which gave rise to differing performance upon heat treatment.

Lignin preparations for carbon fibre

The preferred method of manufacturing carbon fibre from lignin (5,24) involves the preparation of a suitable lignin that is melt-spun into fibre. The fibre is then oxidatively thermostabilized and carbonized. The integrity of the lignin fibre during oxidative thermostabilization depends on its ability to crosslink, so that the T_g of the material is maintained above the processing temperature, ultimately rendering it infusible. The lignin has to be prepared so that it has a low enough softening temperature (T_s) for it to be melt spun without polymerizing, but a high enough T_g for fibre stabilization to proceed at an acceptable rate.

Several features have been found to be apparent in assessing the performance of a lignin polymer for carbon fibre manufacture. Figure 1 illustrates the effect that changing lignin T_g has on melt spinning performance and on carbon fibre conversion. The trends observed in Figure 1(b) also apply to lignins prepared for solution based processes such as for electrospun and solution spun lignin fibres, and in this case the thermal limitations of melt spinning are removed and lignin solvation properties persist so that lignins are optimized for solution processes.

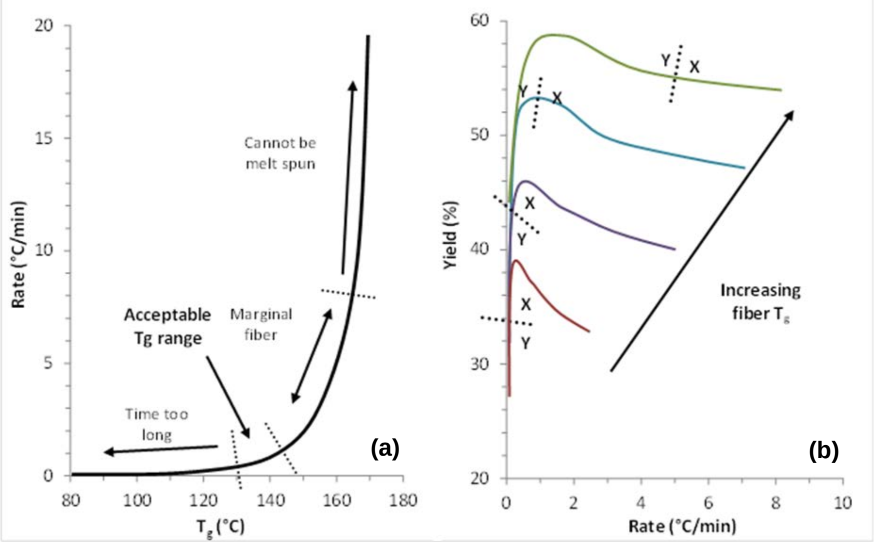

Figure 1. Trends in (a) dependence of melt spinning performance on T_g; and (b) dependence of allowed stabilization rate, conversion carbon yield on fibre T_g, where X denotes the stabilization rate above which fibres fuse and Y denotes the allowed stabilization rates for carbon fibre preparation (5).

Lignins obtained from most industrial processes have a wide polydispersity and thus a large difference is observed between their T_g's and T_s's; they typically contain very high molecular weight components that cause a portion to be infusible, and low molecular weight species and inorganic materials which will cause flaws to arise during conversion to carbon fibre. It is therefore necessary to remove these components. While there are fractionation processes, e.g. organosolv, that provide lignins with more desirable melt properties, the resulting lignins tend to possess low T_gs and substantial carbohydrate contaminants (including chemically bonded) which need to be removed prior to use.

LignoBoost capabilities at Innventia

The traditional process for lignin precipitation and separation from kraft black liquors leads to high levels of impurities. In the LignoBoost Process (Figure 2), a stream of black liquor is taken from the black liquor evaporation plant. The lignin is then precipitated by acidification and filtered. Instead of washing the lignin immediately after filtration, as occurs in traditional processes, the filter cake is re-dispersed and acidified. The resulting slurry is then filtered and washed by means of displacement washing. The LignoBoost process therefore makes it possible to extract high purity lignin efficiently from the black liquor in kraft mills (25).

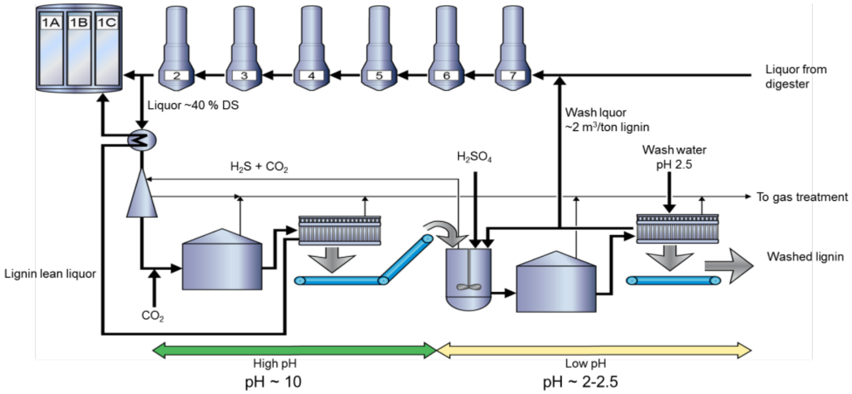

Figure 2. The production of lignin using the LignoBoost process (Source: Valmet).

Innventia has the capability to evaluate black liquors and produce high purity lignin at several scales (10g, 1kg, 10kg, and >1000kg) and in some cases lignins are produced which can be used directly for carbon fibre preparation. This capability has also been extended to include additional process refinements so that tailored lignins can be produced. In each case, the technoeconomic parameters of the process can be defined, assessed in the context of a mill, and lignin quality monitored. Characterization of the lignins is performed in-house to assess purity, structure, and polymeric properties.

Towards a commercial lignin carbon fibre

Innventia have invested significant resources in both personnel and infrastructure to demonstrate the potential that lignins possess to become a viable feedstock for carbon fibre manufacture. Once lignins with suitable properties have been produced using the LignoBoost process and characterised, their melt spinning performance is assessed and conversion to carbon fibre evaluated. Fibre melt spinning performance is first assessed using single filament melt extrusion (DSM Xplore Micro15 Twin Screw Compounder, Netherlands) and rheological profiles obtained (TA Instruments Discovery Hybrid Rheometer, DE, USA; modified for high temperature measurements). Once lignin performance is assessed, melt spinning is performed at the multifilament scale (AJA Fibre Pitch Extruder, SC, USA) where fine fibres can be produced for conversion to carbon fibre. The multifilament extruder is equipped with vacuum degasing, optional mixing and the ability to draw lignin filaments after the spinneret to further reduce fibre diameters.

After fine filaments have been obtained, oxidative thermostabilization of the lignin fibres is done so that carbonization can proceed. To evaluate this, oxidation furnaces have been modified to treat fibre tows batchwise and also with differing levels of tensioning applied to control shrinkage due to crosslinking of the lignin.

Filaments can also be studied to optimize tensioning and thermal treatment parameters using both thermomechanical (Netzsch Hyperion TMA402 1550°C) and thermogravimetric (TA Instruments Q5000IR) analyses and the data used to optimize tow processing. Oxidatively thermostabilized lignin filaments and/or tows can then be carbonized under anaerobic conditions.

To optimally carbonize the stabilized lignin tows, we have the ability to study the effects of thermal treatment programs and tensioning by using either thermomechanical analysis or by using test equipment especially designed to monitor carbonization profiles with either stress or strain control (Figure 3). This information can be used to determine improved carbonization profiles to optimize carbon fibre properties. Carbon fibres are prepared and evaluated for their mechanical properties (Diastron), morphology, and fine structure. Continuous processes for the conversion of lignin fibre to carbon fibre are also being developed to support our growing infrastructure as we continue to improve the quality of the lignins, fibres and carbon fibres we produce.

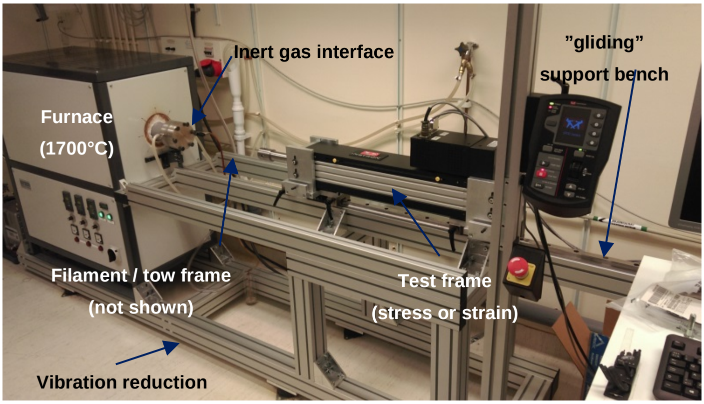

Figure 3. Test frame for measuring carbonization properties of fibre tow.

As a part of our research and development efforts, we have a Vinnova supported carbon fibre test-bed project. This involves representative members from all parts of the value chain, from managed forests through to the automotive industry. The project leverages our collective knowledge towards developing a bid for a continuous carbon fibre development line. The project also interfaces with several engineering groups and equipment manufacturers to assess the needs for such a facility to be placed at Innventia. We believe Innventia is uniquely placed to work with our members and customers to integrate these technologies into their value chains, and make significant contributions to the development and commercialization of bio-based carbon fibres.

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Posters

Yellow Birch Transformation into Butanol and Organic Acids in an Integrated Biorefinery Platform

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Introduction

One of the abundant wood species in eastern Canada is yellow birch, and high volumes of harvested surplus wood and residues (about 4 dry tons/acre/year) exist in several rural and suburban communities. Sustainable utilization of this feedstock by producing biofuels or biochemical such as biobutanol can boost economic transformation of such communities; support jobs retention and/or jobs creation, as well as start-up of several small bioeconomy-based companies. Biobutanol is considered as a biofuel that has superior qualities to ethanol [1-2]. It is also a valuable product for an integrated forest biorefinery platform because it is a precursor for derivatives such as acrylates and acetates [3]. Currently, some of the obstacles for industrial scale production of butanol include the high cost of biomass, pre-treatment and fermentation. There is no record of biobutanol and organic acid production directly from woody biomass and the objective of this study is to establish its feasibility by using surplus yellow birch within an integrated biorefinery platform context. Experiments on biomass pre-treatment using kraft pulp processes similar conditions were carried out, followed by enzymatic hydrolysis to obtain fermentable sugars. Sugar fermentation was performed in an anaerobic jar using *clostridium acetobutylicum*. The results showed that biobutanol yield is as high as 11 g/L while the total Acetone-Butanol-Ethanol (ABE) solvents yield was 23.9 g/L. A preferential utilization of hexose over pentose was identified.

Materials and Methods

Experimental procedure

The process steps to obtain fermentable sugars from yellow birch wood are illustrated in **Figure 1**. Carbohydrate-rich cellulose pulp was generated with an alkali solution of NaOH (10%) and Na_2S (2.6%) that was maintained at 170 °C for 2 hours with a wood to liquor ratio of 1:5. The pulp was subsequently washed and hydrolyzed enzymatically with a cocktail of Accellerase 1500 (cellulase) and Accellerase XY (xylanase), provided by Genencor.

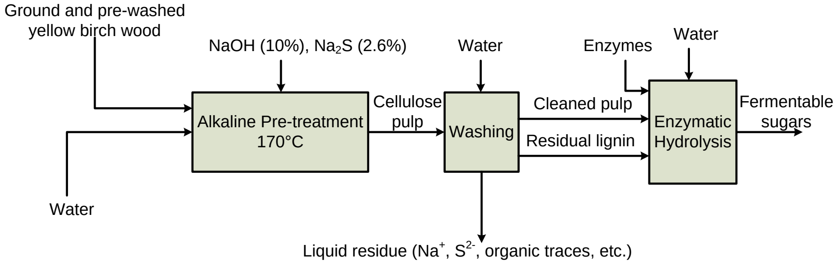

Figure 1. Scheme of process steps for producing fermentable sugars

The sugar solution produced were femented in serum bottles that were enclosed in an anaerobic jar. Clostridium acetobutylicum DSM 792 was used for the microbial culture and the temperature was maintained at 37 °C with agitation at 150 rpm for up to 72 hours. Fermentation tests using synthetic sugar solutions were also performed for benchmarking.

Analytical methods

Sugars and butanol concentrations were measured by HPLC (Shimadzu, Japan), using a Refractive Index Detector and an Aminex HPX-87H 300x7.8 mm column equipped with a Carbo H guard column. The eluent used was 0.005 M H2SO4. Organic acids and solvents concentrations were measured using a Varian CP-3800 GC equipped with a Flame Ionization Detector and an EC-WAX 30m x 0.25 mm, 0.25 µm column (Alltech)

Process Simulation

Three integrated biorefinery process designs were synthesized and simulated using the Aspen Plus® software. Evaluation of their feasibility was made using the energy input, recovery yield of butanol and its purity as criteria.

Results and discussion

The amounts of glucose, xylose and cellobiose obtained after pre-treatment and hydrolysis of the yellow birch biomass is depicted in Figure 2A. The hydrolysis was operated in semi-batch mode with the periodic addition of pulp (when the birch pulp had been hydrolysed) and enzymes (when the rate of sugar concentration became constant). The targeted minimum total sugar concentration (~180 g) was reached after about 450 hours. To prevent substrate inhibition by the sugars, the obtained solution was diluted to ensure that the fermentation medium had only about 60 g/L of C_6 sugars. Samples were withdrawn from the fermentation medium at the start, 4 hr, 48 hr and 72 hr and the results from the analysis are illustrated in Figure 2B. The pH of the fermentation medium was successfully held at about 5.5 with a sodium citrate. However, after about 72 hours, a pH reduction was observed after the production of the solvents (Acetone-Butanol-Ethanol) ceased. The ABE solvent production during fermentation was 8.2 g/L of Acetone, 13.1 g/L of Butanol, 2.7 g/L of ethanol. The concentration of acetic acid was 1.1 g/L and butyric acid 0.2 g/L. Benchmarking tests were performed using synthetic solutions that contained ~60 g/L of glucose and 26 g/L of xylose, 5 g/L of mannose and 1 g/L each of galactose and arabinose. The results obtained were reproducible and comparable to that of yellow birch derived sugar solution. The critical parameters for high fermentation yields ≥ 0.2 g/g (based on total solvent/ dry sugar weight), biobutanol selectivity and longevity of the microorganisms that were determined from the experiments include the maximum tolerable substrate concentration.

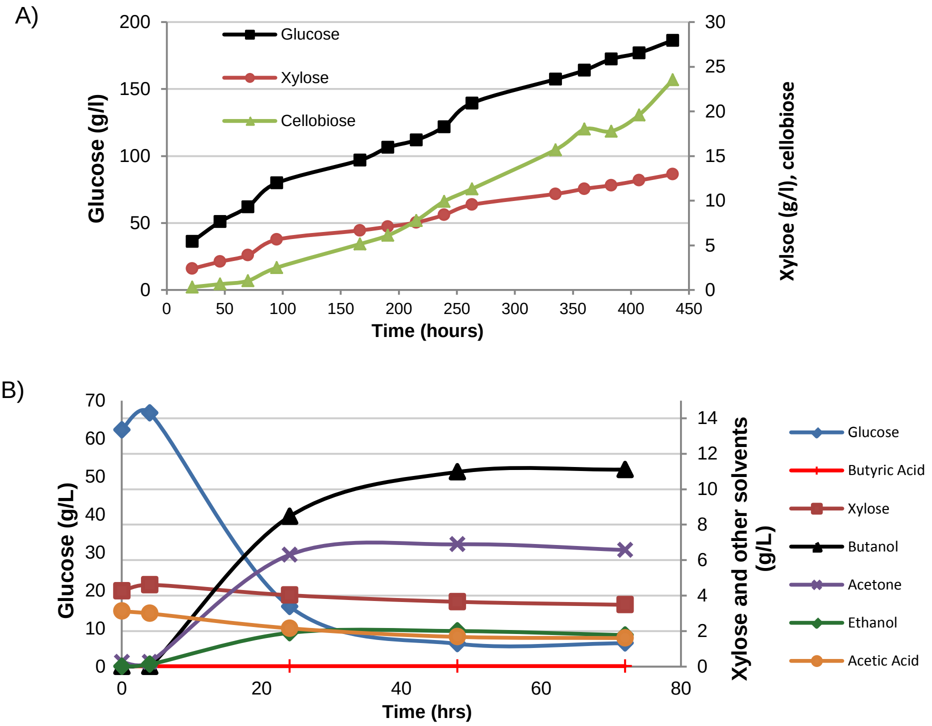

Figure 2. A) Concentration profile of hydrolysed sugars as well as B) Solvents during fermentation

Raising the glucose concentration higher than 70 g/L did not have a positive effect on biobutanol production. Furthermore, a preferential consumption of glucose over the other pentose and hexose that were present was observed. Complete removal of the residual lignin prior to fermentation is necessary for biobutanol production. This was achieved by centrifugation of the solution obtained after enzymatic hydrolysis. The peak growth of the microorganism was observed at about 24 hours.

The three integrated process designs that were developed and simulated to evaluate the feasibility of biobutanol production industrially are summarized in Table 1. It can be seen that although high biobutanol purity (>99%) can be obtained using the different processes, a trade-off based on the energy requirement and recovery yield would always be necessary. Batch fermentation with *in-situ* gas stripping and liquid-liquid extraction offers the lowest energy requirement and highest purity. However, it has a low recovery yield.

Table 1. Comparison of process designs for biobutanol (n-BuOH) production

Process Characteristics	Energy input (MJ/L of BuOH)	Recovery yield of BuOH (%)	BuOH Purity (%)
1. Batch fermentation and distillation	21.77	95.62	99.05
2. Batch fermentation, centrifugation and liquid-liquid extraction	9.63	94.68	99.50
3. Batch fermentation with in-situ gas stripping and liquid-liquid extraction	6.67	75.52	99.88

Conclusion

This work has demonstrated that it is possible to produce biobutanol using the sugars derived from the hydrolysis of pretreated yellow birch. The fermentation yields are similar to that obtained in experiments with synthetic sugar solutions. A detailed economic analysis would be required to determine the most economically feasible processes.

Acknowledgments

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Kraft Lignin Depolymerisation by Base Catalysed Degradation – Effect of Process Parameters on Conversion Degree, Structural Features of BCD Fractions and Their Chemical Reactivity

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Abstract/Introduction

Depletion of crude oil reserves, the increase in the greenhouse gas emissions, as well as economical/ecological challenges of the pulp and paper industry force into the utilization of lignocellulose biomass. Only by economical biomass conversion processes the production of sustainable bio-based materials, chemicals, and semi-finished chemical goods will be reasonable. Lignin (a renewable resource) contains aromatic structures, and has sustainable and economical potential in bio based chemicals and materials. Lignin depolymerisation for the generation of building blocks has been investigated over decades. The degradation of lignins in alkaline solution, so-called "base catalysed degradation - BCD" is based on the selective catalytic cleavage of inter unit linkages (α-*O*-4, β-*O*-4, 4-*O*-5) and methyl-aryl-ether bonds in the presence of strong bases [1-4]. Under defined conditions, the generation of a monomer rich phase (BCD-oil) and of "oligomer polyphenolics" is possible without the formation of char.

Experimental

A detailed study was realized with impure, sulphur containing eucalyptus kraft lignin (25% of ash), supported by DoE (Box-Behnken). The high mineral content of the lignin was used as additional catalytic active component. The experiments were done in a continuous plug flow reactor at T of 300, 325 and 350 °C, with additional NaOH of 1, 2 and 3% and at selected t of 5, 10 and 15 min respectively. The p was in the range of 200-250 bars. The generated BCD-oils and oligomers were analysed (weight, elementary analysis, ^{31}P-NMR, 2D-NMR, TGA). Additionally, the BCD-oils were characterised by GC-MS (monomers: guaiacols (G), syringols (S), catechols, 3-methoxy-catechols (C)) and by infusion MS (APCI) (oligomer composition). Furthermore, the acetylated oligomers were analysed by SEC (M_N, M_W). The 3D assessment of the complex data sets was supported by software Statgraphics centurion XII. The carbon balance was used for the description of the conversion degree into BCD-oil and oligomers. A chemical modification of the oligomers with 2,3-epoxy-1-propanol was done by catalytic epoxide ring opening with phenolic OH-groups. ^{31}P-NMR analyses of the materials were done. GC-MS/FID: monomers were determined according to the method described in [4]. Elemental analysis was performed as described in [4]. ^{31}P-NMR analysis was done as described in [5]. 2D-NMR analysis (HSQC) was done as described in [6]. SEC analysis: M_N and M_W of acetylated samples were determined as described in [7].

Results and discussion

Depending on the process parameters the lignin could be converted into 15-20% of BCD-oil and 30-75% of oligomer polyphenolics.

Results of 2D-NMR (HSQC) and GC-MS/FID analyses

2D-NMR analyses (HSQC) on BCD-oils illustrate the absence of inter unit linkages β-*O*-4, β-β). HSQC analyses on oligomers show an absence of the linkages β-O-4, β-β depending on the process conditions.

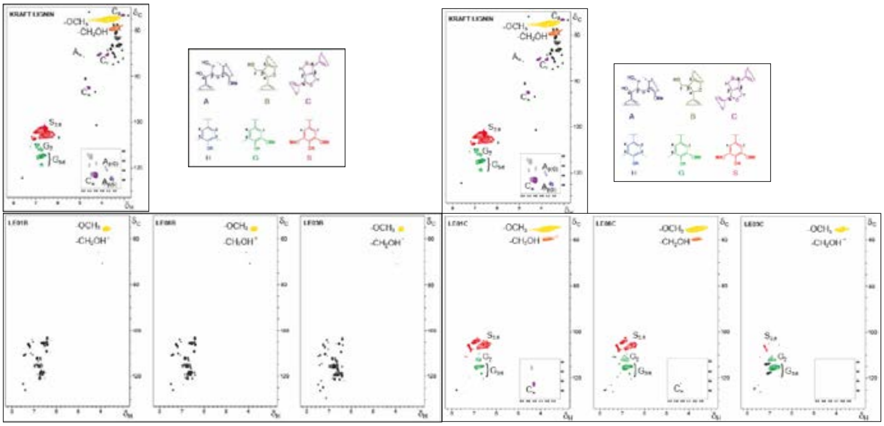

Figure 1. 2D-NMR analyses on kraft lignin (upper left and right), BCD-oils 01, 08, 03 (below, left) and oligomeric cleavage products 01, 08, 03 (below, right).

The liberation of primary cleavage products (Guaiacols and Syringols) and the formation of secondary cleavage products (Catechols) depend significantly on T, t and the concentration of sodium hydroxyde.

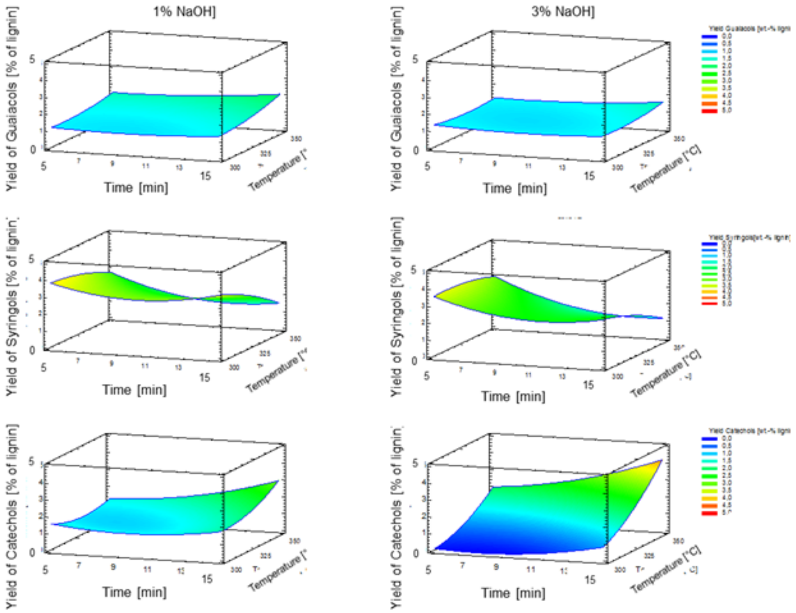

Figure 2. Yield of primary cleavage products (Guaiacols, upper and Syringols, center) and of secondary cleavage products (Catechols, below) depending on the BCD process parameters (T [°C], τ [min], conc. NaOH.

TGA on BCD-oils illustrate that ~ 50-65% of the samples are volatile up to 250 °C. The residues represent the non volatile oligomer fraction in BCD-oils. Infusion MSD Ion Trap analysis on BCD-oils illustrates a complex picture of single and multi charged oligomers in the range from 225 to 500 amu.

Results of ^{31}P-NMR-anylses and SEC- analyses

^{31}P-NMR analyses on BCD-oils and oligomeric polyphenolics were done. ^{31}P-NMR analyses on selected BCD-oils show an increase in the phenolic OH-number depending on BCD process conditions. ^{31}P-NMR analyses on corresponding BCD-tars illustrate more or less the same trend in the phenolic OH-number. The used Kraft-Lignin showed a lower phenolic OH (Table1). The stronger the process conditions (01: 5min, 300 °C → 08: 5min, 350 °C → 03: 15min, 350 °C, const.NaOH:2%) the higher the phenolic OH number, indicating additional de-methylation. An additional de-methoxylation is remarkable. Para-hydroxy phenolic units were also formed (Table 1). During the BCD aliphatic OH-groups were lost (Table 1).

Table 1. Results of ^{31}P-NMR of kraft lignin & of selected BCD-oils & oligomers regarding aliph. & phen. OH-No. (cond. & S, G, C, para-hydroxy-phenyl [mmol/g].

#	aliph. -OH	Cond. & Syringol-OH	Guaiacol-OH	Catechols -OH	para-OH	phen. -OH	Total -OH
K-Lignin	1.58	2.10	0.69	-	-	2.79	4.37
BCD oil 01	0.24	3.30	2.0	0.29	0.20	5.78	6.02
BCD oil 08	0.20	2.88	3.18	0.63	0.39	7.08	7.28
BCD oil 03	0.16	1.26	6.74	0.58	0.80	9.39	9.55
BCD olig 01	0.15	2.64	0.72	0.61	0.27	4.24	4.39
BCD olig 08	0.10	2.39	1.00	1.19	0.38	4.96	5.06
BCD olig 03	0.04	1.16	1.23	1.70	0.62	4.71	4.75

The results of SEC on kraft lignin and on BCD-oligomers illustrate a significant reduction on M_W: 700-1300g/moles and M_N: 300-360g/moles as well as on M_W/M_N: 2. The Kraft-lignin showed following values for M_W: 8569g/moles, M_N: 1351g/moles, M_W/M_N: 6.3 (Figure 3).

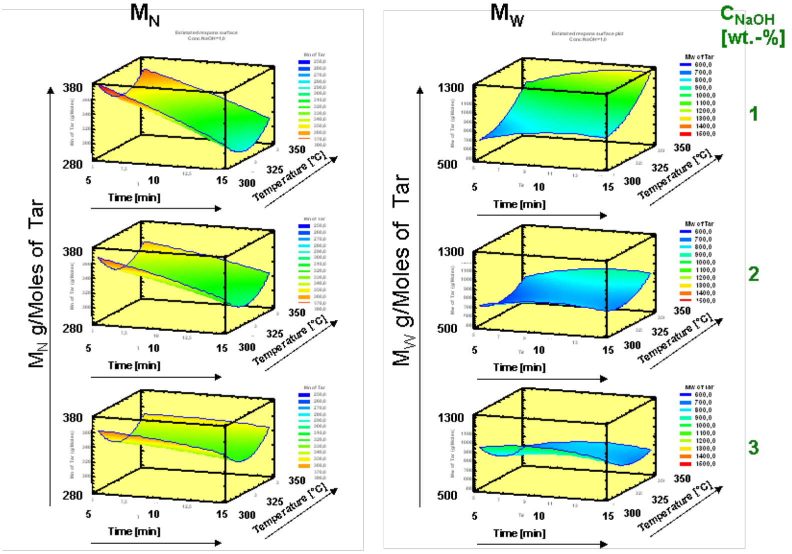

Figure 3. Result of SEC (M_N, M_W) on oligomer cleavage products depending on process parameters, τ [min], T [°C] & NaOH [wt.-%].

Results of chemical modification with 2,3-epoxy-1-propanol

A chemical modification of guaiacol, BCD-oil and of oligomer polyphenolics with 2,3-epoxy-1-propanol was done in ethanol with catalytical amounts of tri-ethylamine according to Figure 5 by reflux cooking at 80-85 °C.The reaction time was 6 h.

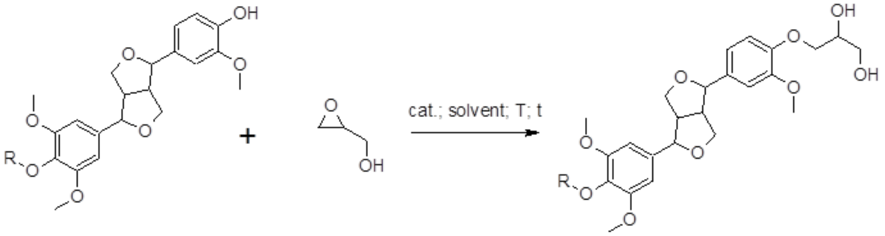

Figure 4. Simplified catalysed chemical modification of BCD-cleavage products.

^{31}P-NMR analyses of the solvent free materials illustrate a significant increase in aliphatic OH-number up to 10 mmoles/g. The cleavage products show a high chemical reactivity.

Table 2. Results of ^{31}P-NMR on BCD-oligomers, on BCD-oil as well as on their synthesis products regarding aliph. & phen. OH-No. [mmol/g].

#	aliph. -OH	Carboxyl -OH	Cond. & Sy-OH	Guajacyl -OH	Catechols -OH	para-OH	phen. -OH	Total -OH
BCD-oligo	0,15	0,49	2,10	0,64	0,58	0,22	3,54	4,19
Oligo-Glyceryl-ether (solid)	4,26	0,04	1,28	0,39	0,24	0,09	2,00	6,31
Oligo-Glyceryl-ether (liquid)	10,42	0,03	0,00	0,00	0,00	0,00	0,00	10,45
BCD-Oil	0,27	0,84	2,83	0,97	1,32	0,21	5,33	6,44
BCD-Oil-glyceryl-ether	9,17	0,03	1,02	0,52	0,05	0,01	1,60	10,80
Guaiacyl-Glyceryl-ether	9,78	0,00	0,00	0,05	0,00	0,00	0,05	9,83

Conclusions

BCD of eucalyptus kraft lignin leads to primary cleavage products (guaiacols, syringols) and secondary cleavage products (catechols, *p*-OH-phenolics) by additional de-methylation and de-methoxylation. The formation of the monomers depends on the parameters: T, τ and NaOH concentration. The inter-unit linkages (β-*O*-4, 4-*O*-5, β-β´ resinol) are not more present in BCD-oils and in the oligomer BCD-fractions depending on the process parameters. The formed oligomer material shows lower M_W, M_N and M_W/M_N than the kraft-lignin, and contains very high amounts of “phenolic-OH”- groups. The “aliphatic OH”- groups will be lost during BCD of lignin. The oligomer main product shows also interesting structures for material applications. A catalytic epoxide ring opening with phenolic groups of oligomeric and monomeric cleavage product leads to building blocks with a high aliphatic OH-number. The properties are adjustable by parameters. The structural features indicate an optional application in resins & PU.

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Enzymatic Challenges in Modern Biorefieries

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Abstract/Introduction

Today, two of the most significant challenges to faster development are the technical and economic hurdles in the scale-up of biomass pre-treatment as well the high cost of enzymes used in the hydrolysis step and further conversion of sugars to biocehmicals. Ea also see strong demand for novel enzymes for lignin valorisation.

An important factor in the efficient use of lignocellulosic biomass is the robust pre-treatment the substrate receives. Pre-treatment refers to the separation of one or more of the four major components of biomass – cellulose, hemicelluloses, lignin and extractives.

The most common pretreatment methods steam explosion and the use of chemical methods such as dilute acids, alkaline solutions, organic solvents, ammonia, sulphur dioxide, and carbon dioxide. Sometimes enzymatic pre-treatments are used in combination with chemical treatments to solubilize the lignin.

In addition to the dozens of different pre-treatment technologies there are numerous types of lignocellulosic biomass. Wood industry residues, corn stover, bagasse, wheat straw and many others sources are all used or have the potential to be used as feedstock for advanced biofuels. While the diversity is desirable in terms of bountiful sources and environmental sustainability it poses a real problem for the economic feasibility of a project. When multiplied by the dozens of pre-treatment methods, we now have more than a hundred potential variations of pre-treated biomass.

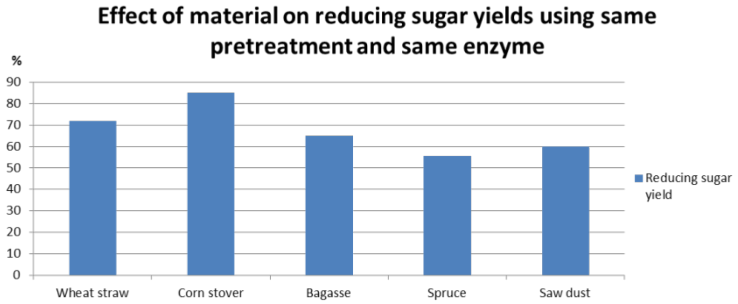

Figure 1. Selection of feedstock and pre-treatment impacts the effect of enzymatic treatment. Commercial cellulases are much more optimized to steam exploded corn stover than similarly treated soft wood.

The goal in the pre-treatment phase of biomass preparation should be on maintaining high concentrations of solids and minimizing the formation of inhibitors, both of which are primary drivers of capital and operating expenditures. Currently, the problem of inefficient hydrolysis due to diverse feedstocks and pre-treatments is primarily solved through enzyme overdosing (primarily cellulase). Unfortunately, this practice keeps the entire biorefinery process economically unfeasible. It’s not reasonable to expect that there will be one magic cellulase or cellulase based cocktail which will be able to convert dramatically different feedstocks with equal efficiency.

We suggest that the second most important consideration (after optimizing existing pre-treatment technologies for a particular feedstock) is to optimize the enzymes specifically for the pre-treated lignocellulosic material.

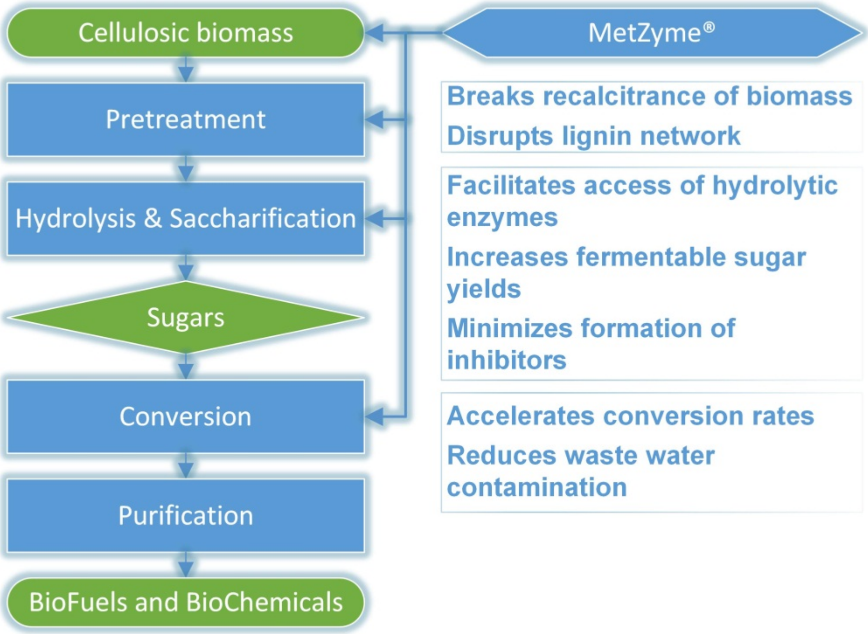

Figure 2. MetZyme® is flexible and adaptive to various processes.

Finland-based MetGen has been developing a method founded on the rational design of enzymes tailored specifically to particular lignocellulosic substrates. In laboratory experiments this approach has demonstrated a dramatic increase in sugar yields and simultaneously a detoxification of the fermentation broth. MetGen is also working on novel enzymes for lignin valorization and further conversion of sugars to valuable biochemicals.

Experiments

Hydrolysis reaction was performed in 24-well plates with 10ml reaction volume. Enzyme mix was added on the substrate to a final consistency of 10%. Plates were shaked for 72h at 50°C and 250rpm. 50µl samples were taken at start and 72h timepoint. 3,5-dinitrosalisylic Acid (DNS) method was applied to samples in order to determine reducing sugar amounts.

MetGen has performed hundreds of experiments using

a) various pre-treted substrates from industrial collaboration partners,
b) various commercial cellulase complexes, such as endoglucanases, exoglucanases and β-glucosidases,
c) various additional enzymes for hemicellulose degradation, such as endoxylanases, endomannanases, β-xylosidases, β-mannosidases, β-galactosidases, α-glucuronidases, α-arabinofurnosidases, α-

galactosidases, acetyl xylan esterases, feruloyl esterases and glucuronyl esterases,

d) additional enzymes for lignin degradation. It requires oxidative enzymes, such as lignin peroxidases, manganese peroxidases and laccases,
e) and several combinations of the different substrates and enzymes above

The Overall objective of the experiments has been to

a) increase the sugar yield and overall productivity of the saccharification and
b) hydrolysis while reducing the technology cost of enzymes in particular.

Cellulose, hemicellulose, lignin and pectin (and even phenols in fermentation broth) need to be enzymatically treated with an optimized cocktail. Pretreatment mechanism, cost and effect needed to be understood in order to optimize the enzymatic solutions. Enzyme cocktails were tailored with specific pretreated feedstock in mind. Also, the processes often require thermostable enzymes. Therefore MetZymes® are optimized for specific customer processes.

As the goal is a low cost enzyme cocktail with high specific activity the aspects to be taken in consideration in desing of experiments are as follows:

a) Understand nature of pretreated biomass and process requirements (pH, temperature, retention time etc). Requirement: Strong analytics skills
b) Tailor genetically individual enzymes to work effeciently both on indvidual wood components and in a mixture (eliminate possible inhibitory effects). Requirement: Genetic engineering and HTS skills
c) Advanced application testing of individual enzymes and mixture to determine optimum proportions and dosage. Requirement: Novel and robust application testing protocols
d) Optimization of production costs (crude formulations, effective production hosts). Production optimization

Results and Discussion

It is interesting to notice that there is a variety of biomass that can be transformed into reducing sugars[1] (Senthilkumar & Gunasekaran, 2005). In addition, it was demonstrated that pre-treatment methods are compulsory steps to include in the reducing sugar recovery process. When proper pre-treatment is applied to specific biomass hydrolysis yield could be improved by 75% (from 15% without pre-treatment to 90% with pre-treatment)[2] (Zheng, Pan, & Zhang, 2**009).**

Results of 72h hydrolysis are shown in figure 3. 72h hydrolysis with recommended commercial cellulase dosage doubled the reducing sugar yield as compared to control sample. 50% reduction of commercial cellulase dosage resulted logically in reduction of hydrolysis yield. However, cellulase dosage reduction can be compensated by addition of MetZyme® SUNO™. Moreover, MetZyme® SUNO™ addition resulted in improvement of the hydrolysis yield by

25%. These results indicate that MetZyme® SUNO™ can improve the valorization of lignocellulosic biomass by reducing the production cost of reducing sugars.

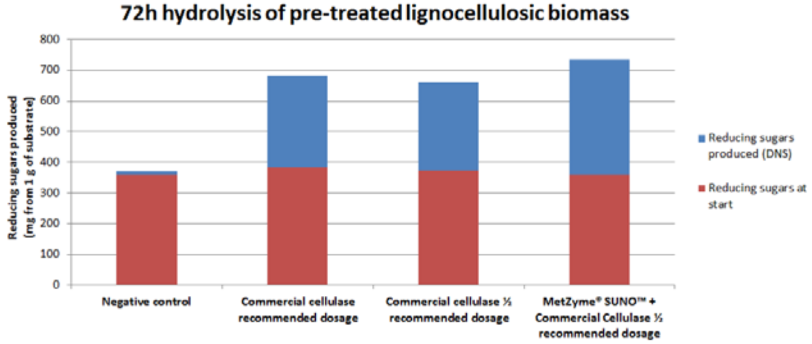

Figure 3. MetZyme® increases sugar yield by 25% with only 50% of cellulase comlex used. Substrate is pre-treated spruce.

The nature of the biomass and the pre-treatment method are intimately linked[3] (Yang, Dai, Ding, & Wyman, 2011). This is due to the role that plays the pre-trement method in facilitating the access for cellulase to sugar chains in the biomass. In addition it was previously shown that oxidoreductases play a clear positive role in the biomass conversion process[4] (Jurado et al., 2009). It is therefore of primary interest to combine properly the 3 parts included in reducing sugar recovery process from lignocellulosic biomass: the biomass, the pre-treatment and the enzymatic solution. Not only that the pre-treatment method play an important role in function of the biomass, the enzymatic cocktail used for the conversion is certainely playing an as important, if not more important, role in the economical equation converting lignocellulosic biomass conversion into value-added.

Conclusions

- There will be no «one size fits all» cellulase cocktail that fits every lignocellulosic process effectively.
- Enzymes and enzyme mixes shall be tailored to customer specific pretreated biomass.
- Enzymes shall be thermostable, robust and price effective
- Formulation shall be crude to save production cost.
- Genetic engineering of enzymes, advanced application testing and price effective production are critical success factors.
- Enzyme Immobilization, cross linkage and on-site production are possible next steps in costs optimization.

- The quest for cheap cellulosic sugars is nascent, highly complex and huge: Partnering across multiple industries and with both small and large players is the name of the game.

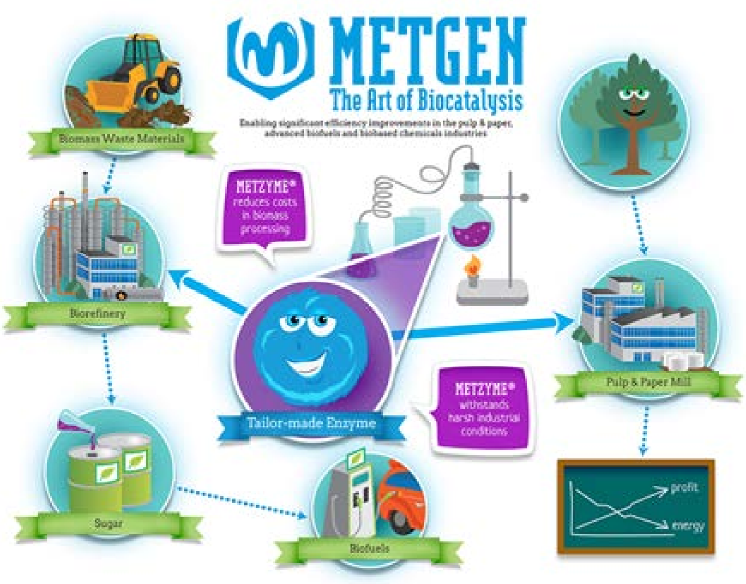

Figure 4. MetZymes® are tailored to bring value from biomass.

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Extraction, Purification, Characterization and Chemical Modification of an Industrial Alkaline Lignin: Towards the Development of New Bio-based Aromatic Building from Lignin

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Introduction

With the gradual depletion of fossil fuels, the use of renewable raw material as a source of chemicals, materials and polymers is expected. Lignin is, second to cellulose, one of the most abundant natural macromolecules. Due to its aromatic structure, it has great potential to serve as an important raw material to replace petroleum-based products. In the pulp and paper industry a large amount of lignin is obtained in the delignification process. It has for a long time been viewed as an energy source. The difficulty of valuing lignin is due to its complex, irregular and variable structure. Those observations make lignin isolation, purification and characterization very challenging.

Results and Discussion

In this context, a valorization of alkaline lignin from industrial pulping liquor supplied by Tembec Innovation is proposed. Before considering any chemical modification or potential applications, it is primordial to elucidate this lignin structure. An efficient 3-step protocol for extraction and purification of lignin from industrial liquor has been established. This protocol leads to high purity sample of lignin (95%) and allows the recovery of 68% of the lignin initially present in the alkaline liquor (Figure 1). Alkaline lignin has been characterized utilizing chemical analytical methods: elemental analysis, infrared spectroscopy (FTIR), size exclusion chromatography (SEC), NMR analysis (^{31}P, 2D-HSQC, ^{13}C) and thermal analysis: differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). The SEC results revealed lignin with considerably low molar mass. The HSQC NMR analysis showed the presence of several linkages like resinol, phenylcoumaran and β-O-4 alkyl-aryl ether and the presence of gaïacyl and p-hydroxyphenyl units[1-4]. The ^{31}P NMR analysis [5][6] also suggested the presence of a majority of phenolic hydroxyls (mainly condensed units and gaïacyl units) and few carboxylic acids.

Chemical modification of alkaline lignin has been done by oxidation in alkaline media. Three major oxidized products have been isolated depending on the solvent extraction: oligomers and aromatic molecules. The SEC analyses have shown a decrease of molar mass confirming the cleavage of the lignin. The ^{31}P NMR analyses have shown a large carboxylic acid formation (functionalization). This functionalization was more obvious for hydrosoluble compounds (93 carboxylic acid functions for 100 C9 units). Finally, aromatic compounds were analysed by GC-MS. Interestingly, this mixture contained 15% of vanillin.

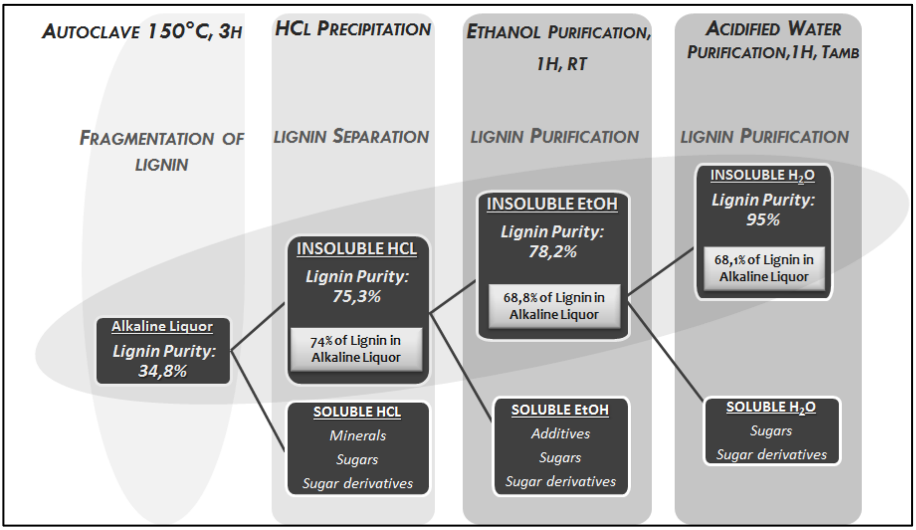

Figure 1. Protocol for extraction & purification of alkaline lignin.

Conclusion

A successfull route to extract lignin from alkaline liquor has been developed. Precipitation in acidic medium followed by ethanol purification and washing with acidified water was found to be an effective procedure to obtain high purity (95%) lignin from alkaline liquor. A detailed elucidation of alkaline lignin structure after extraction and purification was essential to valorize this co-product of paper industry. Chemical oxidative modification and functionalization of alkaline lignin allowed us obtaining value-added bio-sourced chemicals and functionalized oligomers. These substrates will be further investigated in the design of new bio-based polymers.

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Fluidized Bed Fast Pyrolysis and Gasification of Japanese and Australian Woody Biomass

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Abstract

A high temperature experimental fluidized bed (maximum operating temperatures up to 1400 °C) was developed using alumina. By using the bed, fast pyrolysis of various woody biomass samples and the following *in-situ* CO_2 gasification of the produced char were conducted.

The char yield was drastically low compared with slow pyrolysis case, especially for softwoods. Char-bed agglomeration was observed by fast pyrolysis, especially for softwoods, even under higher temperature of 600-1000 °C than that so far reported for bed agglomeration by volatile matter. Characteristic gasification curve was observed only for softwoods char; a distinguish feature of sharply rapid gasification at conversion around 0.05 and then at higher conversion, volume reaction behaviour. The latter two distinguish phenomena especially for softwood was considered to be explained by large quantity of volatiles as well as its quality.

While the gasification rate of red river gum (*Eucalyptus camaldulensis*) increased with temperature up to 1200 °C, gradual decrease in the rate with temperature was curiously observed, which was also explained by the plugging of char holes with calcium released at fast pyrolysis.

Introduction

Recently the research activity on unused woody biomass utilization as a primary energy source for power generation has become hot, because of the purchase price of electric power from it was raised to 40 from 32 JpYen/kWh for 20 years (from this April, only for the capacity smaller than 2 MW; 32 JpYen/kWh was kept unchanged for the capacity larger than 2 MW) while that of solar power was reduced to 27 from 32 JpYen/kWh for 20 years (for larger than 10 kW; in the case smaller than 10 kW, to 33-35 from 37 JpYen/kWh, for 10 yeas) in Japan. The use of biomass had so far been limited to regional energy supply because of its difficulty in collection in Japan, where most of the forest locates at the steep mountain side though forest coverage is as high as 67%.

On the other hand, the forest coverage in Australia is as small as 19%. Most of the land is arid or semi-arid, because of small precipitation. In the area with annual precipitation around 200-250 mm in Western Australia, the present authors have demonstrated for more than 15 years that plantation of wood is possible under such dry condition by modifying soil condition for roots development and by collecting runs off water for tree growth [1]. In the above course, river red gum, *Eucalyptus camaldulensis*, a native species, was found to show high growing rate and good drought resistance. By afforestation of arid or semi-arid area, the carbon in wood is fixed from atmospheric CO_2, which is expected to mitigate climate change issue. The present authors also assessed the feasibility of transportation of liquid fuel produced from woody biomass, from Australia to Japan [2]. It was demonstrated that the liquid fuel may be transported into Japan with reduction of CO_2 emission, however, only under the condition that substantial part of woody biomass is used for power generation in Australia and the produced electricity is used for process energy [2]. Under the present situation, vast amount of biomass is to be harvested and treated efficiently. In order to attain high efficiency the woody biomass is to be continuously fed to gasifiers and the produced gas is to be converted to electricity using gas combined cycles. Under some condition, hybrid processing with coal may be possible/ preferred.

In such processes, biomass is fed into gasifiers and pyrolyzed rapidly, and the produced char and tar are gasified at high temperature. However there are few reports on the behaviour of biomass under the fast pyrolysis at high temperature. In the present paper, various interesting features under the condition are reported.

Experimental

The experimental fluidized bed reactor is shown in **Figure 1**. The main body of the reactor is made of alumina equipped with a distributor made of multi pieces of alumina thin tubes fixed with ceramics cement. The holes of most of the tubes are plugged up while only around ten holes are left open, to keep suitable pressure drop with even fluidization.

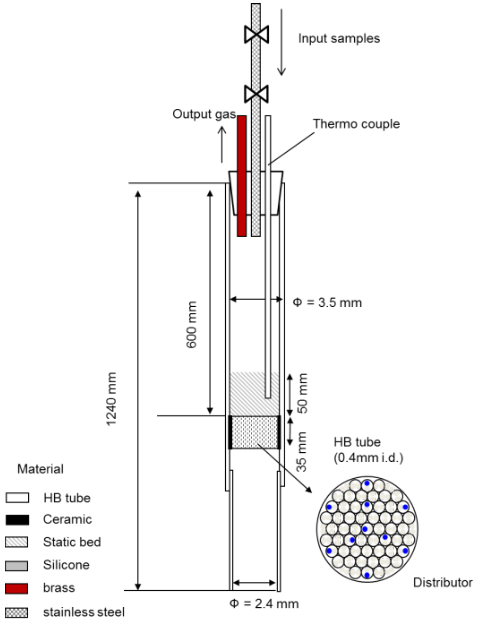

Figure 1. Schematics of fluidized bed.

The proximate and ultimate analyses of the sample used in the present study are shown in **Table 1**. The biomass samples were pulverized and only some fraction was used. Porous activated alumina particles with mean diameter of 215 μm were used as bed materials to get bed height of 5 cm.

Table 1. Properties of biomass samples.

Group	Biomass species (Popular name)	Biomass species (Scientific name)	Proximate analysis (wt % dry)			Ultimate analysis (wt % dry)			
			Volatile	Fixed Carbon	Ash	C	H	N	O (dif.)
Herbaceous plant	Switchgrass	*Panicum virgatum L.*	80.83	14.82	4.35	46.58	5.82	1.54	41.71
	Miscanthus	*Miscanthus spp.*	80.13	17.18	2.69	48.50	5.74	0.07	43.00
Agricultural residue	Bagasse		79.76	15.67	4.57	48.89	5.59	0.41	40.54
	Empty Fruit Bunches		76.47	20.37	3.16	48.25	6.12	0.38	42.09
	Rice husk		64.80	15.81	19.39	-	-	-	-
softwood	Japanese pine, matsu	*Pinus japonica*	82.18	17.25	0.57	49.40	6.33	0.14	43.56
	Japanese cypress, hinok	*Chamaecyparis obtusa*	84.75	15.08	0.17	48.33	5.91	0.00	45.59
	Japanese cedar, sugi	*Cryptomeria japonica*	83.39	16.41	0.20	48.69	6.09	0.00	45.02
deciduous hardwood	Japanese zelkova, keyak	*Zelkova serrata*	79.70	19.18	1.12	47.42	5.50	0.15	45.81
	Red mangrove, obahirug	*Rhizophora mucronata*	81.16	17.95	0.89	45.18	6.03	0.10	47.80
	River red gum, yukari	*Eucalyptus camaldulensis*	78.92	18.50	2.58	48.02	5.99	0.37	43.04

-: NA (because of their small sample amount)

Under the fast pyrolysis condition, 1.0 g of biomass sample was fed from the top of the bed fluidized with 6 u_{mf} nitrogen at 300-1200 °C, while in case of the slow pyrolysis, the bed containing biomass sample was slowly heated at the rate of 10 °C/min under the fluidizing condition. The char sample was taken after cooling the bed. Under the gasification condition, the successive *in situ* gasification was conducted by switching gas to 25% CO_2 gas and the CO and hydrogen production rate was measured by a gas chromatography.

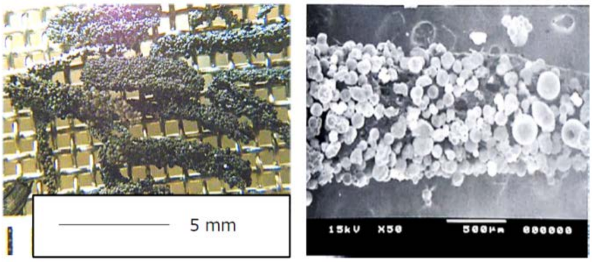

Figure 2. Char-bed agglomerates (cypress, 800 °C).

Results and discussion 1: char yield

The apparent char yield was defined as the weight percent of particles larger than 710 μm in the bed based on fed dry biomass (1.4-2 mm). It was confirmed no char was included in the fraction smaller than 710 μm. Some agglomerates as shown in **Figure 2** were found only in case of fast pyrolysis. So the true char yield was given as [3].

True char yield = Apparent char yield
– Residual ash after combustion of apparent char + Ash by JIS
(all items: dry biomass basis)

As the results of fast pyrolysis, it was found that char yields were drastically low compared with those by slow pyrolysis as shown in **Figure 3**. Furthermore, the char yield from Japanese cypress, a softwood, by fast pyrolysis was lower than those from the other three samples of hardwood, grass and agricultural residue. The other softwoods of Japanese pine and Japanese cedar also gave smaller char yields than any hardwood incl. river red gum, red mangrove and Japanese zelkova, and any of herbaceous plant incl. switchgrass and Miscanthus, and any of agricultural residue incl. bagasse, empty fruit bunches and rice husk, by fast pyrolysis between 400-1200 °C [4]. The present results suggest the drastic increase in volatiles release by fast pyrolysis of softwoods.

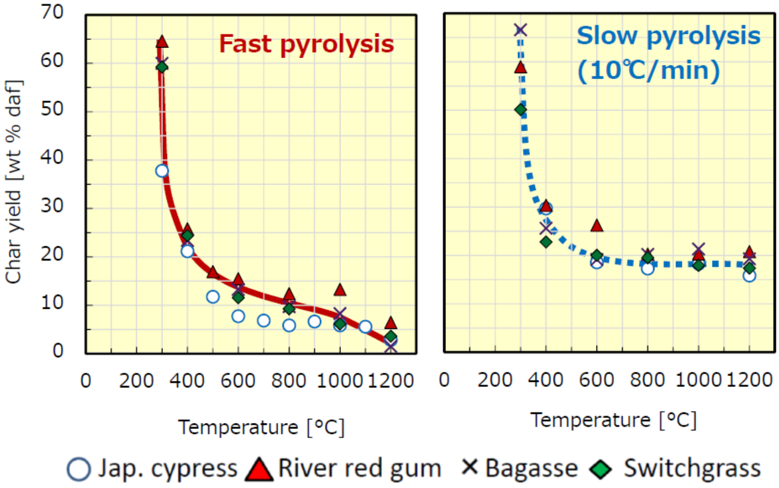

Figure 3. Effect of pyrolysis temperature on char yield.

Results and discussion 2: char-bed agglomeration

The degree of agglomeration was evaluated by the difference between “True char yield” and “Apparent char yield” (namely difference between “Residual ash after combustion of apparent char” and “Ash by JIS”).

The phenomena of char bed agglomeration under the fast pyrolysis in a fluidized bed have firstly reported for Mallee leaf (a kind of Australian *Eucalyptus*) at 300–700 °C and it was demonstrated that the cause of the phenomena is volatile organic materials [5]. And then the present authors have reported that these phenomena are also found by fluidized bed fast pyrolysis of all of the biomass species tested incl. red river gum, a kind of *Eucalyptus*, even at higher temperature [3]. In the present paper the degree of bed agglomeration is schematically shown in **Figure 4**, where the thick colour with less white dots (i.e., softwoods, 800 °C) indicates the degree of agglomeration larger than 60%, while thick with more dots 40-60%, and so on. It should be noted that the significant bed agglomeration was observed drastically, especially for Japanese softwoods by fast pyrolysis, especially at high temperature of 600-1000 °C, not restricted to so far reported agglomeration phenomena for Mallee leaf at lower temperature of 300-700 °C [5]. It is also suggested that the remarkable bed agglomeration found for softwoods is caused by the release of large amount of organic volatiles by fast pyrolysis especially at higher temperature, while the cause of the remarkable agglomeration found only for rice husk at 1200 °C should be attributed to the high temperature melting of ash component such as alkaline or alkaline earth elements with silica.

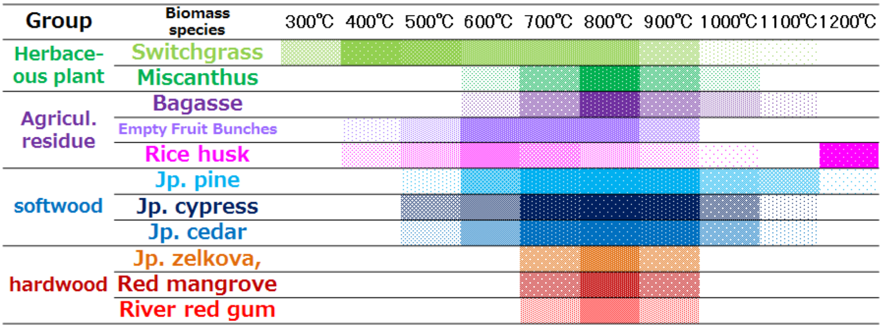

Figure 4. Effect of biomass species on bed agglomeration under fast pyrolysis.

Results and discussion 3: gasification reactivity

The effect of woody biomass type on gasification rate of char produced by fast pyrolysis in fluidized bed at 1000 °C has already been reported in our previous paper [6]. Hardwood char gasification rates were faster than those of softwood samples. Characteristic gasification curve was observed only for Japanese softwood char; a distinguish feature of sharply rapid gasification was observed at conversion around 0.05 and then at higher conversion, it almost followed volume reaction behaviour when porous alumina particles were used as bed materials. The present phenomena are also considered to be caused by the larger amount of volatiles released by fast pyrolysis, especially from softwoods.

Here, the effects of temperature are shown on the gasification kinetics of river red gum char in **Figure 5**. The rate constants determined from the slope of dX/dt vs. X where volume reaction kinetics is applied, were plotted against the pyrolysis/ reaction temperature. While the rate increased with temperature up to 1200 °C, gradual decrease in the rate with temperature was curiously observed. The cross sectional SEMs of fast pyrolysis chars are shown in **Figure 6**. Small fibre-like deposits are sometimes found only on char produced at 1400 °C. The EDX analysis elucidated that the deposit is calcium. Under the high temperature fast pyrolysis, melted metal is suggested to be transferred in the pore with the release of volatiles and onto the surface, which may hinder the progress of gasification.

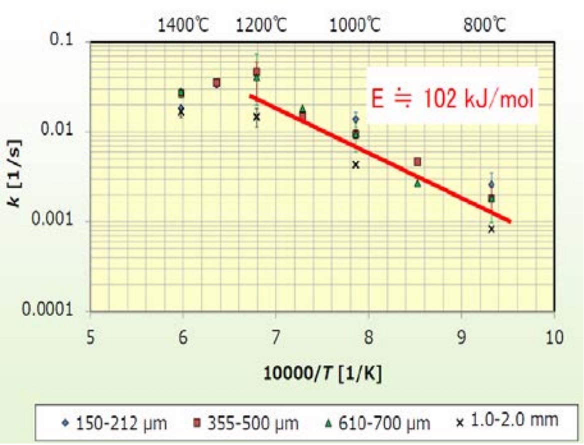

Figure 5. Gasification rate constant of red river gum.

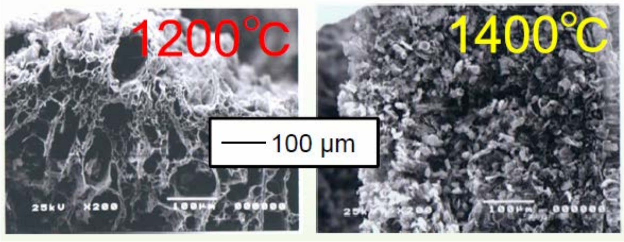

Figure 6. Cross sectional SEM of chars.

Conclusion

Under the high temperature fast pyrolysis and in-situ gasification of biomass in a fluidized bed, various new phenomena were observed different from slow and low temperature case. They may be caused by fast release of much amount of volatiles.

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Application of Enzymes in the Austrian Pulp and Paper Industry

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Abstract

Enzyme catalysed reactions can help to render environmentally harmful process steps in pulp and paper industry more ecologically friendly. For this purpose, enzyme specialists are working together with industrial partners in a project called EnzPap to identify enzyme formulations and conditions relevant for the industry. Through EnzPap, enzyme based process steps in starch conversion, refining, wet end starch treatment and pulp deinking are investigated. Formulations containing amylases, cellulases, proteases, lipases, laccases and xylanases are tested under industrial conditions.

Introduction

The Austrian Pulp and Paper industry plays an essential role in the Austrian economy, providing jobs for more than 8000 people and consuming 4694 GWh electricity, which corresponds to 6.7 % of Austria's electricity consumption in 2013. More than 20 companies are present in the Austrian paper market, with more than 85% of their paper products being exported. The Austrian paper industry is highly exposed to international competition, which makes constant improvement in efficiency necessary. Enzymes can help to reduce energy demand and open up new raw material sources for the industry. Therefore enzymes already used by other sectors of industry, e.g. detergent industry and food industry, came into focus of pulp and paper companies, already many years ago. Today, despite some promising established enzyme based processes, a better knowledge on the effect and potential of enzymes in the individual processes at each company would allow wider implementation. A large cost driver in pulp and paper industry is the material cost.[1] Starch, as third main component in paper, is an important raw material in pulp and paper industry, used in different stages of the papermaking process, to achieve a variety of functions in the end product. Cheap maize starch, in contrast to potato starch, usually contains lipids and proteins which have a negative effect on the application of starch. In wet end processes starch is added to improve strength of the paper and in surface sizing starch is used to adjust porosity and roughness of the paper sheet.[2] EnzPap investigates the usage of amylases, making them better applicable to the paper, the ability of lipases and proteases to remove lipids and protein impurities in starch and cellulases in refining processes to influence fibrillation of cellulose fibres. This will help companies to use maize starch as a cheap source of starch and ensure efficient usage of cellulases in refining.

Cellulases and xylanases mainly used in refining can help to reduce the energy demand in milling, which is one of the most energy consuming steps in paper production. Around 20 % of the total electricity demand is caused by refining, which main goal is the shortening and fibrillation of the cellulose fibre. Cellulases, incubated within the pulp, increase the fibrillation of the fibre and result in decreased milling time and energy uptake [3].

Experimental

Basic characterisation

All Enzymes provided by the company partners had to undergo a basic characterisation, which included protein content determination by the Bradford method, determination of the molecular weight of the enzyme and of possible impurities by SDS-Page and activity measurement on standard substrates [4] [5].

Enzyme assays

To investigate applicability of commercial enzyme formulations under industrial conditions the standard activity tests were adapted to individual situations like water with different degrees of hardness, diverse substrates, temperature and pH

Starch characterisation

EnzPap focuses not only enzymes and their characterisation, but also the characterisation of different cationized starches to replace expensive pure potato starch. Therefore, the content of lipid and protein impurities in different starches is determined by several methods and ability of proteases and lipases to degrade these impurities will be investigated.

Results and discussion

Protein content measurements, performed with the Bradford method, show a high heterogeneity of different enzyme formulations for the same application. [4] **Figure 1** shows the protein concentration measured for enzymes used in wet end starch processing. Differences in protein concentration may result from different amounts of impurities contained and obvioulsy specific activity of the active enzymes. For companies protein determination and activity measurments are an essential information necessary for optimal dosing of enzymes. For companies dosing of enzymes in processes depends on pH, substrtrate, temperature and degree of hydrolosis. Protein content measurments offer a feasible approach to compare different enzymes under real conditions.

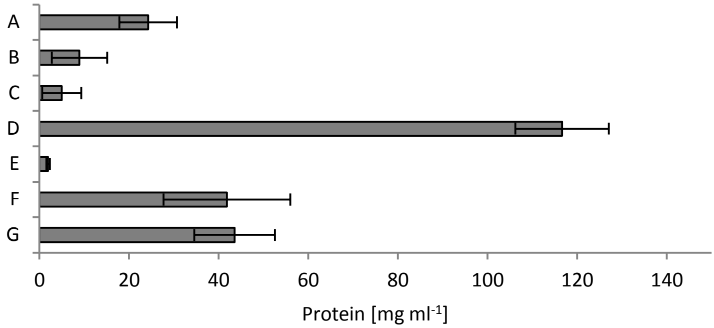

Figure 1. Protein concentration for enzymes used in wet end starch processing.

Purity of commercial enzyme formulations can be investigated with SDS-Gelelectrophoresis. **Figure 2** demonstrates a purity analysis for four different enzyme formulations for refining. Commercial enzyme formulations can contain a mixture of different enzymes and stabilizing agents; this is often the case for cellulases products. Thereby the SDS-Page patterns are more complicated for this group of enzymes compared to other commercial formulations containing different enzymes.

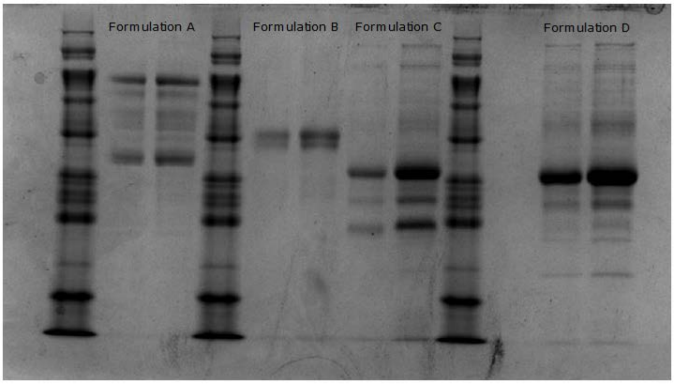

Figure 2. SDS-Page for refining enzymes as part of the basic characterisation.

The used enzyme formulation must withstand special conditions occurring in a paper mill since ideal conditions for enzymes in large scale production processes cannot be maintained permanently. Hence, knowledge about enzyme stability/sensitive to real process conditions is essential, these special conditions must be included, which normally do not play a role in lab scale experiments. One of these considerable factors is the water hardness. The effect of different Ca^{2+} concentrations was investigated for a protease, planned to be used in wet end starch processes. The effect of different Ca^{2+} concentrations is visible in Figure 3. Plants located in regions with hard water have to adopted enzyme dosage. For the evaluated enzyme hard water is decreasing activity to 50 % of the originally value.

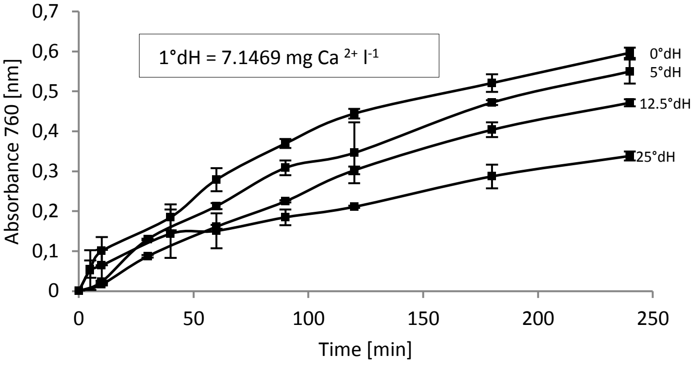

Figure 3. Influences of water hardness on the performance of a protease for wet end starch processes.

According to different types of raw material and pulping processes, different pulps are in use of the paper industry. Raw materials like hard wood, soft wood and agriculture residues can be treated by different processes to obtain pure pulp, which is the starting material for refining. Chemical pulps, produced by the sulphite or Kraft process are pure celluloses and have the highest share in pulping processes. In Europe 65 % of total pulp production derives from Kraft processes. [6] Accessibility of enzymes on pulps is an important factor and may differ for commercial cellulases and thereby must be investigated because of high heterogeneity of enzymes and substrates. **Figure 4** demonstrates differences in activity of a commercial cellulase on different pulps. Long fibre pulps seem to have a higher accessibility for the cellulase formulation used in **Figure 4**. LF 2 and LF 1 derive from different pulping processes. LF 1 was produced by sulphite process and LF 2 derives from Kraft pulping. **Figure 4** demonstrates that the cellulase used here has a higher reactivity on Kraft pulps than to sulphite pulps.

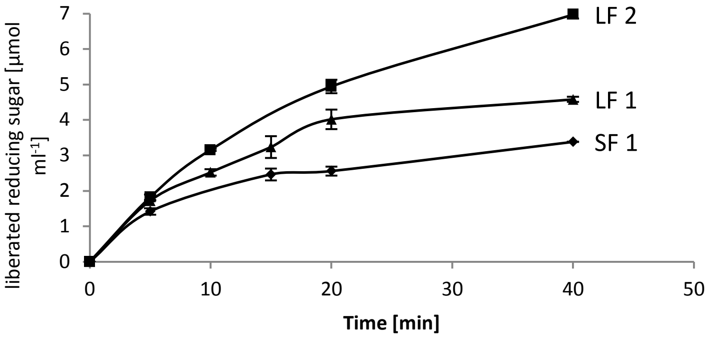

Figure 4. Cellulases activity on different long fibre and short fibre pulps alt pH 4.8 and 40°C.

Starches as important raw material for the pulp and paper industry became into focus, because the paper industry has an enormous need in starches of high purity. Impurities in starches, especially protein and lipids can cause agglutination in the paper machine. To make other starches a useful alternative EnzPap deals with the characterization of cationized starches provided by the Austrian pulp and paper industry. **Figure 5** shows an extraction of starch impurities with solvents of different polarity. The content of extracted impurities is different for different starches and also changes with the solvent. More polar solvents extract more impurities out of starches than non-polar solvents do. Enzymes can be used to remove unwanted impurities by degrading them to products without any sticky properties. In this area, lipases should degrade lipids to fatty acids and proteins should be hydrolysed to their amino acids, by proteases.

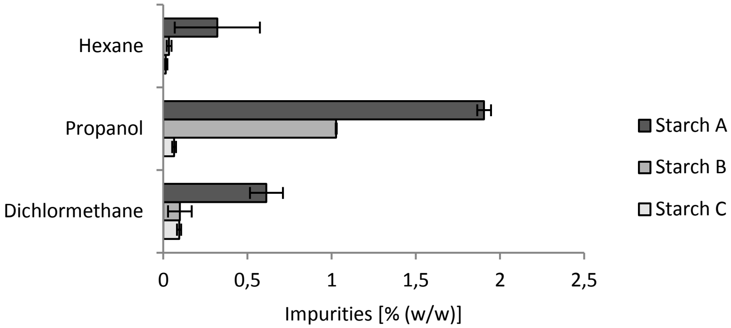

Figure 5. Impurities extraction out of starches with solvents of different polarity.

Due to high number of different enzymes in the pulp and paper industry, standard enzyme assays were adapted to special needs and simple protocols mainly based on photometric methods were developed.

Conclusion

EnzPap provides knowledge and simple protocols for the assessment and implementation of enzymes in various processes of the pulp and paper industry. Dispite the high potential of enzymes processes demonstrated already for many years, implementation can be enhanced by the development of individual solutions and adaptation preferable on-site where many factors play a role ranging from raw materials to process conditions. Ultimately, the efforts of EnzPap should lead to, reductions in energy consumption and material cost as well as to an environmental impact on this industry.

Acknowledgements

We thank all companies of the Austrian pulp and paper industry that participate in our study.

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Molecular Weight Measurement of Kraft Lignin by Size Exclusion Chromatography (SEC) in Organic and Aqueous Systems

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Abstract

This study investigated and compared the measurement of kraft lignin molecular weight (MW) and molecular weight distribution (MWD) using: 1) conventional organic phase SEC (employing linear polystyrene (PS) standards) and on-line refractive Index (RI) or Ultra-Violet (UV) detectors, 2) organic phase SEC with on-line Multi Angle Laser Light Scattering (MALLS) detection, and 3) aqueous phase SEC with on-line RI and viscosity detectors. The comparison was performed using three kraft lignin samples (softwood, hardwood, and modified softwood kraft lignins).

Introduction

The measurement of the MW and MWD of lignin using organic phase size exclusion chromatography (SEC) has been a challenging task for several decades. Common problems include lignin solubility and aggregation as well as excessive binding of the lignin on the column stationary phase [1]. Another source of problems that has been observed in the case of organic SEC, has been the use of PS standards for MW calibration purposes and UV detection for analyzing the eluting peaks. Since lignin is not a linear polymer, the measured lignin MWs have been consistently lower than the actual lignin MWs [2]. Therefore, the purpose of this paper is to discuss ways by which these problems can be addressed. Hence, in an effort to improve accuracy and precision and compare the results obtained from different approaches (organic and aqueous SEC), it was proposed that FPInnovations and PolyAnalytik work in parallel on the analysis of the same series of lignin samples. Therefore, organic SEC-MALLS approach was used at FPInnovations while organic phase conventional SEC-RI and aqueous phase universal SEC-RI/viscosity were used at PolyAnalytik. The results obtained were compared in order to evaluate the relative advantages and disadvantages of each method/approach.

Experimental

Softwood (SW), hardwood (HW), and modified softwood (MSW) kraft lignin samples were produced by FPInnovations using the LignoForce System™ [3]. SW and HW lignins were used without any modification. In an effort to lower the MW of a SW kraft lignin, a pre-treatment under controlled conditions was applied by a university-based group in Canada. Purified kraft lignin samples analyzed by conventional organic phase SEC-RI/UV and SEC-MALLS were first derivatized using an acetyl bromide-acetic acid solution as previously described by Guerra *et al.* [4]. Derivatized kraft lignin samples were prepared at a concentration of 2 mg/mL in THF eluent. However, the kraft lignin samples analyzed using aqueous phase SEC were directly solubilized in 0.1M NaOH. All samples were filtered through 0.2-µm Nylon syringe filters into auto-sampler vials.

Organic Phase Conventional SEC-RI

This approach was used at PolyAnalytik. Three SupeRes SEC columns (PolyAnalytik PAA-104, PAA-103, and PAA-102) having a MW exclusion range of 100-400,000 Da were used as the SEC stationary phase, and THF was used as the mobile phase at a flow rate of 1.0 mL/min at 30°C. The analysis was conducted using a Viscotek GPCmax autosampler, pump, and degasser module and a Triple Detection Array 302 module (Malvern Instruments) which held the SEC columns, the RI detector (wavelength = 633nm), right-angle (90°) and low-angle (7°) light scattering detector, and a four-bridge capillary viscometer with analog pressure transducers in a temperature-controlled oven equilibrated at 30°C. The conventional calibration curve was constructed from the retention volumes of PS standards (PolyAnalytik Inc.) monitored by the RI detector.

Organic Phase SEC-MALLS

This approach was used at FPInnovations. Three Styragel columns (Waters HR4, HR4E, HR1) having MW exclusion ranges from 100 to 600,000 Da (Waters Corp.) were used as the SEC stationary phase and dry, BHT-stabilized THF was used as the mobile phase at a flow of 1.0mL/min at 25°C). The eluting peaks were monitored using three detectors in series: a UV detector from Agilent (254nm); a MALLS detector (laser wavelength = 690nm, equipped with narrowband interference filters on even number detectors to eliminate fluorescence) and a Refractive Index (RI) detector from Wyatt (laser wavelength = 690nm set at 30°C). The RI increment (dn/dc) value of kraft lignin was calculated from the RI detector response factor as a function of polymer concentration using equation (1).

$$\frac{\Delta RI_{Area}}{\Delta c} = \frac{K}{n_0} \cdot \frac{dn}{dc} \cdot c \qquad (1)$$

where RI_{Area} = SEC eluting peak area, c = polymer concentration, K = RI calibration constant, n_0 = refractive index of solvent, and dn/dc= refractive index increment.

Aqueous Phase Universal SEC-RI/Viscometer

This approach was used at PolyAnalytik. One Multi-Solvent SEC column (PolyAnalytik PAM-506) having a MW exclusion range of 10,000-2,000,000 Da was used as the stationary phase and a 0.1M NaOH (pH 12) aqueous solution was used as the mobile phase at a flow of 0.7 mL/min at 30°C. The analysis was carried-out using a Viscotek GPCmax autosampler, pump, and degasser module and a Triple Detection Array 305 module (Malvern Instrument) which held the SEC column, RI detector (wavelength = 633 nm), right-angle (90°) and low-angle (7°) light scattering detector, and a four-bridge capillary viscometer with digital pressure transducers in a temperature-controlled oven equilibrated at 30°C. The digital transducers enabled measurements in mobile phases of a wide pH range (3-12). The universal calibration curve was constructed from Pullulan standards (PolyAnalytik Inc.) using the RI detector and viscometer. The RI increment (dn/dc) value of kraft lignin was calculated from the RI detector response factor as a function of polymer concentration using equation (1).

Results and Discussion

The MW parameters (Mn, Mw, Mz, and Polydispersity index (PDI = Mw/Mn) of SW, HW and MSW kraft lignins were measured by organic phase conventional SEC-RI/UV, organic phase SEC-MALLS, and aqueous phase universal SEC-RI/Viscometer. The results are summarized in Table 1.

As seen in this Table, the MW of SW and HW kraft lignin samples measured with conventional organic SEC-RI and SEC-UV relative to linear PS standards was lower than the MW measured by organic SEC-MALLS which is likely to be due to the branched polymer architecture of lignin. In addition, the polydispersity (PDI) of the lignin samples as measured by the conventional organic SEC-RI was higher than that measured by organic SEC-MALLS. In comparison, the SW and HW lignin samples directly solubilized in 0.1M NaOH and analyzed by universal SEC-RI/viscometer in aqueous phase (0.1M NaOH, pH 12) generated MW results very similar to that obtained by organic SEC-MALLS. The three SEC methods show that SW kraft lignin has a higher MW and a broader MWD as compared to HW kraft lignin. However, a large difference exists between the MW of the MSW lignin sample as measured at FPInnovations and PolyAnalytik using organic SEC-MALLS/UV signals and aqueous SEC-RI signals, respectively. This sample was shown to have an Mw of 252,400 Da and 3,360 Da based on the MALLS and UV detector signals, respectively, when organic SEC-MALLS and SEC-UV were used by FPInnovations, while the same sample analyzed by aqueous SEC-RI system at PolyAnalytik yielded an Mw of 86,341 Da. Hence, assuming that the lignin pre-treatment applied by the Canadian university has led to true lignin depolymerisation, as was expected, the organic conventional SEC-UV seems to provide better information about the outcome of the lignin modification reaction. Based on this observation, more optimization of each SEC approach is needed. In the future, a larger number of lignin samples will be tested in order to have more valid conclusions about the ability of each SEC approach in providing information about the lignin and its derivatives as well as the accuracy and precision of each approach when it comes to the measurement of the true MW.

Table 1. Molecular weight results of Softwood and Hardwood kraft lignin samples as analyzed by three SEC methods and different detectors.

Approach (detector)	ID	dn/dc (mL/g)	Mn (Da)	Mw (Da)	Mz (Da)	Mw/Mn (PDI)
Conventional Organic SEC (RI detector)	SW	N.D.	792	6764	40003	8.533
	HW	N.D.	641	2943	7500	4.613
Conventional Organic SEC (UV detector)	SW	N.D.	1765	9075	31350	5.14
	HW	N.D.	1062	3105	7695	2.92
	MSW	N.D	1250	**3360**	7050	2.693
Organic SEC-MALLS (MALLS detector)	SW	0.21	8210	20710	51690	2.523
	HW	0.20	4500	7470	12660	1.660
	MSW	0.20	181600	**252400**	301800	1.390
Aqueous SEC (RI/Viscosity detectors)	SW	0.075	5462	20901	70636	3.834
	HW	0.075	3881	11072	49527	2.856
	MSW	0.064	20305	**86341**	159189	4.252

In comparison to conventional organic SEC-RI which uses linear PS standards and organic SEC-MALLS that uses no standards, the aqueous phase SEC-RI approach used an on-line viscometer to correct for differences in polymer chain structure (i.e. branching) by measuring intrinsic viscosity (IV), hydrodynamic radius (Rh), and Mark-Houwink parameters (M-H-a and M-H log K) for the lignin samples [5]. The results are summarized in Table 2.

Table 2. Viscometry results for softwood and hardwood kraft lignin samples analyzed by aqueous phase SEC-RI.

Method	Sample ID	IV (dl/g)	Rh (nm)	M-H-a	M-H log K
Aqueous SEC	SW	0.0205	1.64	0.214	-2.591
	HW	0.0303	1.52	0.321	-2.761
	MSW	0.0265	2.66	-0.373	0.074

Given the inverse proportionality between IV and molecular density, the results of Table 2 suggest that the softwood lignin has a molecular density that is higher than the hardwood lignin. This result is consistent with the increased branching found in SW lignin polymer structures compared to HW lignins [6].

Figure 1 (a), (b), and (c) show the SEC elution curves of the SW and HW kraft lignin samples obtained from the RI detector in conventional organic phase SEC-RI, SEC-MALLS, and aqueous phase SEC-RI, respectively.

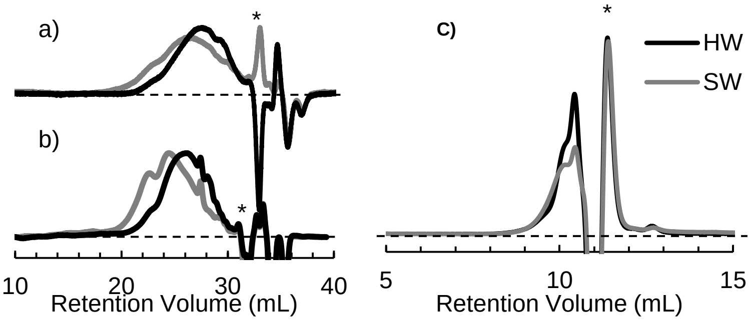

Figure 1. SEC elution curves of SW and HW kraft lignin samples obtained from the RI detector in: (a) organic phase conventional SEC-RI, (b) organic phase SEC-MALLS, and (c) aqueous phase universal SEC-RI (*solvent front).

As seen in Figure 1a) and 1b), SW kraft lignin elutes at an earlier retention volume compared to HW lignin when organic SEC is used, thus indicating its larger molecular size. However, SW and HW lignins appear to co-elute in the chromatogram obtained from the aqueous phase SEC (Figure 1c). In addition, the solvent elutes before the end of separation in aqueous SEC probably because only one SEC column (PAM-506) was used for the separation. Therefore, in the case of aqueous SEC, further optimization is needed – this can be accomplished by having additional lower MW resolution SEC columns to resolve the low MW lignin species in the lignin samples.

As mentioned above, in order to measure lignin MW by organic SEC-MALLS, lignin samples need to be derivatized and the dn/dc of each sample has to be determined prior to analysis. Although this technique might end up providing accurate MW results, the tedious and variable efficacy of the derivatization reaction could present a disadvantage. MALLS measurements of Mn are also overestimated as low MW lignin molecules (<1000 Da) pass undetected due to the weak intensity of scattered light generated by these species which, in turn, underestimates the actual PDI (Mw/Mn) of the lignin samples [8]. The higher sensitivity of conventional and universal SEC analysis to lower MW lignin is expected to provide a more accurate measurement of PDI compared to SEC-MALLS (Table 1).

Conclusions

The Universal aqueous SEC method has the potential of enabling users to simply and fully dissolve lignin samples in 0.1M NaOH solution for direct analysis using an aqueous SEC system. In addition, the use of a viscometer as a detector with this approach adds a new tool for elucidating lignin polymer structure by measuring intrinsic viscosity, hydrodynamic size, and Mark-Houwink-Sakurada parameters. Furthermore, once optimized, the organic SEC-MALLS approach is expected to provide relatively accurate lignin MW results but at the expense of longer sample preparation times and inherent problems that such procedures might entail. Even though, the organic conventional SEC-UV may not be giving the most accurate MW results as compared to SEC-MALLS, it seems to provide the best information with respect to lignin depolymerisation/modification reactions, which might be more useful in many lignin applications than having very accurate lignin MWs. In summary, a large number of lignin samples need to be analyzed in order to have more valid conclusions about the ability of each SEC approach in providing valid information about the polymerization/depolymerisation/chemical modification of lignin as well as the accuracy and precision of each approach over a wide range of MW values.

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Local Filtration Properties of Microcrystalline Cellulose

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Abstract

One of the main challenges with obtaining energy-efficient solid-liquid separation in biorefineries is the formation of compressible filter cakes. In this study the effect of particle surface structure as well as particle surface charge on the local filtration behaviour of microcrystalline cellulose was investigated. The filtration kinetics was found to be affected by the particle surface structure as a rough particle surface increases the specific surface area subjected to drag forces. Similarly, it was found that the filtration kinetics was improved by a low particle surface charge as attractive particle interactions between particles/particle fragments results in a smaller specific surface area subjected to drag. However, filtration of microcrystalline cellulose may result in a rate limiting "skin layer" close to the filter media during conditions were the particle surface is charged and the attractive forces between particles as well as steric hindrance are insufficient to prevent a local collapse of the filter cake. This "skin layer" has a large influence on the required filtration time and/or filter area of the separation, and may not be detected without the use of local filtration properties.

Introduction

Filtration can be expected to be a key unit operation in biorefineries as processes based on solid feedstock oftentimes require energy-efficient solid-liquid separation. The design of filtration units and processes for biorefineries will however present challenges as many organic materials form highly compressible filter cakes. This compressibility may result in the formation of a rate limiting "skin layer" at the filter medium [1, 2], increasing the demand of filtration time and/or filter area to a large extent.

This study investigates the effect of particle surface structure and particle surface charge on the filtration behaviour of microcrystalline cellulose. The particle surface charge was modified through the pH of the suspension with a low surface charge obtained at pH 2.9 while a pH of 6.3 was used to study charged particles

[2]. The surface structure of the particles was modified through mechanical shearing and the corresponding effect of the particle surface structure on the filtration behaviour was studied locally through measurements of the local hydrostatic pressure.

Experimental

Material and sample preparation

This study used a commercially available microcrystalline cellulose, Avicel PH-105 (FMC Biopolymers), with a nominal particle diameter of 20 µm. The particles were suspended in deionised water and the suspension had a solid content of 10 % by volume.

The mechanical properties of the MCC particles were modified through shearing using an IKA Ultra-Turrax T50 with a S50N – G45F dispersing element. This equipment operated at a constant rotational speed of 10 000 rpm and treated the particles for a total of 269 revolutions/g MCC. After the mechanical treatment the pH of the suspension was 6.3, this was adjusted using hydrochloric acid for experiments performed at a pH value of 2.9. The suspensions were then left under constant stirring for a minimum of 12 h before filtration experiments were carried out. Both the ambient temperature and the suspension temperature were constant at 22 °C during experiments.

Characterisation

The particle size distributions of the MCC particles, for initial particles as well as particles subjected to mechanical treatment, were measured using a Malvern Instruments Mastersizer 2000. The effect of the mechanical treatment on the specific surface area of the particles was measured using the BET technique (Micromeritics Tristar 3000, 8-point method). Prior to the BET measurements, a solvent exchange procedure was used prior to drying of the particles in order to preserve the structure of the water-swollen material [3]. The water in the suspension was sequentially replaced by acetone and cyclohexane through repeated displacement washing and the samples were eventually dried in a nitrogen stream before the BET measurements [4]. The particles were also studied using a Zeiss Evo HD 15 scanning electron microscope after drying using the solvent exchange procedure.

Filtration experiments

Filtration experiments were performed in a bench scale equipment designed for measurement of the local filtration properties in the formed filter cakes. The equipment has been described in detail in earlier publications [5, 6] and only a brief summary is therefore given in this paper.

The filter cell is cylindrical and has a diameter of 60 mm and a height of 175 mm, with the lower section composed of a 115 mm high Plexiglas cylinder. The filter cell is pressurised using a piston capable of delivering 6 MPa. The local hydrostatic pressure in the filter cell is measured at 8 different heights in the range 0.5 mm to 12 mm from the filter media using water-filled capillary tubes connected to pressure transducers. The piston position and the local hydrostatic pressures are registered continuously along with the amount of filtrate collected. The equipment can also be used to determine the local solidosity of the filter cake by using the attenuation of γ-radiation from a ^{241}Am source.

The filtration experiments were performed using a hydrophilic polyethersulphone filter (Supor®) with a nominal pore size of 0.45 µm. An additional grade 5 Munktell filter was also used for support. The filtration properties were investigated for applied pressures ranging from 0.15 MPa to 0.7 MPa.

Results and discussion

Characterisation

The effect of the mechanical treatment on the particle surface structure can be observed in the SEM photographs in Figure 1. Subjecting the particle to shearing resulted in an increased surface roughness, thereby increasing the specific surface area of the particles. This effect was quantified by measuring the BET surface area of the particles and the results are presented in Table 1.

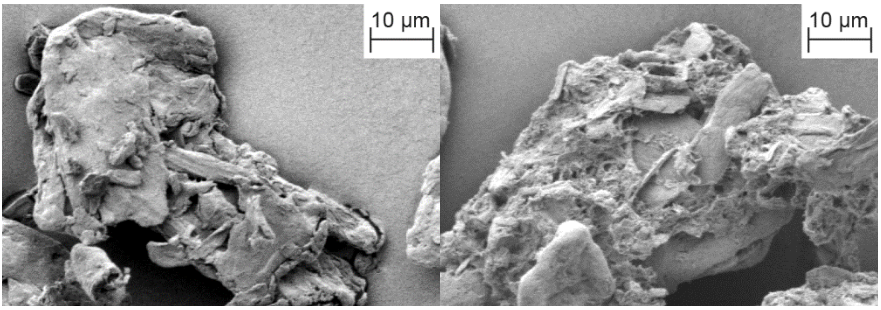

Figure 1. SEM photograph of microcrystalline cellulose particles without mechanical treatment (left) and with mechanical treatment (right) after drying using the solvent exchange procedure.

Table 1. Specific BET surface area measured for microcrystalline cellulose particles dried using a solvent exchanged procedure.

Mechanical treatment	**BET surface area [m^2/g]**
No	43 ± 1
Yes	50 ± 4

Filtration

The accumulated filtrate volume obtained during filtration experiments is presented in Figure 2. The filtrate flow rate decreased to a large extent for particles subjected to mechanical treatment at both the investigated pH levels, an effect of the rough surface structure resulting in a larger surface area subjected to drag forces from the fluid flow [7]. The suspension pH can also be seen to have a large influence on the filtration kinetics of microcrystalline cellulose, both for systems with and without mechanical treatment having affected the particle surface structure.

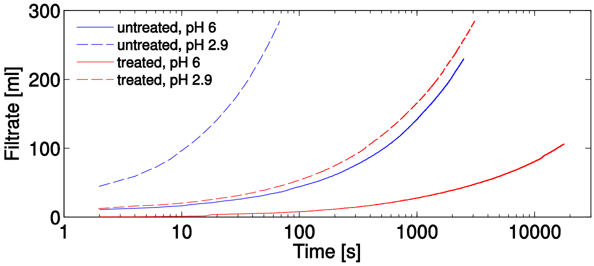

Figure 2. Accumulated filtrate volume during filtration experiments of microcrystalline cellulose with an applied pressure of 0.3 MPa.

The effect of the particle surface charge (as well as charge of the filter media), modified trough the suspension pH, on the local filtration behaviour can be studied through the local hydrostatic pressure in the filter cake at different heights from the filter media, given in Figure 3 and Figure 4. At the neutral pH, Figure 3, the hydrostatic pressure is constant over the filter cake for mechanically untreated particles, indicating a large pressure drop close to the filter media. This results is in agreement with previous studies [1, 2] and indicate that a rate limiting “skin layer” is formed. This effect was not affected by varying the nominal pore size of the filter media in the range between 0.1 µm and 0.8 µm (data not included in this paper).

In Figure 4 the pressure profile in the filter cake is shown when the particle surface charge is lowered by adjusting the pH of the suspension. At conditions with a low particle surface charge the pressure drop over the filter cake is evenly distributed, indicating that the filtration resistance is a result of resistance over the entire filter cake and not only a rate limiting step close to the filter media.

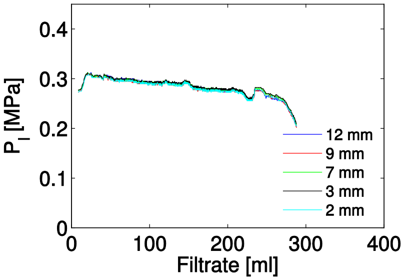

Figure 3. Local hydrostatic pressure profile for filtration of untreated microcrystalline cellulose at pH 6.3.

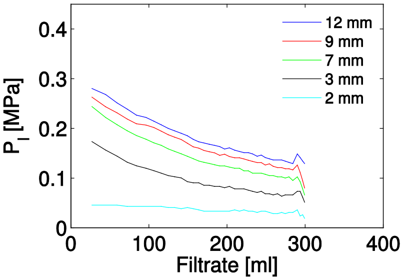

Figure 4. Local hydrostatic pressure profile for filtration of untreated microcrystalline cellulose at pH 2.9.

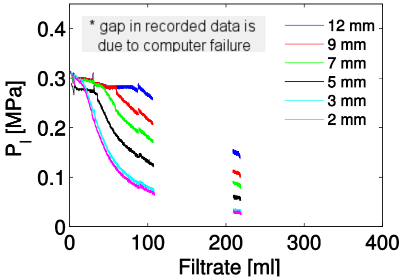

Figure 5. Local hydrostatic pressure profile for filtration of treated microcrystalline cellulose at pH 6.3.

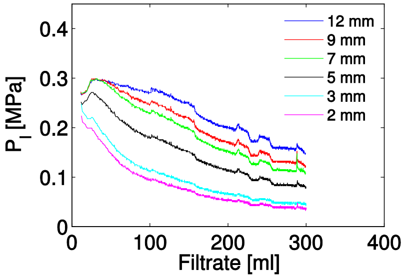

Figure 6. Local hydrostatic pressure profile for filtration of treated microcrystalline cellulose at pH 2.9.

The pressure profiles over filter cakes formed from suspensions subjected to mechanical treatment at the studied pH levels are shown in Figure 5 and Figure 6. A difference compared to suspension without mechanical treatment is observed as the pressure drop is evenly distributed over the filter cake independent of the pH value of the suspension. Increasing the surface roughness of the particles can thus prevent the formation of the rate limiting “skin layer”. This effect could be explained by increased attractive particle interactions and steric hindrance that contribute to the formation of a porous structure and resist cake collapse.

The mechanically treated microcrystalline cellulose did however still show a decreased flow rate in Figure 2 for a neutral pH where the electrostatic repulsive forces between particles are highest. This effect can be explained by the charged surfaces of particles and particle fragments preventing close association between these entities, thereby resulting in a high surface area that is subjected to drag throughout the filter cake. The effect of suspension pH on the filtration kinetics in

Figure 2 thus has different reasons for the untreated and mechanically treated microcrystalline cellulose particles respectively, indicating the need to study the local filtration properties when designing or trouble-shooting filtration operations.

Conclusions

- Mechanical treatment of microcrystalline cellulose particles resulted in a decreased filtration kinetics as the specific surface area subjected to drag forces increased.
- The filtration kinetics of microcrystalline cellulose was improved when the electrostatic repulsion between particles/particle fragments was decreased.
- During filtration of microcrystalline cellulose a rate limiting “skin layer” may be formed close to the filter media. This behaviour was shown to be counter-acted by promoting attractive particle interactions, either by decreasing the electrostatic repulsion between particles or by increasing the surface roughness to increase attractive particle-particle interactions. An increased surface roughness would also counteract collapse of the filter cake by increasing the steric hindrance.

Acknowledgements

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Local Filtration Properties of Kraft Lignin: Influence of Ligning-Carbohydrate Complex

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Abstract

The influence of lignin and xylan interactions on the filtration properties of precipitated LignoBoost lignin is investigated. LignoBoost lignin was dissolved together with added xylan and then re-precipitated. The resulting lignin-xylan suspension was more difficult to filter than the original LignoBoost lignin, although the mix also formed more porous filter cakes. One of the possible explanations suggested by the findings presented in this paper is that xylan is sorbed at the surface of the lignin agglomerates, increasing the contact area between solid and liquid and making the particles local structure more porous.

Introduction

Lignin is the main organic by-product of the Kraft pulping industry: each year, about 50-60 Mt of lignin is dissolved during the Kraft process and incinerated as a biofuel for the recovery of the process chemicals. In modern Kraft pulp mills, at least 10 to 20% of this dissolved lignin can be extracted without disturbing the recovery process. Thus, each year, 5-12 Mt of lignin could be available worldwide for the synthesis of valuable products and chemicals. Different processes exist for the extraction of lignin. The so called LignoBoost process has recently been introduced and using this process, it is possible to obtain a lignin having a high purity and dry content (1, 2, and 3). Cake filtration is one of the major unit operations of the LignoBoost process. For an accurate design of the filtration steps, the filtration properties of the lignin extracted have to be investigated. The compressibility of the material filter cake, i.e. its pressure dependency, is also an important parameter to consider for the best possible design of the filtration units, (4). This can be evaluated during filtration by measuring the local filtration properties.

Depending on the original wood raw material for the Kraft process, the filtration of lignin during the LignoBoost process can vary from being relatively easy and forming weakly compressible filter cake, to more difficult and forming more compressible filter cake. If the precipitation conditions are chosen correctly, it has been shown that softwood LignoBoost lignin is a relatively easy-to-filter material, forming weakly compressible filter cake. Such material is therefore relatively easy to handle in the scale-up of the filtration steps (5). However, other types of lignin have been found to be much more difficult to separate, especially if the precipitation conditions have not been chosen correctly. The reasons behind this are not fully understood and there may be several, but one is related to the content and nature of the residual lignin-carbohydrate complex in the extracted lignin (6).

The objective of this study is to investigate the influence of the xylan content on the local and average filtration properties of LignoBoost lignin. In order to model the influence of xylan content in precipitated lignin, a known amount of hardwood xylan was added to softwood LignoBoost lignin, having a very low original xylan content, using different methodologies. The filtration properties of the solid material in the resulting lignin/xylan suspension were investigated.

Experimental

Material, equipment and procedure

The lignin used in this study is a softwood lignin extracted from black liquor using the LignoBoost process (located in Bäckhammar in Sweden). The xylan used is a 90% pure xylan powder from beechwood (Sigma). The type of softwood lignin used here is known to have a very low content of xylan, which makes it suitable for the study of the influence of xylan addition on the filtration properties of lignin.

The filtration equipment used in this work was designed for cake filtration, expression and washing. Furthermore, it enables the local hydrostatic pressure to be measured during experiment at different heights within the filtration cell, using water filled capillary tubes connected to pressure transducers. The local solid concentration can also be determined during experiment using a ^{241}Am γ-source and detector located at each side of the filtration cell. More information regarding the filtration unit can be found elsewhere (7).

Several different slurries were prepared and subjected to cake filtration. Dissolved and re-precipitated lignin slurries with and without the addition of xylan were investigated, as well as a lignin-xylan mixture slurry (no dissolution/re-precipitation). The results obtained in a previous work regarding filtration of the same LignoBoost lignin (without any xylan addition) were also compared to the new results, (5). A summary of the investigated conditions of the prepared slurries can be found in Table 1. In the tests where lignin and xylan were dissolved in deionized water, the pH was adjusted to 13.8 using sodium hydroxide. Then, the solution was re-precipitated and diluted by lowering the pH to 1.5 using sulfuric acid. The dissolution and re-precipitation were performed at a controlled temperature of 80°C. When no dissolution and precipitation was performed, lignin and xylan were just mixed in deionized water at a pH of 2.4, acidified with sulfuric acid.

All slurries were left under continuous stirring for a minimum of 12 hours before starting a filtration experiment series, which were performed at room temperature (approx. 20°C). The filter media used consisted of a regenerated cellulose membrane filter (Sartoius stedim, type 184, pore size 0.45 µm) placed on a grade 5 Munktell paper filter support. After filtration, the filter cakes were subjected to expression for a minimum of three hours at the applied filtration pressure. The filter cakes were finally collected, weighed and placed in an oven for a minimum of 24 hours. The dried filter cakes were also weighed. These weighs were used to determine the average filtration properties.

Table1. Conditions of the four slurries and corresponding applied filtration pressures investigated. L refers to 'lignin' and X to 'xylan' in the table.

N°	**Slurry**	**Solid concentration [w%]**	**Xylan content [w%]**[3]	**pH**	**Applied pressures [bar]**
1	L+X after dissolution and re-precipitation	8.9	5	1.5	9.7 / 17.3 / 22.5
2	L only after dissolution and re-precipitation	8.9	-	1.5	9.4 / 17.1 / 22.6
3	L+X mixture	9.5	5	2.4	3 / 9.6 / 13.8 / 22.5
4	L [4] only	8.8 / 13 / 21.6	-	2.8	2 to 25.7

In a previous study it was shown that the slurry concentration did not influence the filtration properties of LignoBoost lignin (5).Therefore, the results will not be differentiated based on slurry concentration. Also, the pH variation between the slurries is not expected to have any influence at such acidic conditions, where no substantial dissolution of xylan and lignin is expected.

Particle size measurement

The sizes of the particles/agglomerates were determined by laser diffraction of highly diluted slurry samples with a Malvern Instruments Mastersizer 2000, able to detect particle sizes between 0.02 µm and 2000 µm. The sample were subjected to ultrasounds during 2 min before measurement in order to break down the flocs.

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[3] The xylan content calculated corresponds to the dry mass of xylan divided by the sum of xylan and lignin dry masses.

[4] Data corresponding to previous work (5).

Filtration properties determination

In this study, the local and average solid density of the filter cake, described as its local and average solidosity ($\emptyset$ and $\emptyset_{avg}$) were determined. The local and average flow resistance defined by the local and average filtration resistance (α and α_{avg}) were also calculated. Details regarding these calculations and the evaluation of the experimental errors can be found in a previous study (5).

Results and discussion

Particle size

The results obtained from laser diffraction measurements are presented in Table 2. It was found that the addition of xylan and the dissolution and re-precipitation of lignin and xylan had no significant influence on the particle size.

Table 2. Particle size determined by laser diffraction. $D_{(10)}$ indicates that x% of the particles by number are smaller than the value stated. L refers to 'lignin' and X to 'xylan' in the table.

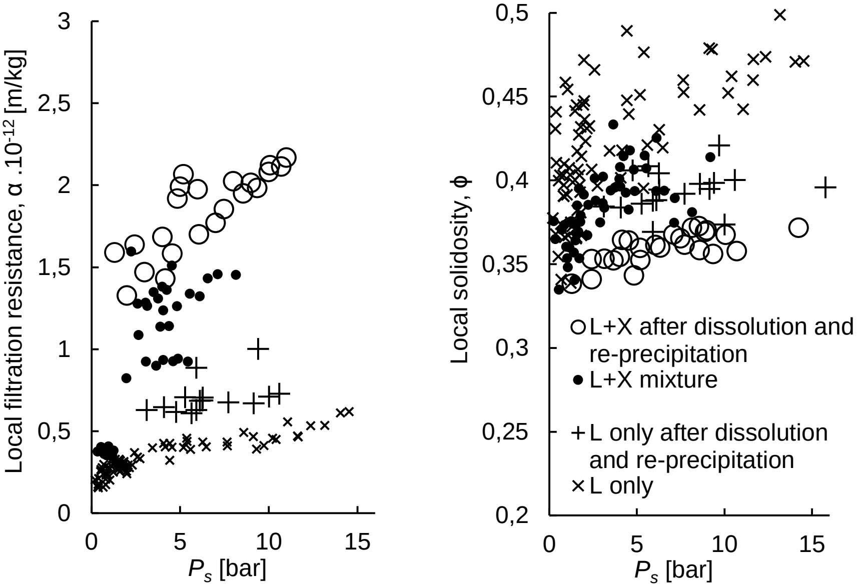
Slurry N°	$D_{(10)}$ [μm]	$D_{(50)}$ [μm]	$D_{(90)}$ [μm]
1	1.4	2.0	3.6
2	1.2	1.8	3.5
3	1.2	1.7	3.0
4	1.2	1.7	3.4

Filtration properties

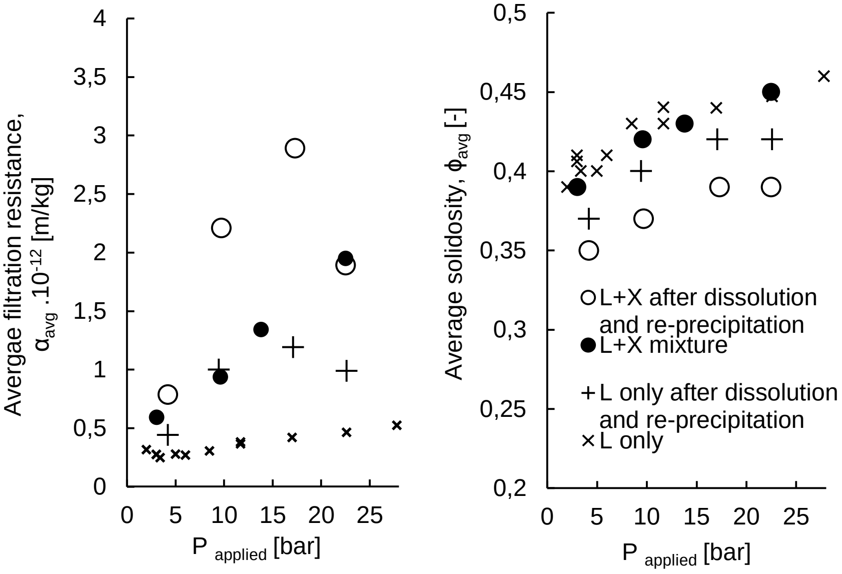
The local filtration properties obtained from the filtration experiments of the different slurries investigated are shown as a function of the local solid compressive pressure P_s in Figures 1 and 2. The average filtration properties are plotted versus the applied filtration pressure $P_{applied}$ in Figures 3 and 4. The relation between P_s, $P_{applied}$, and the measured local hydrostatic pressure P_l is given by Equation1.

$$P_{applied} = P_s(z,t) + P_l(z,t) \qquad \text{Equation 1}$$

where t is the time and z the height from the filter media.



Figures 1 (left) and 2 (right). Local filtration resistance and local solidosity versus local solid compressive pressure obtained for the four different slurries. L refers to 'lignin' and X to 'xylan' in the figures.



Figures 3 (left) and 4 (right). Average filtration resistance and average solidosity versus the applied filtration pressure obtained for the four different slurries. L refers to 'lignin' and X to 'xylan' in the figures.

It was observed that the addition of xylan results in a significant increase of the local and average filtration resistance compared to the slurries containing only lignin, Figures 1 and 3. These results are coherent with results obtained previously in the literature, where the removal of hemicelluloses from the spent liquor of the Kraft process ('black liquor') by membrane filtration, considerably decreases the filtration resistance (6). Furthermore, a significant decrease of the local and average solidosity was observed after addition of xylan, compared to the slurries containing only lignin, and in the case of dissolved and re-precipitated solids, Figures 2 and 4. An increase in filtration resistance and decrease in solidosity can also be noticed if lignin and xylan are dissolved and re-precipitated compared to the cases where these two constituents are just mixed in deionized acid water. This last result indicates that more than one mechanism may be involved regarding the influence of xylan on precipitated lignin filtration.

The obtained higher filtration resistance implies that the contact area between liquid and solid material has increased (higher drag force) and the lower solidosity observed implies that there is a larger liquid volume between the particles (longer average distance between the particles). There are several possible explanations for these behaviors. One is that small xylan particles have been formed and thus give an additional flow resistance. This could be one of the mechanisms involved, at least in the case of lignin and xylan just mixed as solid materials. But it should be kept in mind that the particle sizes (and size distribution) are not very different, Table 2, which makes this explanation less likely to be a major explanation.

Another explanation is that xylan is sorbed at the surface of the lignin agglomerates and interact with lignin in such a way that these agglomerates become locally more open and porous, making the particles more exposed to the flowing liquid, but also hindering a denser structure to be formed within the filter cake. This explanation is particularly feasible for the case where both lignin and xylan are dissolved and then re-precipitated.

Conclusion

The addition of xylan was shown to have a significant influence on the filtration properties of precipitated LignoBoost lignin, especially after dissolution and re-precipitation of the solid mixture. In this case, the filtration resistance increased by a factor three, while the solid density of the formed filter cakes was found to decrease by about 8% when xylan was added. One of the possible reasons to explain these results, which is believed to have a major influence, is that xylan is sorbed at the surface of the lignin agglomerates and interacts in such a way that the solid structure becomes locally more open and porous. This would increase the contact area between liquid and solid and thereby increase the resistance to flow by skin friction. Furthermore, the interactions between lignin and the sorbed xylan are also expected to hinder the formation of a denser structure within the filter cake.

Acknowledgment

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Catalytic Aqueous-phase Reforming of Acetic Acid Solution over Nickel-based Catalysts

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Introduction

The transition from fossil to sustainable and bio-based economy requires novel production processes. However, new feedstock with complex composition requires challenging adaptations of current processes which results in higher investment costs. Biorefineries integrate processes that produce chemicals, fuels, power and heat from lignocellulosic biomass by thermochemical routes including gasification, pyrolysis and catalytic routes, or by biotechnical routes such as fermentation. Biomass-based fast pyrolysis and Fischer-Tropsch reactions have been extensively studied as promising processes for fuel and chemical production from renewable biomass. In spite of the sustainable character of these technologies, the target products are accompanied by large water fractions with organic residues considered as waste streams. The disposal of the water fractions reduces the efficiency of the processes, due to costly conditioning treatments, in addition to upgradeable-product loss. In order to increase the product efficiency, the value of all streams should be maximized.

Currently, there is no efficient technology to convert the diluted organic compounds in the water fractions of fast pyrolysis and Fischer-Tropsch processes. Catalytic aqueous-phase reforming (APR) of organic compounds is a highly potential route to obtain H_2 and CH_4 from these water fractions. However, intrinsic challenges of the process, such as mass transfer limitations and low concentrations of the reactants, as well as performance and stability of catalysts require considerable research effort.

Aqueous-phase reforming

Aqueous phase reforming has been proved to be more energetically efficient than other technologies used for water processing, such as steam reforming [1]. The efficiency is derived from the suppression of the evaporation step which lowers the energy requirement [2]. APR of oxygenated hydrocarbons (1) occurs at lower temperatures below 300°C and below the bubble pressure point of the feed to ensure liquid phase. Low temperatures reduce the presence of decomposition reactions, and high pressure facilitates downstream treatments [3]. Nonetheless, this reaction scenario introduces kinetics and mass transfer limitations, and selectivity challenges that could be overcome by selecting appropriate operation conditions and suitable catalysts.

$$C_nH_{2y}O_n \leftrightarrow nCO + yH_2 \tag{1}$$

$$CO + H_2O \leftrightarrow CO_2 + H_2 \tag{2}$$

$$CO + 3H_2 \leftrightarrow CH_4 + H_2O \tag{3}$$

$$CO_2 + 4H_2 \leftrightarrow CH_4 + 2H_2O \tag{4}$$

$$(2n+1)H_2 + nCO \rightarrow C_nH_{2n+2} + nH_2O \tag{5}$$

$$(2n)H_2 + nCO \rightarrow C_nH_{2n} + nH_2O \tag{6}$$

Water gas shift (WGS) reaction (2) plays a significant role in APR. Water dissociation takes place at similar conditions than aqueous phase reforming, producing of H_2 and CO_2 mixtures with low CO concentration [3]. Additionally, side reactions facilitated at low temperature, such as methanation (3) and (4), and Fischer-Tropsch (5) and (6), produce methane and other short chain alkanes [4].

Materials and methods

Catalyst preparation

Nickel-based catalysts supported on TiO_2 and β-SiC were prepared by incipient wetness impregnation of the $NiCl_2$ precursor, and subsequent calcination at 400°C. The third catalyst used in the experiments was a commercial Ni/Al_2O_3. The catalyst particle, between 200 and 300 µm, were diluted with inert sand (50 wt-%). Previous to the reaction, the reduction of the catalysts was conducted at atmospheric pressure and with flow rate equal to 0.2 ln/min of H_2:N_2 = 1 for 2 h. The reduction temperature varied between 390 and 600°C according to the specific activation needs of each catalyst.

Experimental

Acetic acid was used as a model compound for aqueous phase reforming. The reaction was conducted in a continuously operated tubular reactor, 550 mm long and with an inner diameter of 9,4 mm. The liquid product was collected in a sampling system consisting of three glassy bottles. Off-line total organic carbon (TOC) and gas chromatograph (GC) were applied for liquid phase analysis. The total organic carbon was determined with a TOC-L Shimadzu device, and the composition was determined with a GC-7820A Agilent device, with FI detector and HP-FFAP 50mx0,2 mm column. Furthermore, on-line gas analyses were carried out with a microGC Agilent 3000 A by thermal conductivity detector (TCD).

The 5 wt-% acetic acid solution was fed up-flow into the reactor at a constant flow rate of 2 ml/min with a HPLC pump. Nitrogen was fed to the system downstream the reactor to sweep the outlet gases, and as an internal standard to calculate the total flow of outlet gases. The reactions were carried out at 230°C and 34 bar during approximately 2 hour.

Formation rate, and yield of hydrogen and methane were the main parameters utilized to analyse the results. The formation rate was calculated as the volume of component formed per time unit. Yield of hydrogen and methane were calculated with equations (1) and (2) respectively. Additionally, turnover frequency (TOF) and production rate (PR) were evaluated.

$$H_2 yield\ (\%) = \frac{H_2\ experimental\ (mol/min)}{H_2\ theoretical\ (mol/min)}\ x\ 100 \tag{1}$$

$$CH_4 yield\ (\%) = \frac{CH_4\ experimental\ (mol/min)}{CH_4\ theoretical\ (mol/min)}\ x\ 100 \tag{2}$$

Results

The formation and production rate of hydrogen was superior to methane over the three catalysts tested (Table 1). The hydrogen production improved depending on the support applied according to the following sequence: Al_2O_3 < TiO_2 < β-SiC. Conversely, the methane production rate had opposite trend to the production of hydrogen. Furthermore, the reaction yield and TOF was significantly low in every case (Table 1). No carbon monoxide was detected in the outlet gases, which indicates important activity of the WGS reaction. C2 components were detected in the order of traces when TiO_2 was used as support. The output was assumed to be entirely gaseous, since unreacted acetic acid was the only component found in the liquid samples. The concentration of acetic acid in the liquid samples was considerably lower than predicted. According to the yields, the conversion was expected to be close to zero. However, conversion values up to 90% indicate that part of the unreacted acetic acid possibly left the system in the gas form. In order to avoid confusion, we will not include the results of conversion in this paper.

Table 1. Flow rate and yield of APR of 5 wt% AcOH at 230°C and 34 bar.

		Ni/SiC	**Ni/TiO$_2$**	**Ni/Al$_2$O$_3$**
H$_2$	ml/min	1,3	0,9	0,5
	Yield (%)	0,8	0,5	0,3
	TOF (min^{-1})	1,8E-4	1,2E-4	4,1E-5
	PR (µmol/min*gCat)	18	12	7
CH$_4$	ml/min	0,02	0,05	0,2
	Yield (%)	0,1	0	1
	TOF (min^{-1})	4,4E-5	1,1E-4	2,6E-4
	PR (µmol/min*gCat)	0,3	0,7	2,8

Conclusions

Leaching due to the chemical features of the reactant, and sintering due to high pressure are the main causes of catalyst deactivation in APR. However, the catalysts tested in this work showed low initial activity. The low values of yield hindered the evaluation of the effect of the support in the performance of the catalysts. Therefore, broader catalyst screening, and testing of different model compounds and operational conditions are proposed in order to improve the gas yield of APR.

The analysis of liquid products indicated deficiency in the separation of phases, observed in the low concentration of unreacted acetic acid. Thus, modifications in the gas-liquid separation system are encouraged to enhance the reliability of the results in further experiments.

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Controllable HDO of Lignin Model Compounds via Aqueous Phase Reforming

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Abstract

The depolymerisation of lignin into its monomeric constituents is a promising route to the production of aromatic bulk chemicals from lignocellulosic biomass and lignin-containing waste streams (e.g. from the paper industry). In order to obtain an industrial product, further downstream processing of the monomeric mixture is required. Therefore, the selective removal of methoxy (-OMe) and hydroxy (-OH) groups from mixtures of monomeric lignin model compounds over Pt-based catalysts in the aqueous phase was investigated. This hydrogenolysis / reforming approach promisingly yielded a narrow range of products, the composition of which, can be controlled via the system hydrogen concentration. Optimisation of the hydrogen supply during the reaction is crucial to direct the reaction towards phenol while simultaneously preventing ring hydrogenation. It was found that at temperatures of *ca*. 250 °C, using a Pt-based catalyst,-OMe groups were converted to -OH groups, in turn reacting with H_2O to produce CH_3OH (MeOH). This MeOH is then instantly reformed over the Pt catalyst to produce $3H_2$ and CO_2, thus providing an in-situ supply of hydrogen directly at the active sites of the catalyst, facilitating -OMe and -OH abstraction. Therefore, the amount of -OMe groups in turn limits the supply of hydrogen. It is important to note that aromatic ring hydrogenation does not occur as the hydrogen is produced in-situ and consumed simulataneously at the catalytic site. It was found, as expected, that the addition of small quantities of MeOH at the beginning of the reaction accelerates the conversion, although nevertheless the hydrogenation of phenol seems to be the slowest reaction in the reaction pathway, making it a promising product of the process. Pt nanoparticle catalysts supported on traditional support media, including γ-Al_2O_3, ZrO_2, TiO_2, and activated carbon (C), were investigated along with a more cost effective / sustainable Ni/C alternative. Pt/ZrO_2 showed the best results regarding conversion followed by Pt/C and Pt/γ-Al_2O_3. Pt/TiO_2 and Ni/C catalysts showed no significant conversion toward the desired products. Reactions were performed over 10 h, with the product distribution analysed via liquid phase sampling at hourly intervals. The main process problems encountered in these investigations concerned the formation of coke and polymerisation, whilst adoption of a continuous process provided insight into the severity of these side reactions.

Introduction

Lignin, one of the main constituents of woody biomass, is a promising mixture of aromatic compounds which has the potential to serve as a source of bulk chemicals or as a substituent for phenols in, e.g phenyl formaldehyde.[1] Depolymerisation or usage of the low-molecular weight fraction of lignin gives a reasonable feed for a process which aims at the selective reforming of these compounds toward a more homogeneous product composition. The liquid phase reforming of lignin (and model compounds) over supported Pt catalysts have been reported previously with varying degress of success,[2–4] and as such there remains scope for further catalyst and process optimisation, particularly with regard to the development of a continuous process.

Experimental

Chemicals and Catalysts

All chemicals were purchased from Carl Roth or Sigma-Aldrich and used as received. The investigated supported Pt and Ni catalysts were prepared using an aqueous phase, incipient-wetness impregnation of the support material (e.g. ZrO_2), using hexachloroplatinic acid hexahydrate ($H_2PtCl_6 \cdot 6H_2O$) and nickel nitrate hexahydrate ($Ni(NO_3)_2 \cdot 6H_2O$) as metal precursors respectively. The loading of Pt and Ni was 3 wt% and 10 wt% respectively.

Characterisation and Analytics

Product analytics was performed using Gas Chromatogprahy (GC). The gas phase was analysed via TCD and the liquid phase with an FID. For the preparedcatalysts, the solid materials were analysed using N_2 sorption, XRD, and SEM-EDX. For more specific details concerning these procedures please refer to Ref.[5]

Batch Reactions

An autoclave (Carl Roth stainless steel (X6CrNiMoTi17-12-2 or AISI 316 Ti); Art.-No.: 2094.1) equipped with a heating jacket and a magnetic stirrer was used for batch reaction testing. To be enable liquid phase sampling during the course of the reaction, a sampling device was designed and integrated into the autoclave. This device enabled the withdrawal of aliquot of the complete reaction mixture (including catalyst). For all reactions deionised H_2O was used as solvent. The aromatic compounds (syringol, guaiacol, catechol, and phenol) were dissolved in equi-molar amounts relative to 1.5 wt% guaiacol (i.e. 0.24 mol/L). MeOH was added equal to 1/3 of the -OMe groups present in the feed. Before starting the reaction, the reactor was purged with N_2 several times and then pressurised to 5 bar N_2, followed by heating to the reaction temperature of 245 °C over 60 mins. A magnetic stirrer was used at a rotation speed of 550 rpm. At hourly intervals, liquid aliquots were drawn from the reaction mixture via the custom built sampling device. After 10 h the heating jacket was turned off and the system cooled to room temperature. Sampling of the gas phase was then performed. The reactor was subsequently opened for sampling of the remaining liquid phase, catalyst, and solids.

Continuous Reactions

Reactions were performed on a self-constructed test-rig with a 20 mL plug-flow reactor. The reactor was placed inside an oven and heated to the desired temperature. Four axially placed thermocouples attached to the reactor provided temperature profile information. Pressure was kept constant with a back-pressure valve in the gas phase. Gas phase samples were taken via a 25 mL high pressure vessel and liquid samples were withdrawn over a system of magnetic valves.

Results and Discussion

Table 1 shows the final conversion of the reactions performed under batch operation. Pt/ZrO_2 showed the highest conversion after 10 h and was found to be stable under hydrothermal conditions. Therefore it was chosen to be used with the addition of MeOH, which acted to provide additional H_2 and drive the reaction further towards phenol.

The liquid samples taken during the course of the reactions showed that there is no significant change in concentration after *ca*. 150 min. Coking of the catalyst was assumed and a continuous reaction showed that the conversion gradually declines over time. After converting three times the mass of guaiacol compared to the mass of catalyst its activity was down to 20 % of its original capacity. A reactivation of the catalyst by combustion at 550 ^{o}C of the formed coke in air was found to be possible.

Table 1. Conversion and yield of the liquid products of the reactions with Guaiacol (G) and Syringol (S) under hydrothermal conditions with different catalysts. Starting concentration 0.12 M, reaction time = 10 h at 245 °C.

Reactant + Catalyst	**Conversion**	**Yield**				
		1,2-Benzenediol, 3-Methoxy	Guaiacol	Catechol	Phenol	Coke & Poly
(G) Pt/ZrO_2	0.96	-	-	0.45	0.27	0.24
(G) Pt/ZrO_2 + MeOH	0.90	-	-	0.30	0.45	0.14
(G) Pt/γ-Al_2O_3	0.43	-	-	0.31	0.07	0.06
(G) Pt/TiO_2	0.34	-	-	0.00	0.00	0.34
(G) Pt/C	0.84	-	-	0.46	0.04	0.31
(G) Ni/C	0.36	-	-	0.02	0.00	0.34
(G) ZrO_2	0.00	-	-	0.00	0.00	0.00
(S) Pt/ZrO_2	0.29	0.14	0.02	0.01	0.00	0.15
(S) Pt/ZrO_2 + MeOH	0.74	0.09	0.05	0.19	0.10	0.36

Conclusion

A range of supported Pt catalysts were employed under hydrothermal conditions to direct the product spectra of aromatic compounds derived from lignin and associated model compounds were found to be a promising tool. H_2 supply and concentration were found to play a key role in the selectivity of the aqueous phase reforming process. Understanding the principles pathways of this reaction network is necessary in order to direct the reaction toward the desired final product(s). However, coking of the employed catalyst remains a major issue in process development and will be adressed in future investigations via choice of catalyst support pore structure and the usage of appropriate additives.

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Bioethanol Production from the Green Alga *Ulva Rigida* and the Brown Algae *Macrocystis Pyrifera*

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Abstract

Macroalgae are suitable bioresources to be explored as raw material for bioethanol production, as about 40 wt.% of its mass is composed of carbohydrates and they completely lack lignin. In this work the simultaneous saccharification and fermentation (SSF) of the green alga *Ulva rigida* and the brown alga *Macrocystis pyrifera* was performed. The algae were initially pretreated in deionized water or diluted sulfuric acid at 125°C in an autoclave for 60 min, respectively. Commercial cellulolytic enzymes and yeast were used for ethanol production. The carbohydrate composition of the fresh alga, pretreated alga and glucose and ethanol concentrations in the SSF processing are given. The water pretreatment solubilized 82 wt.% of the ulvan (rhamno-glucuroxylan) contained in *U. rigida* and 73 wt.% of the glucan remained in the residue. The diluted acid treatment removed 93 wt.% of the carbohydrates contained in *U. rigida*. The SSF of *U. rigida* pretreated with water produced 0.47 g EtOH/g sugar, with a 92 wt.% theoretical yield. In turn, water and diluted acid pretreatment of *M. pyrifera* increased 8.4 and 14.8 fold the carbohydrate content in the pretreated alga compared to the SSF of the fresh alga. The SSF of *M. pyrifera* pretreated with dilute sulfuric acid produced 0.15 g EtOH/g sugar, 29 wt.% theoretical yield. The production of ethanol was demonstrated for *U. rigida* and *M. pyrifera* with mild pretreatments. Especially in case of *U. rigida* simple water treatment allows to isolate ulvan for other purposes and efficiently ferment the remaining fibers.

Introduction

The need of food, energy and goods are expected to grow exponentially since the world population is still increasing, especially in developing countries. Hence, it is of paramount importance to find new resources since our supplies of fossil fuels are rapidly decreasing and the effect of its use is continuing damaging our ecosystem. Consequently, these new resources must be renewable to avoid depletion. In this context, production of biofuels from biomass is a promising choice to meet this challenge. Back in the first half of twentieth century, Sweden pioneered the production of cellulosic ethanol from lignocellulosic biomass, but competitiveness to oil prices forced to shut down the mills. A couple of decades later again a turmoil on oil prices encouraged the production of bioethanol from crops, leaving Brazil and the United States as the worldwide leaders in the production of this type of biofuels. However, some issues regarding the use of land for energy purposes instead of food production were brought up, encouraging the scientific community to focus its efforts back towards the second generation biofuels. Even though there are some industrial applications of this type of biofuel currently operating, the revenues are highly dependent on the price of enzymes for cellulose hydrolysis and the valorization of the non-cellulosic fractions. Moreover, the presence of lignin induces the need of a pretreatment carried out at harsh conditions to obtain high production yields [1].

In order to meet the above mentioned challenges, new efforts have been placed on the production of third generation biofuels which are derived from algae. Essentially algae are marine photosynthetic organisms that grow at much more higher rates compared to terrestrial plants, contain substantial amounts of carbohydrates and completely lack lignin [1]. Admittedly, algae do not contain substantial amount of cellulose as terrestrial plants do. Instead, they contain starch to some extent, but more importantly of sulfated polysaccharides such as ulvan (rhamno-glucuroxylan), carrageenan (galactan) and fucoidan (fucan) [3]. Further, they also contain polysaccharides with jellifying properties such as alginate (polysaccharide containing uronic acids) and agarose (galactan) [2]. Particularly alginate is of special interest for the food industry. Some of these carbohydrates are water soluble, which is of high interest under an industrial perspective, but its depolymerization needs acid catalysts or enzymes. The later ones are, however, not yet commercially available. Unfortunately, the open literature is still very scarce on the development of such enzymes and uronic acids fermentative microorganisms [1].

In this work, we present the fermentation of the green alga *Ulva rigida* and the brown alga *Macrocystis pyrifera*. Complete characterization of the carbohydrates contained in the fresh and after pretreatment samples is given, as well as bioethanol production yields using a commercial cellulolytic enzymatic complex and commercially available yeast. This work is an initial step to further research on the fermentation of the different carbohydrates contained in both algae.

Experimental

Materials

Ulva rigida (C. Aghard 1823 Chlorophyta, Ulvaceae) was kindly donated by Prof. Mario Edding from the Research and Technological Center in Applied Phycology (CIDTA), Northern Catholic University. The algae were collected in 2009 from submerged marine rocks located in Coquimbo, Chile. The samples were dried in oven at 40°C overnight and milled to 90 % - # 30 mesh. Once received, samples were stored in a freezer and freeze dried prior to analyses. In turn, *Macrocystis pyrifera* was grown in Chiloe Islands, Chile. Algae were harvested in December 2013 and kindly donated by Prof. Alejandro Buschmann, University of Los Lagos. The algae were dried at room temperature and cut into 10-15 mm long and 5-10 mm wide chips, with cutoff sieve up to 3.5 mm.

Pretreatments

4 g of dry *U. rigida* was pretreated in a 1:10 ratio (wt) either with 1 vol-% sulfuric acid (DSA1) or with only deionized water (DI Millipore, DW), respectively. In the case of *M. pyrifera*, 4 g of algae was pretreated in a 1:3 ratio (wt) either with 2 vol-% sulfuric acid (DSA2) or with only deionized water, respectively. The algae and solvent were introduced into glass flask and put into autoclaved and kept at 125°C and 1.5 bar for 1 hour. Subsequently, algae were washed with 80 mL DI water eight times. *U. rigida* fibers were collected by filtration, whereas *M. pyrifera* fibers were recovered by decantation, and subsequently freeze dried overnight.

Fermentation

0.75 g of either fresh algae or pretreated algae were fermented each with 2 mL of medium (sodium acetate 500 mM, yeast extract 50 g/L, $MgSO_4x7H_2O$ 0.25 g/L and $(NH_4)_2HPO_4$ 5g/L), 460 µL of cellulases (Sigma), 62 µL cellobiases (Sigma), 0.2 g yeast LALVIN EC1118 (Lallemand) and 27.48 mL of DI water in 50 mL flasks. The fermentation was performed at 40°C and 38°C for *U. rigida* and *M. pyrifera* samples in a G24 Environmental incubator shaker, New Brunswick Scientific Co., Inc., for 3 days, respectively.

Analytical

The amount of glucose, cellobiose and ethanol were quantified by HPLC of samples filtered through a 0.22 µm pore size filter. The analyses were conducted with an Agilent 1100 Series HPLC System. Biorad Aminex HPX-87H column was used with 5 mM H_2SO_4 using a flow rate of 0.6 mL/min and column temperature of 45°C. Standard solutions of glucose, cellobiose and ethanol were prepared (1 to

10 mg/mL). The content of pectins and cellulose was determined using the acid methanolysis and the acid hydrolysis methods, respectively, as described in [4].

Results and discussion

Pretreatment of algae

The sugar composition of fresh and pretreated algae is presented in Table 1. The pretreatment with DI water clearly favored ulvan dissolution in *U. rigida*, as proposed by Ray & Lahaye [3], removing up to 82 wt.% of the ulvan contained in the fresh alga. On the other hand, the glucan content was increased by 35 wt.%, and up to 73 wt.% of the glucan remained in the alga. On the contrary, the DSA1 treatment lead to substantial carbohydrate dissolution of *U. rigida* samples, with a 93 wt.% yield. Consequently, such acidic treatment was not suitable for subsequent fermentation of the remaining alga, because of small glucan content (33.7 mg glucose/g alga). In turn, when *M. pyrifera* was treated with DW water, the amount of carbohydrate increased by 20 wt.%. Moreover, when *M. pyrifera* was treated with DSA2 the carbohydrate content increased up to 51 wt.%, which was 40 wt.% more than in the fresh alga. Further, fucan and mannitol were substantially solubilized during the process. On the contrary, alginate and glucan were not much degraded as expected. Still, the glucan content was 3 fold increased in the DSA2 pretreated sample up to 25.3 wt.%.

Table 1. Sugar composition in fresh and pretreated algae samples[5].

Sugars	*Ulva rigida* Fresh alga	*Ulva rigida* Pretreated DI water 60 min - 125°C	*Ulva rigida* Pretreated 1 vol-% H_2SO_4 60 min - 125°C	*Macrocystis pyrifera* Fresh alga	*Macrocystis pyrifera* Pretreated DI water 60 min - 125°C	*Macrocystis pyrifera* Pretreated 2 vol-% H_2SO_4 60 min - 125°C
Alg	18.0 ± 6.1	9.6 ± 1.0	17.4 ± 0.2	218.9 ± 27.4	286.4 ± 8.5	243.5 ± 58.0
Fuc	0.1 ± < 0.1	< 0.1 ± < 0.1	< 0.1 ± < 0.1	16.7 ± 0.9	5.6 ± 1.0	1.6 ± 0.2
Gal	11.7 ± 0.1	13.1 ± 1.4	4.1 ± 0.3	10.7 ± 1.6	10.5 ± 0.8	5.6 ± 0.8
Glu	184.2 ± 1.1	248.9 ± 40.4	33.7 ± 3.2	81.5 ± 10.0	108.9 ± 12.9	253.1 ± 14.7
GluA	62.3 ± 0.9	14.0 ± 1.7	3.3 ± 0.4	6.6 ± 1.3	6.4 ± 0.2	1.6 ± 0.3
Mol	0.9 ± 0.8	0.2 ± 0.1	< 0.1 ± < 0.1	16.0 ± 1.6	7.6 ± 0.2	0.6 ± 0.2
Rha	81.2 ± 2.5	19.0 ± 1.1	0.4 ± < 0.1	0.8 ± < 0.1	0.6 ± 0.1	< 0.1 ± < 0.1
Xyl	38.5 ± 1.1	40.6 ± 1.3	17.1 ± 1.0	3.2 ± 0.2	2.2 ± 0.5	0.3 ± < 0.1
Total	400.5 ± 14.2	350.6 ± 47.6	84.8 ± 5.8	361.3 ± 23.8	434.5 ± 6.4	508.5 ± 45.0

Saccharification & fermentation of fresh and pretreated algae

The results of the SSF of the fresh and the pretreated *U. rigida* and *M. pyrifera* as glucose and ethanol concentration profiles as a function of time are depictured in Figure 1. The fermentation of the fresh alga of both species was not successful.

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[5] Values in [mg/g of alga]; Alg: alginate, Fuc: fucose, Gal: galactose, Glu: glucose, GluA: glucuronic acid, Mol: mannitol, Rha: rhamnose, Xyl: xylose.

The maximum concentration of ethanol produced from fresh *U. rigida* was 1.33 g/L after 4 h, corresponding to 0.09 g EtOH/g sugar, which corresponds to 17.3 wt.% of the theoretical yield for glucose fermentation. In turn, the SSF of *U. rigida* pretreated with DW at 125°C and 2 bar for 1 h obtained a maximum concentration of 6.2 g/L after 4 h of fermentation, corresponding to 0.47 g EtOH/g sugar, 92.3 wt.% of the theoretical yield. The fermentation of pretreated *U. rigida* attained 5.3 fold better yield than that obtained with the fresh alga, showing great efficiency of glucan saccharification and further fermentation. Korzen et al. reported the in-situ saccharification and fermentation of fresh *U. rigida* under mild sonication at 40 kHz and 37°C, obtaining a production yield of 0.33 g EtOH/g glucose [5]. The sonication aided SSF appeared to be promising, though thermal pretreatment looked to be more effective, since ulvan is removed and accessibility of enzymes to glucan is increased, thus improving ethanol production yields.

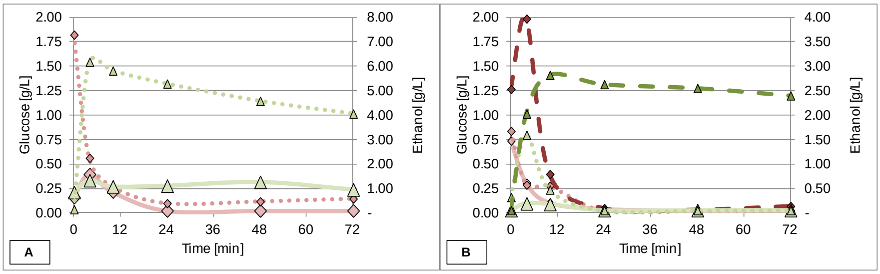

Figure 1. Concentration of glucose and ethanol produced in the simultaneous saccharification and fermentation of fresh and pretreated alga[6].

The SSF of fresh *M. pyrifera* produced very low ethanol concentration 0.19 g/L, corresponding to 0.01 g EtOH/g sugar and 2.7 wt.% of the theoretical yield for glucose fermentation. Admittedly, *M. pyrifera* doesn't contain much glucan compared to *U. rigida*, thus it was not surprisingly that the ethanol production was lower in *M. pyrifera* compared to *U. rigida*. Further, the SSF of *M. pyrifera* pretreated with DW produced 1.59 g/L of ethanol, corresponding to 0.10 g EtOH/g sugar and 19.1 wt.% of theoretical yield. This result was 8.4 fold higher than those obtained with the fresh alga. Since the amount of carbohydrates contained in the *M. pyrifera* pretreated with DW didn't vary much from that in the fresh alga, as it was shown in Table 1, the water treatment most likely opened the biomass matrix without causing further carbohydrate dissolution. In turn, when *M. pyrifera* was pretreated with DSA2, the amount of ethanol produced reached a concentration of 2.82 g/L, corresponding to 0.15 g EtOH/g sugar and 29.0 wt.% of theoretical yield. This result was 14.8 fold higher than the yield obtained for fresh alga and 1.7 fold higher than the yield obtained with DW. The theoretical yield of ethanol production

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[6] A: *Ulva rigida*, B: *Macrocystis pyrifera*. Fresh alga: ─◊─ glucose, ─▲─ ethanol. DI water pretreatment (DW): ····◊···· glucose, ····▲···· ethanol. Diluted sulfuric acid pretreatment 2 wt.% (DSA2): - - -◊- - - glucose, - - -▲- - - ethanol.

to glucan availability of pretreated samples was 76.5 wt.% and 58.2 wt.% for DW and DSA2, respectively. Lee *et al.* processed *Saccharina japonica* with 0.06 wt.% H_2SO_4 at 170°C for 15 min and subsequent SSF with yeast, and obtained 67.4 wt.% theoretical yield of EtOH to glucan [6]. Notwithstanding, the amount of glucan of *M. pyrifera* is low compared to others algal species, but there is substantial amount of alginate. Therefore, efficient enzymes to hydrolyze alginate and also microorganisms capable to produce ethanol using uronic acids as a carbon source are required. Our group has earlier demonstrated the use of cellulases and alginases for the saccharification of pretreated *M. pyrifera* [7].

Conclusions

The production of bioethanol from green and brown algae containing glucan was demonstrated. Particularly, the simultaneous saccharification and fermentation of the green alga *Ulva rigida* pretreated with deionized water rendered 0.47 g EtOH/g sugar. Most of the ulvan (82 wt.%) was dissolved during the pretreatment. In turn, simultaneous saccharification and fermentation of *Macrocystis pyrifera* rendered 0.15 g EtOH/g sugar when pretreated with dilute sulfuric acid in an autoclave. This result is interesting because ethanol production from glucan in this brown alga was demonstrated, and there is still room for increasing the yields by the development of alginate saccharification enzymes and uronic acid fermentative microorganisms.

Acknowledgments

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Deep Eutectic Solvents and Ionic Liquids in Enzymatic Lignocellulose Hydrolysis

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Abstract

Deep eutectic solvents (DESs) and ionic liquids (ILs) have been shown to be effective chemicals for lignocellulose pretreatment in sugar platform biorefineries. ILs are, however, known to significantly inactivate hydrolytic enzymes. In this paper, we compare the stability of hydrolytic enzymes in a set of different DESs and [EMIM]AcO, a cellulose-dissolving IL. The efficiency of these solvents in lignocellulose pretreatment is assessed in different process pathways, by carrying out enzymatic total hydrolysis on a) untreated substrates, b) pretreated and washed substrates, c) pretreated substrates in 30 % of DES/[EMIM]AcO and on d) pretreated substrates in 80 % of DES/IL. Microcrystalline cellulose, dissolving pulp, shredded barley straw and spruce saw dust were used as substrates. The results show that some of the DESs were stabilizing for the enzymes, whereas [EMIM]AcO was the most efficient pretreatment chemical under the used mild conditions. However, in the combined hydrolysis with DES/IL present, [EMIM]AcO inhibited enzymatic hydrolysis to a significantly higher degree than the DESs. The enzymatic hydrolysis yields were generally lower in DESs than in buffer, even if the enzymes showed significant stability in the DESs.

Introduction

In a lignocellulosic biorefinery, the plant cell wall polysaccharides of the feedstock may be enzymatically hydrolysed into monosaccharides, which thereafter are converted to chemicals or fuel molecules by *e.g.* fermentation. Typically, the lignocellulosic feedstock is very recalcitrant towards enzymatic hydrolysis, why an initial pretreatment is needed. Conventional pretreatment techniques are categorised as *e.g.* physical, chemical or physicochemical pretreatments. In pretreatment technology several bottlenecks remains. Especially in finding more effective methods for wood hydrolysis, there is still much room for technological improvement.

Ionic liquids (ILs) are salts with low melting points (by definition < 100 °C). ILs are excellent solvents as they can combine charged and organic character in the same solvent. ILs became interesting for lignocellulose processing in 2002, when they were reported to dissolve cellulose.[1] Their use in cellulose regeneration was also reported to increase its enzymatic digestibility considerably.[2] Different lignocellulosic materials have been pretreated in ILs with subsequent successful enzymatic hydrolysis as recently reviewed.[3]

The group of multicomponent solvents of interest in lignocellulose processing was recently enlarged with the deep eutectic solvents (DESs), which have many similar properties as the ILs. DESs generally have three components, of which a salt acts as hydrogen bond acceptor, and an uncharged component acts as hydrogen bond donor. To date, DESs have not been reported to dissolve cellulose, but they dissolve other biopolymers, which makes them interesting for lignocellulose processing.[4] The main advantages with DESs as compared to ILs are their generally cheaper price, ease of synthesis and in many cases lower toxicity. One clear disadvantage with cellulose-dissolving ILs is their inactivating effect on cellulases, which are used in lignocellulose hydrolysis.[3] In a two-step IL pretreatment with a subsequent separate hydrolysis step after washing, the IL inactivation is not a problem. To save processing steps and washing water a one-pot hydrolysis has been proposed, in which the IL pretreatment and enzymatic hydrolysis are performed in the same step.[5] The one-pot hydrolysis will, however, require that compatible IL and enzyme combinations are found. Although much less studied with enzymes than ILs are, DESs appear to some extent to be more enzyme-compatible. In this paper we provide a detailed comparison of the use of DESs and ILs in lignocellulose pretreatment in both the separate pretreatment and hydrolysis and in the one-pot hydrolysis procedures.

Experimental

Stability measurements

Enzyme stability measurements were done by incubating the enzyme in 85 % (w/w) DES or [EMIM]AcO solutions or in 0.050 M citrate buffer, pH 5.0 (reference) at 50 °C under gentle agitation. Samples were withdrawn at set time points and their residual activity was measured. The endoglucanase activity was measured with a 1 % (w/v) carboxymethylcellulose (CMC) solution as substrate in citrate buffer (0.050 M, pH 5.0), at an assay temperature of 50 °C, a reaction time of 10 min and with the quantification of formed saccharides during the assay with a 3,5-dinitrosalicylic acid (DNS) assay and colour formation measured at 540 nm. Xylanase activity was measured with a similar protocol but using beach xylan as substrate and a reaction time of 5 min, and CBH1 activity was measured with 30 min reaction time using a 1 mM 4-methylumbelliferyl-β-D-cellobioside as substrate and fluorometric detection.

Enzymatic hydrolysis of pretreated samples

As pretreatment, the substrates were subjected to a mild DES, [EMIM]AcO or buffer (reference) treatment. The samples were mixed gravitationally in 90 %

(w/w) DES or IL, or 100 % buffer at 80 °C at a consistency of 5 % (w/w). After the 24 h treatment time, the mixtures were cooled to room temperature, mixed with water for 30 min and thereafter washed several times with water.

For enzymatic hydrolysis experiments an enzyme cocktail was composed of the four *T. reesei* enzymes studied in the stability measurements, and supplemented with an excess of β-glucosidase. The mass proportion between the enzymes was Cel5A 15 %, Cel7A 60 %, Cel7B 15 % and Xyn11 10 %. The enzyme dosage in the hydrolysis experiments was 15 mg of protein/g of substrate (by dry weight).

The hydrolysis of untreated or pretreated samples was done in 2 % (w/w) solid consistency at 45 °C for 48 h in buffer. The hydrolysis was stopped by boiling for 600 s and the solids were separated from the liquid. The hydrolysis yield was determined based on a DNS assay made on the hydrolysis liquid and taking into account the carbohydrate composition of the starting material for each reaction.

For one-pot hydrolysis the starting material was treated in 90 % (w/w) DES or [EMIM]AcO solution or 0.050 M citrate buffer (pH 5.0) at 80 °C. After 24 h pretreatment, the samples were cooled to 45 °C and further diluted with buffer to form solutions with either 30 or 80 % (w/w) of DES or IL. The pretreated and diluted mixtures were hydrolysed by the composed enzyme cocktail with hydrolysis conditions, stopping, work-up and analysis as for hydrolysis in buffer.

Results and discussion

The stability of the four monocomponent *Trichoderma reesei* hydrolases, *i.e.* the cellobiohydrolase Cel7A (CBHI), the endoglucanases Cel5A (EGII) and Cel7B (EGI) as well as the xylanase Xyn11 (XYNII) was studied in 85 % (w/w) DES or [EMIM]AcO solutions with reference measurements done in citrate buffer. The enzyme stability in DESs and ILs was necessary to study in order to understand whether the enzymes' could be expected to perform at all in the selected solutions and conditions, and in the extension, to study whether enzyme stability would correlate with good performance in hydrolysis. Interestingly, the stability of the enzymes varied greatly in buffer. Cel7A had a good stability in buffer, with > 60 % residual activity after 6 d incubation, whereas the xylanase lost its activity in a day, and the two endoglucanases were between these two extremities. In [EMIM]AcO, which is a very efficient cellulose solvent, all enzymes lost their activity rapidly, but surprisingly the xylanase retained some residual activity in this oslution for several days, underlining that enzymes from the same organism can react very differently to the presence of ILs (**Figure 1**). The acidic DES1 inactivated all enzymes very rapidly, probably due to its acidity. In contrast, the two glycerol-containing DES2 and DES3 stabilised the cellulases, although not the xylanase, significantly. In DES3, the endoglucanases were stabilised at 40 – 60 % residual activity with virtually no inactivation taking place after the initial decrease.

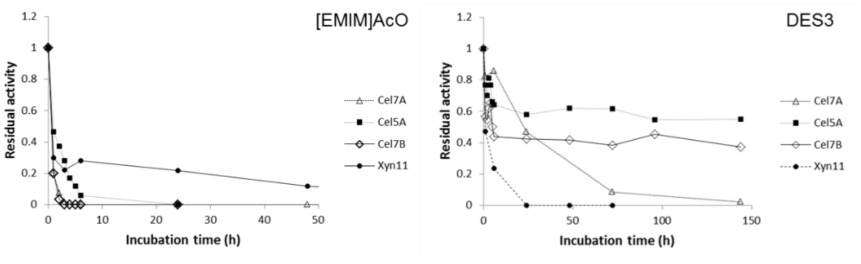

Figure 1. Enzyme stability curves 90 % (w/w) solutions of [EMIM]AcO (left) and the glycerol-containing DES3 (right) at 50 °C.

One of the main aims of this study was to compare the separate pretreatment and hydrolysis process to the one-pot procedure. In addition, it was of interest to study the differences between using a powerful cellulose-dissolving IL and less harsh DES solutions. The pretreatment was very mild, with only 90 % (w/w) DES or IL solution instead of using a 100 % solution, and a low temperature of 80 °C.

From the hydrolysis results, it can be seen that all DESs and [EMIM]AcO were effective in the separate pretreatment and hydrolysis procedure (**Table 1**, 0% column). [EMIM]AcO was by far the most effective in pretreatment, with virtually full hydrolysis yield from the polysaccharide fraction of every pretreated lignocellulose. The DESs cannot be ordered according to pretreatment efficiency, the efficiency of each DES depended on the substrate. In the case of dissolving pulp, a clear swelling was noticed during pretreatment, and in subsequent composition analysis the cabrohydrate content was found low, suggesting that most of the pretreated pulp weight was absorbed DES or IL. For this reason, the very high (> 100 %) yields are likely due to the difficulty of making a reliable composition analysis of samples containing little carbohydrates and lignin.

In the one-pot hydrolysis (**Table 1**, 30 % column), in which 30 % (w/w) of DES or IL was present during the enzymatic hydrolysis, the inactivating effect of [EMIM]AcO is clearly seen with hydrolysis yields of only a few percent in this medium. The DESs are comparably less toxic to the enzymes, but nevertheless the hydrolysis yields are lower in 30 % (w/w) DES than those obtained from the untreated or pretrated and washed substrates hydrolysed in buffer. In comparison, the inactivating effect of the DES or IL is a stronger factor than the benefit of their use in pretreatment, if the hydrolysis is done in the one-pot setup. There were some differences in hydrolysis yield depending on which DES was used in the 30 % (w/w) one-pot hydrolysis, but it varied in an arbitrary way for the different substrates. In the 80 % (w/w) one-pot hydrolysis, saccharide traces or yields of up to a few percent could be observed, but it was clear that these hydrolysis conditions were too harsh for the selected enzymes to work in.

Table 1. Hydrolysis yields in different hydrolysis setups with pretreatment in DES or IL.

Starting material	Pretreatment	Hydrolysis yield (%) in different concentrations of DES or IL		
		0 %	30 %	80 %
MCC	Untreated	48.5	NA	NA
	DES1	49.1	15.5	0.0
	DES2	65.5	9.0	Traces
	DES3	65.6	12.1	Traces
	Buffer	56.6	57.0	NA
	[EMIM]AcO	103.3	0.0	2.30
Dissolving pulp	Untreated	61.7	NA	NA
	DES1	97.2	16.2	Traces
	DES2	130.6	18.8	Traces
	DES3	102.7	22.5	Traces
	Buffer	59.8	60.4	NA
	[EMIM]AcO	130.3	1.6	0.0
Wheat straw	Untreated	17.5	NA	NA
	DES1	33.2	14.3	Traces
	DES2	18.9	5.3	1.2
	DES3	17.7	7.9	1.2
	Buffer	15.1	15.1	NA
	[EMIM]AcO	95.8	3.0	Traces
Spruce saw dust	Untreated	8.1	NA	NA
	DES1	13.5	9.1	0.0
	DES2	13.8	5.3	1.4
	DES3	13.5	4.7	1.5
	Buffer	9.9	10.7	NA
	[EMIM]AcO	100.5	1.5	1.6

Conclusions

In this study a set of three DESs were compared to a powerful cellulose-dissolving IL in both the separate pretreatment and hydrolysis and the one-pot hydrolysis protocols. The separate pretreatment and hydrolysis process was found to be more efficient in terms of hydrolysis yield than the one-pot hydrolysis in the studied conditions. [EMIM]AcO was far superior to the studied DESs as pretreatment chemical, but on the other hand it was too inactivating to be used with the chosen enzymes in the one-pot system, in which the DES performed better than the IL.

The strong inactivation of the enzymes observed in [EMIM]AcO solutions was supported by the stability measurements. The stability measurements also indicated an acidic DES to be very inactivating, but this DES was nonetheless not more inhibiting than the other DESs in one-pot hydrolysis. High enzyme stabilization was observed in the glycerol-containing DESs, but in the one-pot hydrolysis these DESs also inhibited the enzymatic hydrolysis. Thus it can be concluded, that having high cellulase stability in a solution does not necessarily mean that the enzyme will perform well in the hydrolysis of a realistic solid substrate.

Although this study would not indicate the DESs to be very effective as pretreatment chemicals, several considerations should be made. Firstly, the DESs were rather arbitrarily chosen due to the lack of knowledge on their interaction with lignocellulose, whereas [EMIM]AcO, which the DESs were compared against, is a very efficient cellulose-dissolving IL. Secondly, the pretreatment conditions were relatively mild and 10 % (w/w) water was added, which likely further reduced the pretreatment efficiency of the DESs, which in extension means that the full potential of these DESs still has not been fully explored in pretreatment. Thirdly, although the yields from the one-pot hydrolysis were not better than those obtained directly from the untreated substrate, it was shown than the DESs were significantly more enzyme-compatible than [EMIM]AcO.

Acknowledgements

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Chemometric Study on Alkaline Pre-treatments of Wood Chips Prior to Pulping

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Introduction

Biorefinery processes integrated with chemical pulp mills have gained a great interest during the last decades [1]. One of the most promising alternatives for producing value-added by-products comprises alkaline pre-treatments prior to pulping, allowing especially the recovery of hemicelluloses- and lignin-derived components from wood chips [2]. The isolated organic fractions can be used for producing chemicals and fuels, thus enabling a more effective utilization of wood feedstock. However, the pre-requirement for being an economically and technically attractive process, the chemistry of pre-treatments should be known in detail.

Chemometrics is a scientific discipline utilizing mathematical and statistical methods for producing chemically relevant information from a wide range of results obtained from chemical experiments by visualizing, representing, and displaying these kinds of data instead of just reporting raw numerical values [3]. Especially principal component analysis (PCA) has been proved to be a very powerful tool for describing and visualizing chemical phenomena observed during the chemical pre-treatments of wood chips.

In this study, a PCA model for the dissolution of lignin (*i.e.*, molar mass distribution or MMD) and the alkaline pre-treatment conditions were calculated for birch and pine chips, respectively. Based on the correlation consideration, a representative chemometric model for describing chemical phenomena taking place in alkaline pre-treatments was developed.

Experimental

Pre-treatments

Screened birch and pine chips were pre-treated in an oil-heated batch digester with liquor-to-wood ratio of 5 L/kg. Chips were heated at two temperatures (130°C and 150°C) for four treatment times (30, 60, 90, and 120 minutes) and six alkali charges (1, 2, 3, 4, 6, and 8 % NaOH on o.d. feedstock).

Chemical and chemometric analyses

- MMDs of the dissolved lignin: a gel permeation chromatography
- (GPC/HPLC-PDA) system.
- PCA models: Unscrambler® X software package.

Main findings

- During alkaline pre-treatments 2.1-16.5 % (hardwood) and 2.0-13.6 % of initial o.d. feedstock (softwood) was dissolved.
- The amount of dissolved lignin corresponded to a mass loss of 0.6-3.4 % and 0.8-4.4 % of the o.d. hardwood and softwood, respectively.
- The weight average molar masses of the dissolved lignin were slightly higher for softwood lignin (2,260-7,050 Da) than for corresponding hard-wood lignin (2,200-5,550 Da).
- PCA calculated for both wood species (Fig. 1) illustrated clear differences between the dissolution behavior of softwood and hardwood lignin.
- Alkali charge was found to be the most influential parameter (PC1) ex-plaining 75 % and 83 % of the MMD changes taking place during the pre-treatments of birch and pine chips, respectively.

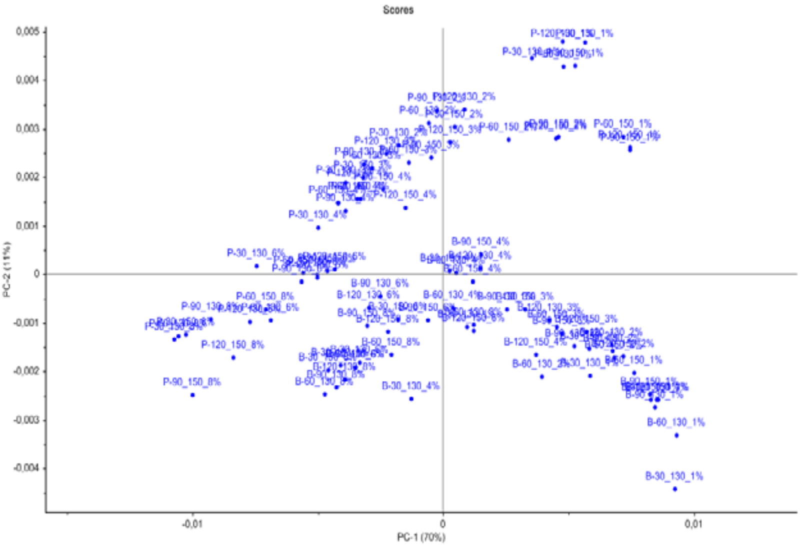

Figure 1. PCA model for lignin MMD for birch (B) and pine (P).

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Improved Ethanol Production from Lignocellulosic Biomass through Membrane Bioreactors

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Abstract

Ethanol production from lignocellulosic biomass is considered more beneficial than its production from starch and sugar based crops, considering the energetics and environmental advantages as well as the readily availability of the feed stock. However, the recalcitrant nature of lignocellulosic materials makes its ethanol production more challenging. Common methods of hydrolysis and fermentation of lignocellulosic materials to ethanol is through the separate hydrolysis and fermentation method (SHF) and the simultaneous saccharification and fermentation method (SSF). During SHF, product inhibition of the enzymes occurs as the sugar concentration increases during the hydrolysis, the process is also associated with increased contamination risk. SSF process makes use of suboptimal conditions for the hydrolysis and the fermentation; also the fermenting organism cannot be reused since it has been mixed with the lignocellulosic biomass. In this study, a new method was developed for hydrolysis and fermentation of lignocellulosic materials to ethanol, called simultaneous saccharification, filtration and fermentation (SSFF). The method allows both the hydrolysis and fermentation at optimum conditions with the use of a membrane bioreactor. It also allows the fermenting organism to be reused for several batches. The method was applied on pretreated spruce using a flocculating yeast strain and also on pretreated wheat straw using encapsulated genetically modified yeast. SSFF was compared with SSF as one of the conventional method, both on 10% suspended solids basis. From pretreated spruce, similar ethanol yield was obtained. Interestingly, from the pretreated wheat straw, 90% ethanol yield of the theoretical value was obtained during the SSFF while just 53% was obtained during the SSF. The study shows that the newly developed method of SSFF has the potential to replace the conventional methods and to improve ethanol production from lignocellulosic biomass.

Keywords: Lignocellulosic biomass, Ethanol, Hydrolysis, Fermentation, Membrane bioreactors, SSFF.

Introduction

Ethanol is an important biofuel in the transportation sector, it can be produced from starch and sugar based crops as well as from lignocellulosic biomass. Its production from lignocellulosic biomass is considered more advantageous than its production from starch and sugar based raw materials. This is due to the environmental benefits and the availability of the raw materials [1, 2]. However, the recalcitrant nature of lignocellulosic materials makes its ethanol production process more challenging than its production from starch and sugar based raw materials. Pretreatment, hydrolysis, fermentation and distillation are the necessary steps involved. Commonly applied methods of hydrolysis and fermentation are; separate hydrolysis and fermentation (SHF) and simultaneous saccharification and fermentation (SSF) [3]. Product inhibition of the enzyme as the hydrolysis progresses, sub-optimal processing conditions as well as the non re-usability of the fermenting organism are some of the challenges confronting the SHF and SSF methods [4]. Hence there is need for a method which can eliminate the challenges and improves ethanol production.

Membrane bioreactors (MBR) are commonly used for producing quality water and in waste water treatment. Membranes are used for separation processes based on their permeability selectivity [5]. Recently, MBR have been used in biological processes such as biogas and ethanol production for achieving high cell densities [6]. This study investigates the use of MBR in a novel way for hydrolysis and fermentation of lignocellulosic materials with a method referred to as simultaneous saccharification, filtration and fermentation (SSFF). The method was investigated on pretreated spruce with a flocculating strain of *Saccharomyces cerevisiae* as the fermenting organism and also on pretreated wheat straw with encapsulated genetically modified strain of *S. cerevisiae* as the fermenting organism.

Experimental

Lignocellulosic biomass

Spruce chips, a softwood lignocellulosic biomass from Swedish forests were used. The chips were chemically pretreated with SO_2 impregnation and exposed to a pressure of 22 bars, 215°C for 5 min (SEKAB E-Technology, Sweden) and delivered as slurry. It had pH 2.0, 15.9% suspended solids (SS) and 23.8% total solids (TS). The slurry was stored in a cold room of 5°C until use. The composition of the liquid fraction of the slurry was 22.8 g/L glucose, 25.3 g/L mannose, 13.7 g/L xylose, 5.8 g/L galactose, 4.7 g/L arabinose, 5.7 g/L acetic acid, 1.8 g/L HMF, and 2.0 g/L furfural. The solid fraction of the slurry had 46.5±0.1% cellulose, 46.1±0.3% acid insoluble lignin (AIL), 5.01±0.1% acid soluble lignin (ASL) [3]. Wheat straw, an agricultural residue lignocellulosic biomass from a Swedish farm was used as well. It was chemically pretreated with dilute H_2SO_4 (0.3-0.5%), at

185°C for 8 min and delivered as slurry with pH 1.9, 14.9% suspended solids (SS) and 22.2% total solids (TS). The composition of the liquid fraction of the slurry was 33.4 g/L xylose, 8.5 g/L glucose, 1.5 g/L mannose, 3.1 g/L galactose, 4.9 g/L arabinose, 8.9 g/L acetic acid, 1.1 g/L HMF, and 9.2 g/L furfural. The solid fraction of the slurry had 43.6±0.5% cellulose, 34.81±0.1% acid insoluble lignin (AIL), 5.1±0.1% acid soluble lignin (ASL) [7]. The slurry was stored in a cold room of 5°C until use.

Enzymes and Yeast strains

Cellic® CTec3 and Cellic® Ctec2 enzymes (Novozymes, Denmark) was used for the hydrolysis of the spruce slurry and wheat straw slurry respectively. A flocculating strain of yeast *Saccharomyces cerevisiae* CCUG 53310 (Culture Collection University of Gothenburg, Sweden) was used for the spruce slurry experiment. The yeast was maintained at 4°C on YPD agar plate containing 20 g/L agar (Scharlau), 20 g/L D-glucose (Scharlau), 10 g/L yeast extract (Scharlau) and 20 g/L peptone (Fluka). Prior to fermentation, 100 mL preculture in YPD medium containing 20 g/L D-glucose, 20 g/L peptone and 10 g/L yeast extract in 250 mL flask was provided. This was incubated in a shaking water bath (Grant OLS 200, Grant instrument ltd, UK) at 121 rpm and 30 °C for 24 h. Genetically engineered strain of *Saccharomyces cerevisiae* (T0936) was used for the wheat straw slurry experiments. The yeast was maintained at 4°C on a YPD agar plate containing 20 g/L agar, 10 g/L D-glucose, 10 g/L D-xylose, 10 g/L yeast extract, and 20 g/L peptone. Prior to the fermentations, 100 mL preculture in YPD growth medium containing 25 g/L D-glucose, 25 g/L xylose, 20 g/L peptone and 10 g/L yeast extract in 250 mL flask was provided. This was incubated in a shake-bath at121 rpm and 30 °C for 48 h.

Membrane bioreactor (MBR) with simultaneous saccharification filtration and fermentation (SSFF)

The MBR with the SSFF method allows the hydrolysis and the fermentation to be performed at different optimum conditions, Enzymes is added to the pretreated lignocellulosic biomass and pumped through a cross-flow membrane, so that a clear sugar-rich filtrate continuously drops into the fermentation reactor. Simultaneously, the volumes are kept in balance by continuously circulating the fermentation broth between the hydrolysis and fermentation reactors (Fig. 1). Retention of the fermenting culture is essential and this is achieved by the use of a flocculating yeast strain and encapsulated genetically modified yeast strain. The SSFF is composed of three parts of hydrolysis, filtration and fermentation (Fig. 1). The hydrolysis and the fermentation were performed at separate optimum temperatures of 50 °C and 30 °C respectively, pH of 5.0 was used in both processes [3, 7].

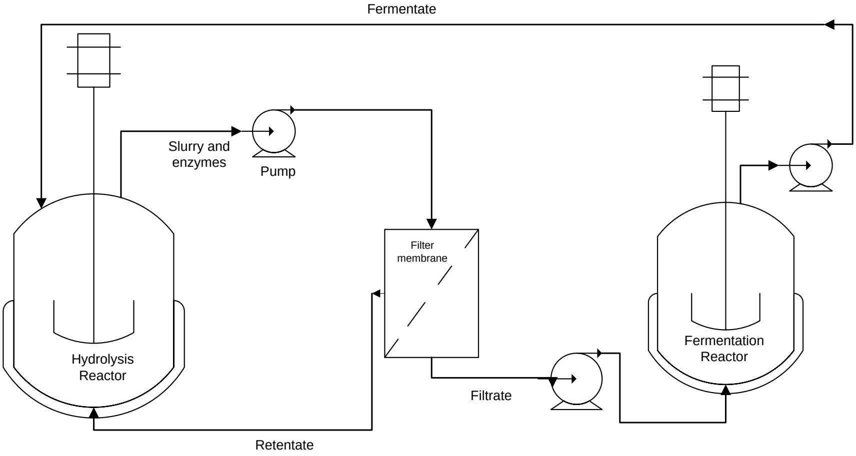

Figure 1. Schematic representation of the MBR with the SSFF process, adapted from [5].

Result and discussion

Application of MBR in lignocellulosic ethanol production through the SSFF method (Fig. 1) combines the advantages of SSF and SHF methods and eliminates their disadvantages. The method allows the hydrolysis and fermentation to be performed at their separate optimum conditions; it also provides the possibility to reuse the fermenting cells, which is an important factor for a successful ethanol production process. The method was performed using pretreated spruce with flocculating yeast strain after which pretreated wheat straw was used with genetically modified yeast strain. A comparison with commonly applied method of SSF was also performed.

Comparison of MBR via SSFF method with commonly used SSF method using pretreated spruce

MBR via SSFF and SSF methods were carried out with the same amount of pretreated spruce on 10% suspended solids basis and the respective results are compared in Figure. 2a. Almost identical amount of ethanol production is observed from both methods at the end of the fermentation, corresponding to 84% and 85% of the theoretical yield for SSFF and SSF, respectively [3]. This indicates that SSFF produced almost the same amount of ethanol as SSF with the same input of enzymes and carbohydrates., However, the amount of xylose at the end of SSF was higher than in SSFF which implies that more sugars was consumed during SSFF than SSF, which may be due to lactic acid formation in SSFF. Glycerol formation in SSFF was also lower compared to SSF. With similar ethanol yields, it can be interpreted an advantage for SSFF over SSF, if all the process units are well controlled and optimized since it is not necessary to supply new yeast for each batch.

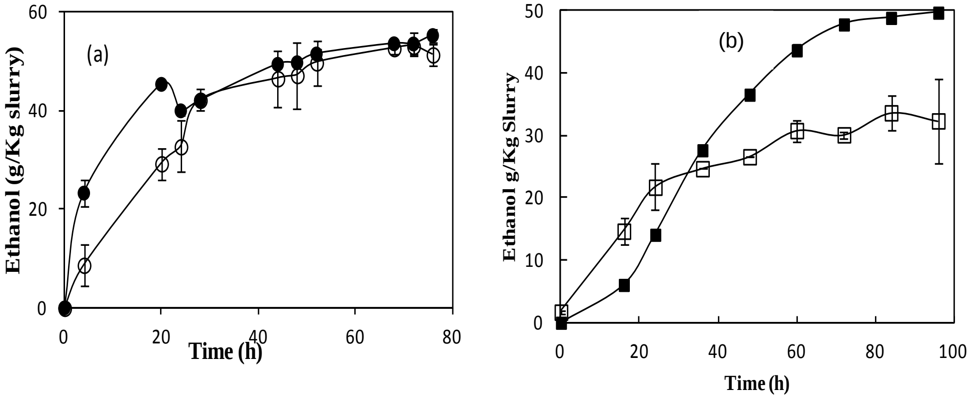

Figure 2. Comparison of ethanol produced per supplied amount of slurry during MBR via SSFF method with SSF method using (a) pretreated spruce; SSFF is represented by (○) while SSF is represented by (●), (b) pretreated wheat straw; SSFF is represented by (■) while SSF is represented by (□).

Comparison of MBR via SSFF method with commonly used SSF method using pretreated wheat straw

During the experiment with pretreated wheat straw where encapsulated genetically modified yeast was used as the fermenting organism. The experiment was also based on 10% suspended solids. It was observed that ethanol concentrations of 37 g/L and 22 g/L were produced at 96 h during SSFF and SSF respectively, which are equivalent to 50 g/Kg and 32 g/Kg produced ethanol during SSFF and SSF respectively (Figure 2b). These values correspond to 90% and 53% of the theoretical ethanol yield for SSFF and SSF respectively, an indication that SSFF process improves the ethanol yield for about 40.0% more than the commonly applied SSF method [7]. This observation indicates that SSFF could be more advantageous for lignocellulosic ethanol production than SSF.

Conclusion

Membrane bioreactor (MBR) was applied for lignocellulosic ethanol production via the simultaneous saccharification, filtration and fermentation (SSFF) method. It was applied on pretreated spruce using a flocculating yeast strain and also on pretreated wheat straw using encapsulated genetically modified yeast. MBR via SSFF was compared with SSF as one of the conventional method, both on 10%

suspended solids basis. Similar ethanol yield was obtained from pretreated spruce during SSFF and SSFF, from the pretreated wheat straw, 90% ethanol yield of the theoretical value was obtained during the SSFF while just 53% was obtained during the SSF. The study shows that application of MBR via SSFF method in lignocellulosic ethanol production has the potential to improve the ethanol yield.

Acknowledgements

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Chemical Pretreatment of Wood Chips: a Comparative Study of Mild Steam Explosion and Hot Water Extraction

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Abstract

Pretreatment of wood is a prerequisite for an efficient separation and utilization of its building blocks in future biorefinery concepts. Inherent recalcitrance of the cellulose-hemicellulose-lignin matrix of the cell wall poses huge challenges on separation of these components and implies usually a need for a broad set of methods targeting different components and providing as well chemical as morphological alterations. Mild steam explosion and hot water extraction are examples of typical pre-treatment methods enabling extraction of hemicelluloses and facilitating further processing of wood. Both are based on autohydrolysis of lignocellulosic material at high temperatures, but involve generally different conditions, the most prominent difference being a rapid disintegrating discharge employed in the steam explosion treatment, rendering morphological changes and altering structure accessibility compared to the physically less disruptive hot-water extraction. In this study we compare the key features of both of these methods and present that their effects on wood are somewhat non-uniform.

Introduction

The concept of wood material biorefinery aims at efficient separation and recovery of wood structures in order to fulfill future needs for renewable raw materials. Due to its inherent recalcitrance the solid wood is for this purpose nomally treated in several steps. In each of these steps the physical structure and chemical composition of the wood tissue is changed.

Among the treatments aiming at enhanced accessibility with the minimal degradation of the wood components two methods were selected: mild steam explosion (STEX) and hot water extraction (HWE). Those treatments rely on autohydrolysis of lignocellulosic material at high temperatures, but involve generally different conditions with rapid pressure release in STEX causing morphological changes facilitating structure accessibility and relatively physically less disruptive HWE [1, 2]. Both of the selected methods result in extracting some of the hemicelluloses and thus give the possibility to utilize them for development of new materials.

There is a need to understand changes of the wood tissue during those processes so that the proper method could be chosen, optimized and modified according to specified demands.

In this study we aim at comparing the key features of both of these methods with focus on induced local variations in chemical composition. It is a part of a larger study in which investigations of molecular weight distribution, porosity analysis and environmental scanning electron microscopy are among the others employed in order to elucidate chemical and physical processes in wood associated with these pretreatments.

Materials and methods

Materials

The samples consisted of industrially-cut wood chips of Norway spruce (*Picea abies*). The wood chips were manually selected to provide preferable size and avoid dirt, knots and bark. The demanded size was at least 6 mm in thickness, 3 cm in width and 4 cm in length.

Methods

Mild steam explosion

The equipment used for mild steam explosion is constructed with a modified steel autoclave (approx. 1.2 L) fitted in an insulated container. The autoclave's lid is equipped with inlet and outlet for steam and a temperature sensor. The valve on the outlet allows rapid release of the pressure into a collection vessel (approx. 15 L). The autoclave was filled with 50 g of o.d. wood chips and water corresponding to wood to water ratio of 4:1, the experimental conditions were chosen to be 150 °C and 15 min. Pre-treated wood chips were washed primary with approximately 5 L of warm water and subsequently with cold water for one week.

Hot water extraction

The extraction with hot water is performed in steel autoclave (approx. 1.2 L) placed in pre-heated PEG bath. The amount of wood and wood to water ratio was same as in steam explosion. The sample was kept at 150 °C for treatment time of 60 min. The washing procedure was the same as for STEX treatment.

Chemical characterization

To investigate how different parts of the wood chip are affected during STEX and HWE treatment different sections of the chips were analyzed separately. Prior to analysis treated and washed wood chips were oven dried and cut with a saw. The parts damaged during chipping were removed and sections were collect from the corner of the wood chip, outer edge and the middle. The obtained fragments were then sliced into layers using microtome so that outer and inner lamella could be analyzed separately (see Figure 1).

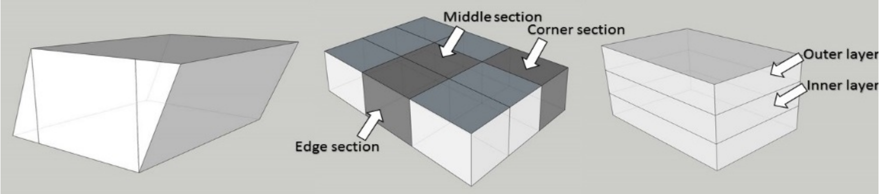

Figure 1. Sectioning of wood chip: removal of damaged parts, selecting sections from corner, edge and middle, dividing fragments into layers.

The selected wood fragments were milled in Wiley-type mill, oven dried and subjected to complete acid hydrolysis with use of 72% sulphuric acid. Typically 30 mg of sample was used. The residual material was considered to be Klason lignin and its amount was determined gravimetrically. The filtrate from the hydrolysis was used to determine the content of acid soluble lignin (ASL), the carbohydrate and acetate content.

The amount of ASL was calculated based on the absorbance measured with UV at a wavelength of 205 nm in a Specord 205, Analytic Jena, assuming the absorptivity constant equal 110 $dm^3g^{-1}cm^{-1}$ [3].

The carbohydrate composition was determined as the amounts of monomeric sugars with help of high performance anion exchange chromatography (HPAEC). The system consist of Dionex ICS-5000 equipped with CarboPacTM PA1 column and electrochemical detector and NAOH and NaOH + NaAc as eluents. The software was Chromeleon 7, Chromatography Data System, Version 7.1.0.898. The detected amounts were corrected to the hydrolysis yield and amount of anhydro sugars was calculated from sugar monomers [4, 5]. The polymeric content of the sample was calculated according to procedure described by Jedvert et at. [6].

The analysis was performed on several wood chips for each method (four STEX and three HWE), running all tests on duplicate samples.

Results & discussion

Pre-treatments

The initial study showed that the wood composition and morphology is affected differently by the studied treatments. As presented in Figure 2 wood subjected to HWE gained a dark brown colour while STEX chips became only a shade darker than untreated wood. Moreover, analysis of the HWE and STEX liquors shows that extraction yield is significantly higher for HWE being 5.1% of initial wood mass compared to 1.7 % for STEX. Considering the elevated temperature and acidic conditions during the treatment (pH 4.3 for STEX and 3.3 for HWE-extraction liquid, i.e. the 10 times higher H^+ concentration for HWE) we can assume that the main reason behind this difference is more extensive autohydrolysis in the case of HWE.

Figure 2. Wood chips, from left native, STEX and HWE treated.

The results of carbohydrate analysis on multiple samples of untreated wood show that selected method displays standard deviation of ± 1.5% on cellulose, 1.0 % on GGM and 1.4 % on lignin (Table 1.). This deviation is caused not only by the uncertainty of the method but also by the inherent inhomogeneous composition of the material.

Table 1. Results of composition analysis on untreated wood (*the values are relatively low in comparison to literature data).

	NATIVE	
	Average	std.dev.
Cellulose*	35,9	1,5
GGM*	16,6	1,0
AGX	5,2	0,6
Klason	27,6	1,4
ASL	0,8	0,1
Unknown	13,9	2,3

Table 2. The acetate content in weight % of sample.

	Outer layer	Inner layer
HWE	1,22	1,40
STEX	1,69	1,62
native	2,06 ± 0.07	

Corresponding examination of the treated wood reveals that for the both treatments cellulose and lignin are principally preserved while the amount of hemicelluloses is affected to different extents, especially in the HWE-treated samples. There is a clear decrease in the (galacto)glucomannan content while it is moderate for arabinoglucoronoxylan.

Local effects of HWE and STEX treatment

Compositional analysis of the selected sections of the chips indicates that various parts of the wood chip are subjected to different changes. In spite of the longer treatment time, the variations are more pronounced in the HWE samples than in STEX and are detectable mostly as variations in hemicellulose content between outer and inner region. e.g. showing more pronounced decrease in GGM content in outer parts (Figure 3.).

Similar variation between the layers could be observed in changes of acetyl content upon STEX and HWE, since hemicelluloses are subjected to deacetylation during the treatments and the change in acetate content reflect the extent of the treatment. However, only wood subjected to HWE displays a variation in acetyl content between the outer and inner layers (Table 2.). This may be a consequence of a mass transport in HWE, which in case of STEX is enhanced by the disintegrating impact on morphology.

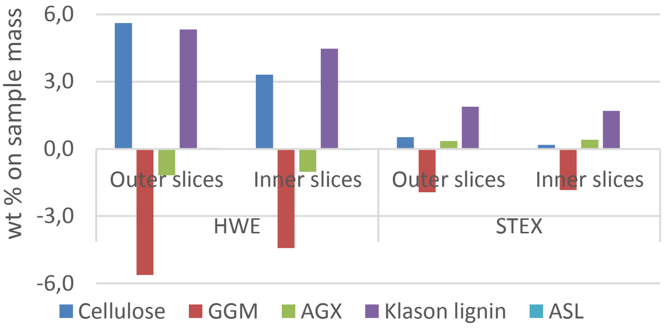

Figure 3. Changes in composition of selected layers within STEX or HWE treated wood chips.

The variations in composition are not only visible when comparing inner and outer layers of the chip, but also among the different sections within the same layer (middle, edge and corner of each layer - visualized in Figure 1.). The differences appear as relative increase of the cellulose and lignin amount and decrease in GGM and AGX content and are more pronounced in the inner layer this may be related to the slow mass transport. The results show that the GGM is to a higher extent preserved in the middle parts of a layer. On the other hand in the corners the local composition variations showing bigger changes in relation to untreated wood. The results are presented in Figure 4 as an average change of composition in relation to the untreated wood. The standard deviations between samples in different regions were up to 3.5% on cellulose, 1.7% on GGM, 0.3% AGX, 1.8% Klason and 0.4% ASL for HWE treated samples and 3.8% on cellulose, 2.3% on GGM, 1.1% AGX, 2.7% Klason and 0.2% ASL for STEX samples and can be deduced to heterogeneity of the wood material, related to origin, localisation in the tree, etc. as well as chipping effects.

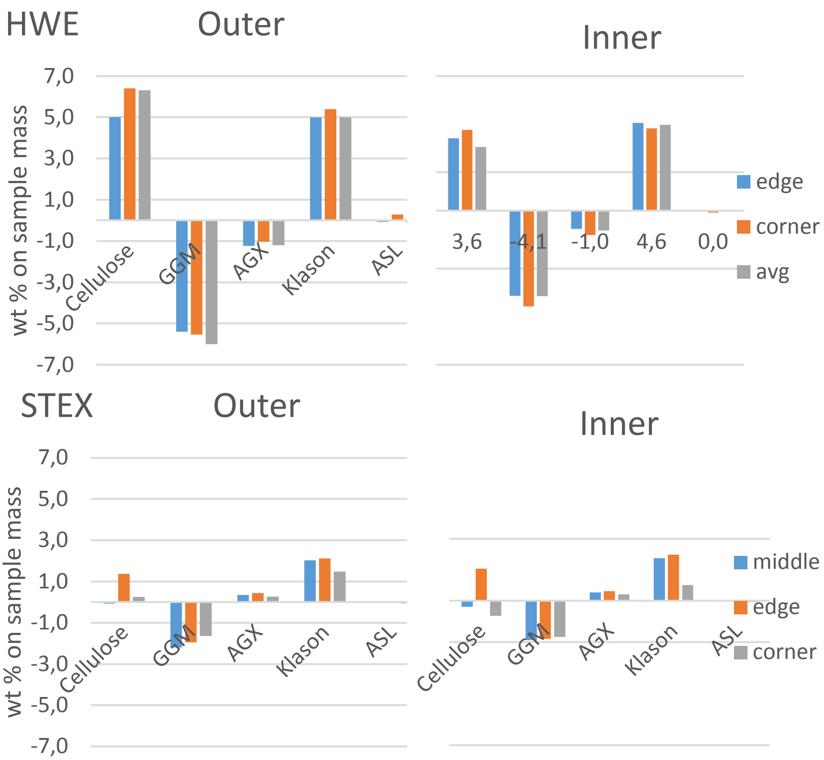

Figure 4. Results of composition analysis on selected fragments of treated wood chip as changes in composition (in wt % of the sample) in relation to the untreated wood.

Conclusions

HWE treatment shows significant local variations in progress within the treated wood chip, leaving the inner part of the tissue significantly less affected. On the other hand STEX treatment accomplishes more even removal of hemicelluloses in a shorter treatment time. The difference in amount of extracted material is ascribed to the different process conditions.

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Fast Pyrolysis of Differently-treated Spruce (*Picea Abies*) Sawdust by Py-GC/MSD

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Introduction

Fast pyrolysis of lignocellulosics has been investigated under a variety of conditions and from several points of view, since by this straightforward technique it is possible to produce liquid biofuels and chemicals [1]. On the other hand, biomass pretreatment technology plays an important role in many biorefinery processes based on lignocellulosics. According to an integrated forest biorefinery (IFBR) concept, one interesting approach, mainly for recovering valuable carbohydrates-derived material, is to apply hot-water extraction (HWE) ("autohydrolysis") of wood chips or sawdust prior to pulping [2]. Besides utilizing the pretreated wood material for delignification, it might also be a potential feedstock for thermochemical conversion [3,4]. In this study, the fast pyrolysis of untreated (S_{ref}) and hot-water-extracted (S_{HWE}) spruce (*Picea abies*) sawdust as well as the soda-anthraquinone(AQ)-cooked pulps of untreated (P_{ref}) and of hot-water-extracted (P_{HWE}) spruce feedstocks was investigated by pyrolysis-gas chromatography with mass-selective detection (Py-GC/MSD). The main idea was to detect differences in the thermochemical behavior of these feedstocks with varying chemical composition for evaluating their suitability for pyrolysis.

Experimental

Pretreatment stages

Hot-water extraction was performed as three stages; i) 160°C for 40 min, ii) 170°C for 60 min, and iii) 180°C for 180 min [5].

Soda-AQ cooking

170°C, 30 min, NaOH charge 20% on o.d. feedstock, AQ charge 0.1% on o.d. feedstock, and liquor-to-feedstock ratio 5 L/kg. Yields for P_{ref} and P_{HWE} were 60.0% and 64.9%, respectively [5].

Analyses of feedstock materials

Extractives (TAPPI T 280 pm-99), acid hydrolysis (TAPPI T 249 CM-00) and monosaccharides by GC/FID, lignin (TAPPI T 222 om-98 and TAPPI T 250 UM). The chemical compositions of differently-treated sawdust samples are presented in Table 1.

Pyrolysis conditions

Fast pyrolysis (with a CDS Pyroprobe 1000 heated filament pyrolyzer coupled to an HP 5890 II GC, a capillary column ZB-35HT): 500°C and 700°C, residence times 5 s and 20 s with a heating-up time of 20°C/ms. The effects of temperature and residence time on the peak area% of the pyrolytic products are shown in Figure 1.

Table 1. The chemical composition of differently-treated sawdust samples (% of the feedstock dry solids) (monosaccharide units are presented as their anhydro forms).

Component	S_{ref}	S_{HWE}	Pulp$_{ref}$	Pulp$_{HWE}$
Carbohydrates	60.6	59.4	76.1	61.8
Arabinose	1.4	0.0	0.7	0.0
Galactose	1.4	0.6	1.2	0.6
Glucose	40.0	55.4	61.3	59.9
Mannose	11.9	1.0	6.9	0.3
Xylose	5.9	2.4	6.0	1.0
Lignin	29.8	36.6	17.8	37.4
Klason lignin	29.4	36.4	17.3	37.1
Acid-soluble lignin	0.4	0.2	0.5	0.3
Extractives	1.2	4.0	0.5	0.8
Others	8.4	-	5.6	-
Total	100.0	100.0	100.0	100.0

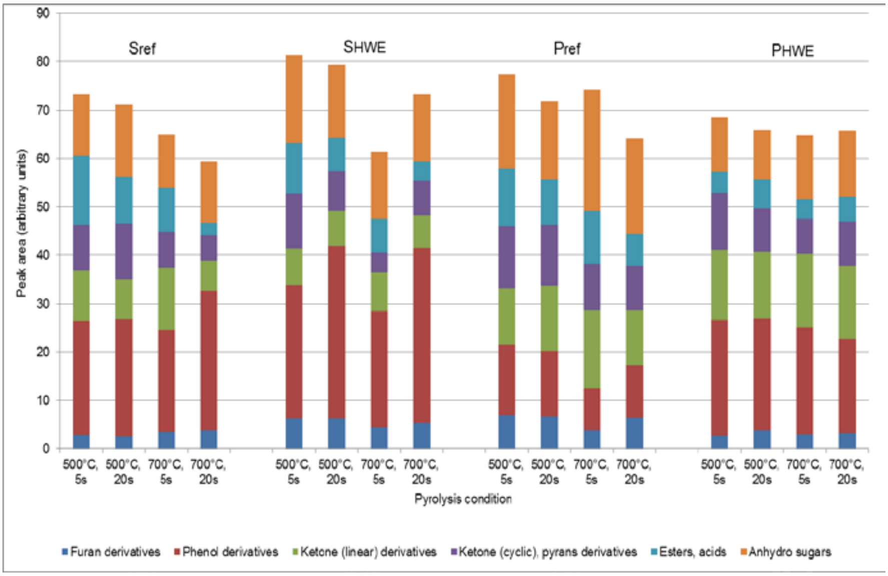

Figure 1. The effects of temperature and residence time on the area peak of pyrolysis product groups.

Main findings

- Major GC-amenable pyrolysis products were classified into several compound groups (mainly furans, phenols, ketones, anhydro sugars, and carboxylic acids including their derivatives) and changes in the relative portions of these monomer-related fragments were determined under varying conditions. The formation of the main products was shown to be characteristically dependent on feedstock and reaction conditions.
- Examples of the similar “fingerprint” compounds derived typically from lignin and carbohydrates (cellulose and hemicelluloses) were acetic acid, 1-hydroxy-2-propanone, furfural, 5-(hydroxymethyl)furfural, phenol, 2-methylphenol, 1,3-cyclopentadione, guaiacol, 2-*p*-cymenol, 4-propyl guaiacol, and levoglucosan.
- The content of major compounds tended to increase with reducing the reaction temperature from 700°C to 500°C (residence time 5 s).
- The highest relative peak areas for levoglucosan and its degradation products in pyrolysis products of P_{ref} were obtained at 700°C (5 s) corresponding to almost the value that was determined for glucose in P_{ref} by wet-chemical analysis.
- The highest relative peak areas of phenol derivatives in pyrolysis products of S_{ref} were obtained at 700°C (20 s) corresponding to the slightly higher value that was determined for lignin in S_{ref}.
- Pyrolysis tests under the conditions applied led to reproducible results.

Acknowledgment

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Present Value Flows in Swedish Forest-based Industry

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Abstract

Forest biomass represents large physical as well as economic flows through the forest industry value chains. This paper presents the results from a survey of economic values related to the forest biomass flows from the forest through the forest-based economy in Sweden. The study is based on published market and industry data as well as information from stakeholders in the forest industry value chains. The flows are illustrated graphically.

Introduction

Large changes of the energy systems on both global and local scales are necessary in order to accomplish a transition from an economy based on fossil raw materials to a renewables-based bioeconomy. A larger share of nationally available renewable energy in the energy supply is also advocated as a means to increase energy security and reduce dependence on imported energy. Forest resources are economically important in forest-rich countries such as Sweden and Finland. Today, forest biomass is used as raw material mainly for production of sawn products and pulp and paper for the global market. Waste-products from forest industries as well as some of the residual forest biomass that can be extracted directly from the forest are being utilized for e.g. heat and electricity production.

The Swedish forest industry is under pressure to change; part of its infrastructure is coming of age and competition from other regions with newer production units and faster-growing feedstock increases. Also, the traditionally important market segment of printing and writing paper is in decline. Hence, the industry is looking to develop new value-added products, while at the same time there is a call for new, renewables-based solutions to replace fossil resources.

The objective of the present study is to give an overall view of the economic values related to the main physical biomass flows through the Swedish forest industry. Thereby it aims to provide a better understanding for the bioeconomy structure and the values added within it.

Data collection

The approach has been to combine existing information on physical feedstock flows with economic data from available statistics and literature. Existing market and forest industry production statistics on timber and pulpwood as well on many energy assortments (logging residues, stumps, young trees from pre-commercial thinnings and energy wood) were compiled.

The data collected comprised of three levels of information:

- Level one: Overview based on national economic accounts
- Level two: Aggregated values for key flows and product groups, based on published market data, trade statistics, stakeholder survey and assumptions.
- Level three: Increased detail for certain products.

The surveyed data sources included information from authorities, industry organizations and individual industry representatives. Organizations included the Swedish forest agency (www.skogsstyrelsen.se), the Swedish forest industries federation (www.skogsindustrierna.org), Trä- och möbelföretagen – TMF (www.tmf.se), the forest industry's IT company (www.sdc.se), the Swedish energy agency (www.energimyndigheten.se), the Forestry research institute of Sweden (www.skogforsk.se/), Statistics Sweden (www.scb.se), the Swedish petroleum and biofuels institute (www.spbi.se). A survey was sent to representatives from forest companies and forest owners associations. Forest industry representatives were interviewed.

Delimitations

Data were collected for the year 2009. In general, the study is not complete in the sense that it does not include all costs and revenues, but rather focuses on the values of the main forest products flows. For example, it includes the value of paper produced by the paper industry and the cost that the industry has for wood feedstock. However costs for other inputs, such as pulping chemicals and filler materials are not included, nor are labor and capital costs. The studied flows of forest products may also contain significant amounts of non-wood materials, for example, paper products often contain varying levels of mineral fillers and coatings. This study does not attempt to provide a full account of the cost and income structure of the studied sectors.

The sectors included are; forestry, (i.e. wood production and supply), the wood products industry, the pulp and paper industry, the pellets industry and the wood-based panels industry. Further use and refining of the wood in sectors such as construction, furniture manufacture, newspaper and print industry, packaging industry etc., was not covered in the study. The information collected for wood supply is more complete as it covers the most relevant forestry costs. Also, a complete picture of the forest-based industry is given on a much more aggregated level by input-output data from the Swedish national accounts.

Results

The results of the value flow analysis are shown in tables and illustrated with Sankey diagrams[7].

Figure 1 gives an overview of the economic flows to and from key sectors of the forest-based economy in Sweden in 2009, based on the symmetric input-output table from the national economic statistics. The values generated (1), which drive the system, are manifest in three groups: 1a) Final domestic consumption, i.e. what consumers spend on products and services to satisfy the needs and wants, 1b) exports, i.e. the income from goods that are exported for final consumption or further refinement outside the Swedish border, and 1c) gross capital formation, i.e., domestic values that are created but not consumed, such as constructed buildings. On the other end of the diagram (2), the value flowing through the economy ends up in two main categories: 2a) imports, where money leave the system as compensation for imported goods and 2b) an aggregated class composed of added value such as compensation to employees, operating surplus and taxes paid to society. The values generated also have to compensate for the consumption of fixed capital. The flows in the input-output tables are defined by products and services and aggregated into groups of related products and services, roughly reflecting different sectors of the economy. All net input and output flows to and from selected sectors were included in the diagram: 3) The primary production of wood in forestry and related services; (4) the primary wood processing industry divided into 4a) wood and products of wood, including for example the production of sawn wood products and 4b) paper and paper products, including the products of the pulp and paper sector; and (5) important downstream users of wood and paper products: 5a) construction and construction works, 5b) furniture and other manufactured products and 5c) printing, recording and publishing services. In addition, the net flows between these sectors and other parts of the economy (6) were included and grouped into: 6a) Energy, including electricity, gas, steam, air conditioning, coke and refined petroleum products; 6b) Transport services; 6c) Chemicals; 6d) other products; and 6e) other services. The diagram shows net flows. Flows with a magnitude smaller than 1000 MSEK are not shown.

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[7] A Sankey diagram is a graphical illustration of flows, where each flow is represented by a line and the width of the line reflects the magnitude of the flow. We have opted to show where the money comes from and where it goes, i.e. the direction of the value flow is opposite to the physical flow (of, for example, wood).

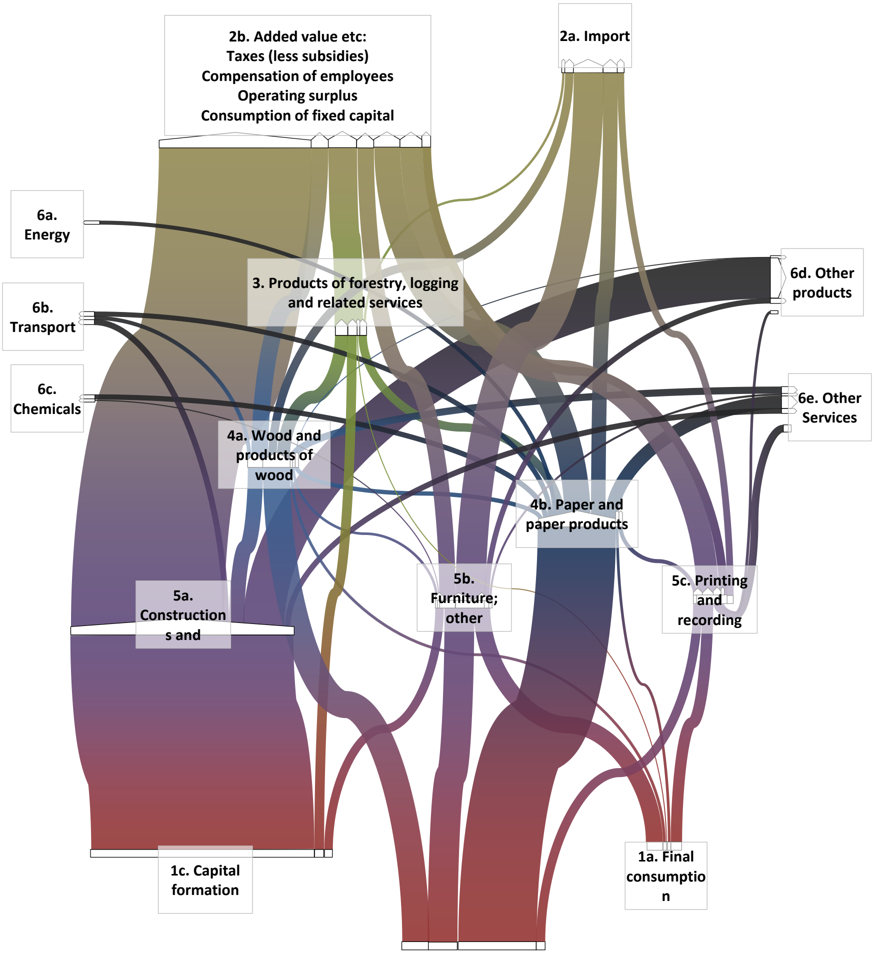

Figure 1. Overview of economic flows through the forest-based economy based on the Swedish national accounts.

The diagram is dominated by the large capital formation in construction and construction works. The flow from construction to other products was in total about 63000 MSEK out of which 27% to wood products. Wood and paper products have their main economic inflow from exports. The main net economic inflows to forestry came from wood products industry (14000 MSEK), from pulp and paper industry (9000 MSEK) and from capital formation (11000 MSEK). Compared to the production of wood products, the production of paper products have a more diversified cost structure, and the economic flow to the forestry sector is relatively small in comparison to the total value flow from the sector. The value flows to the forest industry sectors from the sectors of furniture and other manufactured goods and printing, recording and publishing services are small compared to the total turnover of these two sectors.

Figure 2 shows the value flows for the forest-based economy sectors in greater detail. The magnitudes of the flows were calculated by combining data on physical flows with economic data. Unlike Figure 1, Figure 2 is not complete, in the sense that it focuses on the part of the economic flows directly referable to biomass-containing physical flows. Costs for non-wood feed-stock and energy, personnel etc. are not shown. Hence, the in- and outputs do not balance.

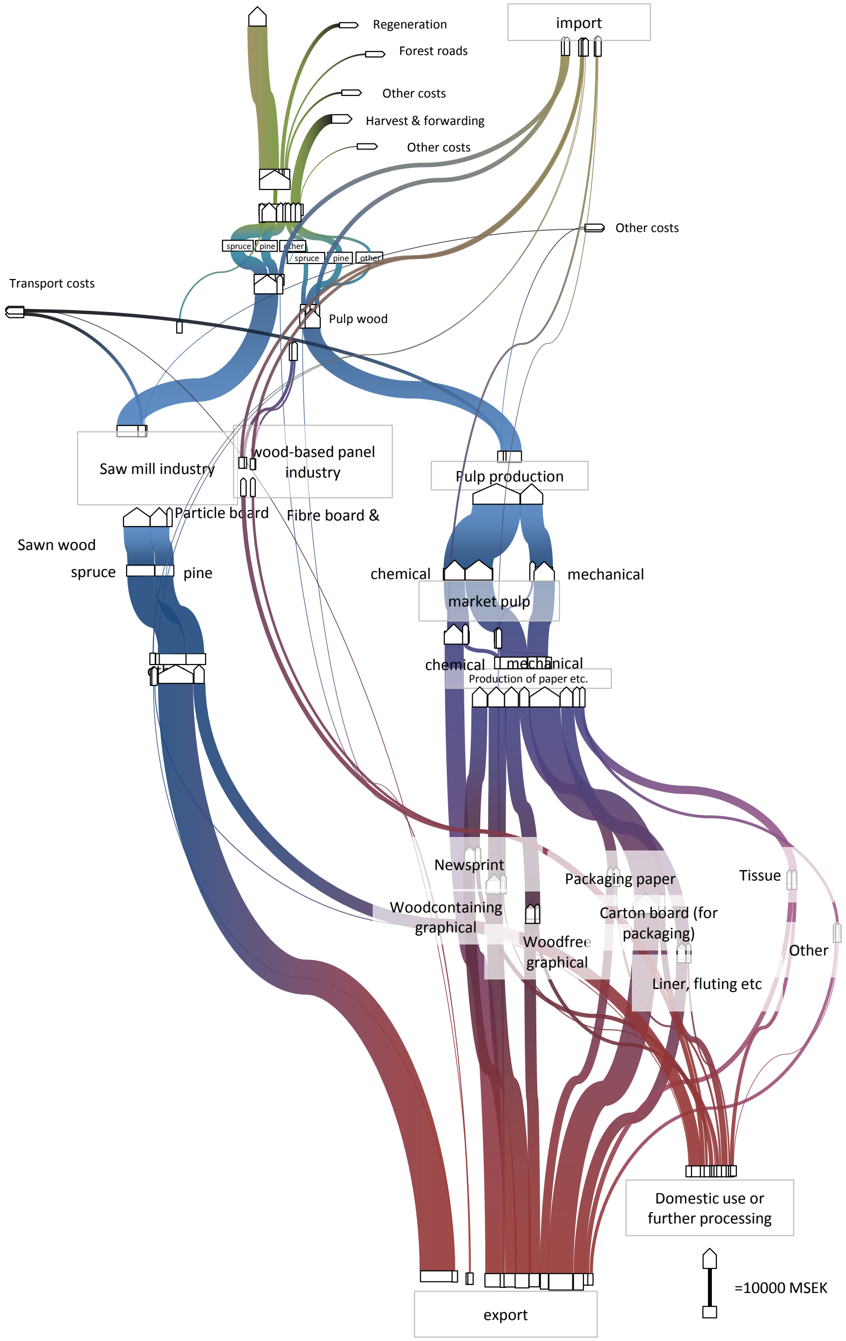

Figure 2. Economic flows divided by product groups.

Summary and conclusions

This paper has presented a graphical view of the economic values related to forest-based flows through the economy in Sweden. The objective is to improve the understanding of the forest-based economy and its value creation processes. This could serve as a starting point in efforts to transform the forest industry sector that are called for, both to improve the competitiveness of the sector and to contribute to a transition from a fossils-based economy to a bioeconomy. Further details and conclusions from the study will be described in a forthcoming report [1].

Acknowledgements

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Aqueous Phase Oxidative Treatment of Saw Dust

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Abstract

Regarding the utilization of lignocellulosic residues and solid waste biomass, partial wet oxidation (PWO) provides an alternative treatment to produce sugars or carboxylic acids. This paper investigates the impact oxygen, temperature and alkali metal (sodium carbonate) on the PWO of wood particles in a single reactor. The experiments were followed by measuring the yields of solid residues, carboxylic acids and sugars, pH, total organic carbon and average oxidation stage of carbon after the reaction. These data give insight to the reaction mechanism. The results show that increase in temperature up to 230 °C increases the solid dissolution and yields of sugars and organic acids. On the other hand, the alkaline catalyst cause retarded hydrolysis step during PWO. The presence of oxygen increases the acid yields by accelerating hydrolysis and introducing more intermediates to the system compared to the absence of oxygen. From the process viewpoint, this single-stage setup is more effective than two-stage process including cooking as a pre-treatment.

Introduction

Due to the environmental issues and the increasing need of using renewable carbon sources, the utilization of waste biomass has significant importance to fulfil needs of chemicals and energy without compromising other sectors, such as food or forestry products. One type of solid biomass is fine-sized wood particles, such as by-product of saw mills, grinding or mechanical pulping.

In the literature, the treatment methods for solid wood particles mainly include torrefaction, gasification, hydrothermal decomposition or partial wet oxidation (PWO). However, torrefaction and gasification are energy-intensive since drying of high moisture content of wood is necessary. Therefore, the methods suitable for wet biomass might be suitable for wood waste provided that mass transfer limitation of dissolution is addressed. In some recent studies PWO of black liquor has been investigated [1, 2]. The implementation of PWO to solid particles involves two steps: the dissolution of solid and thermal decomposition/oxidation of the dissolved organics. Mudassar&al. (2014) studied saw dust treatment in two steps, cooking followed by partial wet oxidation [3].

This study investigates PWO of wood particles in a single reactor. The purpose is to determine the impacts of temperature, oxygen and sodium carbonate catalyst on dissolved solid percent, the yields of sugars and carboxylic acids, pH, total organic carbon (TOC), average oxidation stage of carbon (AOSC).

Materials and Methods

The raw material used in this work is softwood processing waste with fine size particles. The moisture content of this feedstock was 55.4 %. 28 runs were performed in total: with only oxygen, with oxygen and catalyst, with only catalyst and neither with oxygen nor catalyst under various temperatures from 130 to 270 °C.

The same reactor described by Mudassar&al. (2014) [3] was used in the experiments. First, solid particles and distilled water were added to the reactor with the ratio of 1:10 by weight. Sodium carbonate was used as a catalyst and added in the concentration of 10 g/L. The rest of the reaction procedure is similar to the description in Mudassar&al. (2014) [3]. The reactor was heated to the reaction temperature in 30 minutes. The temperature was kept constant for 30 minutes and meanwhile the pressure was maintained at 5 bar above the corresponding vapor pressure at that temperature by pressure control of oxygen bottle. The partial pressure of oxygen was approximately 5 bars during the reaction. Afterwards, the reactor was cooled down in 5 minutes to 25 °C. Solids were separated from the reaction mixture by sieving. The solid phase is washed with 10 mL water, which was mixed to liquid phase as well. Then, the separated solid phase was dried in oven at 105 °C and the weight of remaining solid was measured to obtain the dissolved amount.

The liquid phase was analysed for TOC, COD, pH, acids as described by Mudassar&al. (2014). In addition, sugar analysis was performed with the methodologies described by Sipponen (2015) [4]. Briefly, carbohydrates solubilized by the PWO were hydrolyzed to monomeric sugars by mixing 2.5 mL of PWO liquor with 2.5 mL of 8 % (w/v) sulfuric acid in a crimp cap glass vial. The reaction in the closed vial was conducted at 121 °C in an autoclave during 1 h. An aliquot of the obtained acidic hydrolysate was supplemented with D-xylitol as an internal standard, and adjusted to neutral pH by calcium carbonate. The liquid fraction was passed through a 0.45 μm disc filter, and sugars were analyzed with an HPLC system comprising a Micro-Guard De-Ash pre-column (Bio-Rad, USA), an SPO810 column (Shodex) coupled to a refractive index detector (Shimadzu). Deionized water delivered at flow rate of 0.7 ml/min was used to elute the column at 60 °C. Monosaccharides were identified and quantified based on their retention times and peak areas relative to external standard calibration constructed for D-xylose, D-glucose, D-galactose, L-arabinose, and D-mannose. Sugar recovery standards subjected to the acid hydrolysis were used to correct for sugar degradation that occurred.

Results and Discussion

The reaction mechanism of the oxidation involves two main steps: hydrolysis of polymeric structures (i.e. the dissolution) and further decomposition of monomers. Hydrolysis of cellulose and hemicellulose generates soluble sugars and the decomposition of lignin produces guaiacol and some other phenolic fractions. In addition, oxidative degradation of lignin produces phenolic aldehydes such as vanillin and syringaldehyde as well as some oligomeric fragments. The further decomposition reactions can occur either as oxidation and thermal decomposition without oxygen through free radical mechanism. These reactions produce intermediates, such as aldehydes, alcohols, furanes, aromatic hydrocarbons and carboxylic acids.

The further processing of the product liquid may be for example fermentation to produce bioethanol (requiring high sugar content and low concentration of inhibitors such as furfural) or evaporative crystallization to recover carboxylic salts. However, if the liquid is dilute, crystallization may become unfeasible due to energy-intensive evaporation, as investigated by Özdenkci&al. (2014) [5]. In order to evaluate the performance of partial wet oxidation, the important considerations to note are the percentage of dissolved solids and the yields of sugars and acids.

Dissolved Solid Percent, TOC and AOSC

Dissolved solid percentage indicates the rate of hydrolysis. TOC and AOSC (average oxidation stage of carbon) indicate the organic content and the extent of oxidation relative to thermal decomposition without oxygen. AOSC can be calculated with molar TOC and chemical oxygen demand as shown in [2].

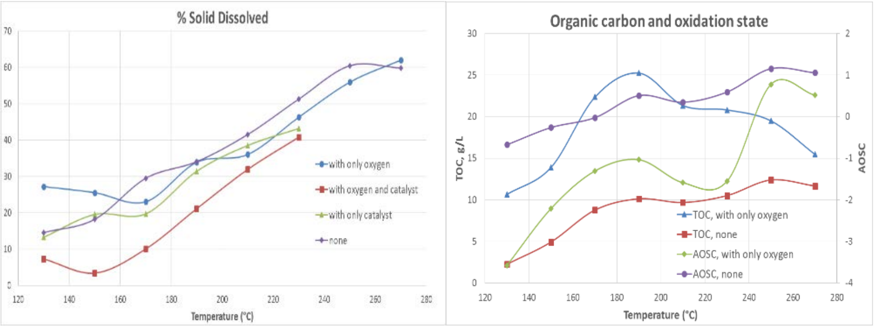

Figure 1. Dissolution of solid versus temperature for all four cases and TOC and AOSC for two cases.

Figure 1 shows the trend of dissolution as well as TOC and AOSC in liquid fraction after PWO of wood particles. As temperature promotes the reaction kinetics, the dissolution increases almost linearly with temperature after 150 or 170 °C in all cases of oxygen and catalyst. However, dissolution decreases from 130 to 150 °C except the case with only sodium carbonate catalyst. TOC increases with increasing treatment temperature as well. On the other hand, even though the dissolution are close or higher in the absence of oxygen, TOC is much higher for the case with oxygen. Moreover, AOSC is higher for the case with no oxygen and reaching positive values at 170 °C and higher temperatures.

These trends together demonstrate that oxygen is promoting hydrolysis reactions. In the absence of oxygen, side carboxyl groups and other groups with relatively more oxidized carbon dissolve faster than the monomer dissolution through hydrolysis. Then, these groups are oxidized to carbonates and carbon dioxide when there is less sugar and more of these kind of groups in the liquid. Therefore, lower TOC was obtained in the absence of oxygen and AOSC is higher than with oxygen present. In contrast, hydrolysis is faster in the presence of oxygen and then more various intermediate reactions occur rather than dissolved carboxyl groups being oxidized to carbonates and carbon dioxide. Especially, the percentage dissolutions at low temperature below 200 °C confirms this statement as well: dissolution with oxygen is much more pronounced. Either in the absence or presence of oxygen, the sodium carbonate causes decrease in percentage of dissolution suggesting that alkaline conditions retards the hydrolysis step.

Sugar Yields

Sugar yields measure the relative rate of hydrolysis and the further decomposition of sugar monomers. For fermentation purposes, it is desirable to interrupt the reaction chain after hydrolysis and maintain more sugars in the liquid.

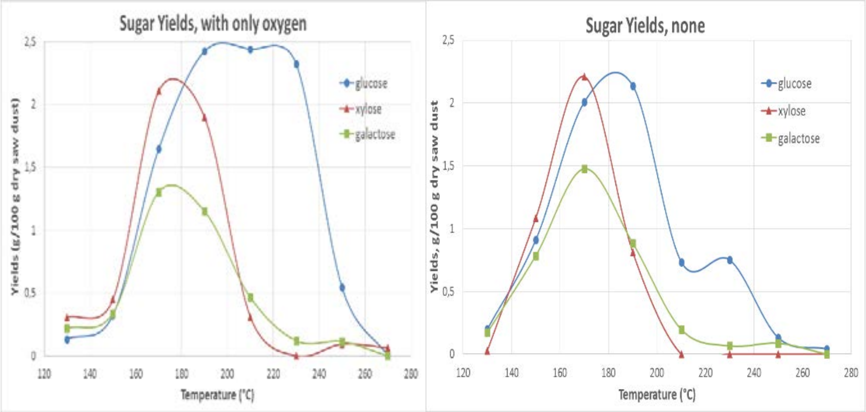

Figure 2. Sugar yields for the two PWO treatments.

Figure 2 shows the trends of some soluble sugars derived from cellulose and hemicelluloses. The yields of glucose are slightly higher with oxygen whereas the yields of other sugars are similar. However, the yields and concentrations (not shown here) are not sufficient for profitable production of bio-ethanol through fermentation. In addition, very high temperatures decrease the sugar yields due to promoted reactions of further decomposition. The low sugar concentration was due to high liquid to solid ratio of 10 used due to limitation with the stirring in the reactor.

pH and Acid Yields

Acids are generated through thermal decomposition of monomers and other intermediates both in the absence and the presence of oxygen. pH is a measure of overall acid content of the liquid, starting from alkaline and decreasing during the reaction.

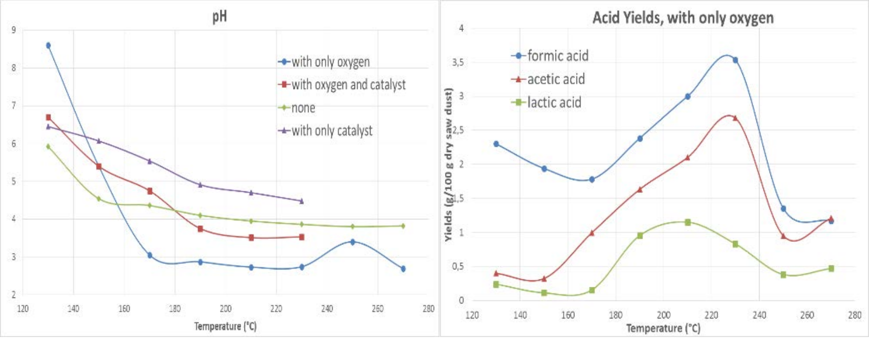

Figure 3. pH of the product liquid for all cases and acid yields for one case.

Figure 3 shows pH of liquid fractions collected after the PWO of wood particles. The values sharply decrease with temperature for all alternative treatments, *i.e.* temperature promotes acid formation. Nevertheless, temperature does not have major impact when increased beyond 210 °C. The results show that the alkali catalyst does not promote the acid formation due to slower hydrolysis and the shifting speciation towards carboxylate ions. Figure 3 also shows the yields of three major carboxylic acids for the treatment without catalyst in the presence of oxygen.

From the processing viewpoint, a single-stage process gave higher acid yields than the two-stage process which consisted of cooking softwood particles with alkali followed by partial wet oxidation of the formed solution as studied by Mudassar&al. (2014) [3] with the same feedstock. In addition, this single-stage process has less operating and investment costs as well.

Conclusion

This study investigated partial wet oxidation of wood particles. Temperature, sodium carbonate catalyst and oxygen partial pressure are the parameters which influences the process. Regarding the further use of the product, sugar content and acid contents are the important parameters. In addition, the solid dissolution percent is a useful measure for understanding the rate limiting step of the reaction mechanism.

The results indicated that the presence of oxygen promotes hydrolysis reactions in acidic conditions. However, even though alkali metals promotes the decomposition reactions in higher pressure and temperature (e.g. in sub- or super-critical water gasification), sodium carbonate causes alkaline effect which slows down the hydrolysis step and reduces the acid yields under the conditions studied in this work. Temperature increases the percentage dissolution, and yields of soluble acids and sugars. On the other hand, increasing temperature after 230 °C decreases the yields and TOC due to oxidation to carbonates and carbon dioxide. In addition, oxygen also reduces the energy demand of the process since the wet oxidation process liberates heat; instead, the thermal decomposition without oxygen is endothermic.

From the processing viewpoint, the single-stage process has given higher yields than the previously presented two-stage process of cooking and partial wet oxidation. As to future aspects, different types of catalysts can be tested and higher solid/water ratio can be used in order to improve the concentrations in the product. The utilisation of the solid residue could be studied for pellet production or further thermochemical conversion, such as gasification or combustion.

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The Evaluation of Extraction Yield on Black Liquor for Korean Native Miscanthus through Soda Pulping Process

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Abstract

Some factors affecting the behavior of black liquor derived from Korean Native Miscanthus by the caustic-soda pulping process have been investigated. The black liquor, which is by-product derived from the pulping process, is contained mainly lignin and a partial of hemicellulose. By an acid hydrolysis, acid insoluble lignin (AIL) in black liquor is precipitated, used to pellet additive. In addition, the hemicellulosic fraction can be broken down into xylose, Inhibitor. In this study, Soda pulping of the feed-stocks with NaOH was performed using oil-bath equipment with 33ml cylindrical stainless steel reactor. The oil-bath reactor were loaded with 2g of dry base Miscanthus. The total LS (Liquid/Solid) ratio was approximately 6, 8, 10:1 w/w. To investigate the effect of various condition during soda pulping, the H-factor and NaOH concentration were tested on 500-1100(170~190℃) and 1-15%. The focus of this study is pulp yield on the optimization of static time, temperature, alkali concentration and LS ratio in soda pulping.

Introduction

In the worldwide, around 95% of all raw materials used by the paper industry to obtain cellulose pulp consists of hardwood or softwood. The other raw materials used for this purpose are known as ‘non-wood’ materials [1, 2]. Among the treatment processes for obtainment of cellulose pulps, there is a predominance of sulfate (Kraft) and sulfite methods, which makes up two-thirds of the world production of paper pulps [3]. However, the use of sulfurated chemical agents in these methods brings with a serious environmental impact due to the released sulfur compounds, and the bleaching with chloride derivatives that produce highly toxic organochloride compounds [4].

Nowdays, by-products, which was affected in environment, were avoid or reduced on effluents environment standard. The use of soda solutions constitutes an alternative method for producing chemical or semi chemical pulps from non-wood lignocellulosic materials, without this problem [5, 6]. Besides, a pulping process performed with high efficiency led to a reduction in the amount of chemical reagents necessary for pulp bleaching and a concomitant reduction in the pollutants discharged from bleach plant [7]. However, delignification processes and the resulting pulps are influenced by several parameters such as the liquid-to-solid ratio, H-factor and NaOH concentration [8].

In this study, an experimental design was used to evaluate the pulp yield and black liquor composition of the operation condition (NaOH concentration, H-factor and Liquid-to-solid ratio) used for miscanthus soda pulping, with the aim of identifying the optimization on soda-pulping operation.

Experimental

Korean Native Miscanthus (KNM)

Perennial grasses, as miscanthus (Miscanthus x giganteus) and wheat straw, were generating much interest in Europe and China, as new sources of biomass for energy production [9]. The KNM used in this study were obtained from the Muan-gun, Jeollanam-do in South Korea. The used miscanthus stalks were cleaned from leaves, roots, branches, calyxes and soil.

Soda Pulping

Soda pulping, which purpose of delignification from Miscanthus, was performed 10mesh (2mm) miscanthus with NaOH using oil-bath and racking reactor. Experimental condition was shown **Table. 1**. The dried miscanthus 2.0g was added to racking reactor with NaOH solution. After that reactor was placed in an Oitl bath [10-13]. After pulping, the reacted sample were separated liquid and solid respectively. After that solid was dried oven at 105℃ during 24h, and analyzed according to National Renewable Energy Laboratory (NREL)/TP 510-42618(Structural Carbohydrate)[14].

The highest temperature for the extractions was 170-190℃ for target H-factors of 500-1100 h at each chemical loading. The H-factor is a kinetic model applicable to alkaline pulping that expresses cooking time and temperatures a single variable. The H-factor equation is given by Eq. (2):

$$\mathrm{H-factor} = \int_{t_0}^{t} e^{[43.19-(\frac{16113}{T})]}dt \qquad (2)$$

(2) where time (t) is given in hours and the temperature (T) is given in Kelvin. The numerical constants in the expression are related to the activation energy of 134 kJ/mol for delignification during soda cooking.

Table 1. Experimental condition of soda pulping.

Parameter		
Liquid Solid ratio (w/w %)	6, 8 and 10: 1	
NaOH concentration [%]	1, 8, 15	
H-factor	Temperature [℃]	time [minute]
500	170	41.30
	180	23.30
	190	16.30
700	170	54.30
	180	29.18
	190	19.12
900	170	67.30
	180	35.12
	190	22.00
1100	170	80.30
	180	41.00
	190	24.42

Acid Hydrolysis

An acid hydrolysis step was required after soda pulping extraction to hydrolyze oligomeric sugars into monomeric sugars for analysis solid composition and lignin recovery. The samples, which were black liquor, were hydrolyzed at pH 0.5 with sulfuric acid in an autoclave (HEMOSS, Korea) for 60 min at 121℃. The extracted black liquor was hydrolysed to produce partially hydrolyzed monomeric sugars and acid insoluble lignin was precipitated to solid. After that samples were separated liquid and solid respectively. Solid were dried oven at 105℃ and weighted lignin composition from black liquor. Liquid were analyzed sugar components and organic acid by HPLC.

Composition Analysis

The KNM was analyzed quantitatively for their composition according to the NREL analytical procedures: NREL/TP-510–42618 (structural carbohydrates) and 42623(sugars, byproducts, and degradation products in liquid fractions) [14, 15]. The lignin and extractives in the raw woodchips and extraction liquor were analyzed quantitatively for their composition according to the NREL analytical procedures: NREL/TP-510–42618 (lignin in biomass) and 42619(extractives in biomass) [14, 16].

High Performance Liquid Chromatography (HPLC)

The concentration of sugars and organic acid in black liquor was quantitatively analyzed using HPLC equipped with refractive index (RI) and UV detection. The HPLC system (Shimadzu Co., Nakagyo, Kyoto, Japan) used to measure carbohydrate content had an Aminex HPX-87Hcolumn (300 mm × 7.8 mm), (Bio-Rad Laboratories Inc., Hercules, CA). The column was maintained at 60℃, with a 5 mM H_2SO_4 eluent at a flow rate of 0.6 mL/min. All of the sugar peaks were detected by refractive index and UV absorption (280 nm), and compared to retention times of authentic standards. This study was used a Bio-Rad Aminex HPX-87H analytical column, which allows the concurrent analysis of liquid samples for the presence of acetic and lactic acids as well as sugar degradation products such as furans. The sample was respectively analyzed during 50 min.

Results and Discussion

Miscanthus chemical composition

The KNM chemical composition was shown **Table 2**. The KNM composition was 43.15% glucan, 26.39% XMG, 3.28% arabinan, 9.41% Klason lignin and 6.18% Extractive. The carbohydrate fraction was predominantly composed of glucan and XMG, while arabinan was a relatively minor component. Analysis of the KNM showed that lignin available for extraction accounted for more than 9.41% of their content on a dry basis.

Table 2. Miscanthus Chemical components.

Component	Raw material
	Dry basis (% wt/wt)
Glucan	43.14
XMG(Xylan + Mannan + galctan)	26.39
Arabinan	3.28
Total sugar	72.81
Klason lignin	9.41
Extractive	6.18
Total non-carbohydrates	15.59
Total (Total sugar + Total non-carbohydrates)	88.40

Acknowledgements

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Behavior of Wood Powder and Pellets in a Horizontally Rotating Cylinder with Internal Screw Cylinders: Cold Model Experiment

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Abstract

Cold model experiments on gas and solid movement were conducted using two scales of horizontally rotating cylinders specially designed for woody biomass drying, pyrolysis and gasification. Their inner diameters were 400 mm and 200 mm equipped with two pairs of 131 mm i.d. internal screw cylinders and a single 65 mm i.d. cylinder for shuttling/transporting pelletized particles and discrete biomass powder, respectively. The air tight bigger rotating cylinder experiment revealed that the operational range for good gas-solid contact was narrow because the gas passes not through but over the particle layer under the low packing of particles inside the internal cylinder. Hence in the present paper various modification ways of the particle entrance of the internal cylinder were proposed and their improvement effects on the increase in packing were demonstrated using small scale model, to enable stable pressure drop and good gas-solid contact in the internal cylinders.

Introduction

The technologies for practical use of fossil-alternative resources should be urgently developed because fossil resources such as petroleum will dry up in the near future. In addition, the international community has the responsibility to reduce the greenhouse gases such as CO_2 emitted by the energy conversion of fossil resources. Hence, the woody biomass attracts attention as a fossil-alternative resource because it is reproduced by photosynthesis in a relatively short term by absorbing CO_2 when it grows up (carbon neutral) and furthermore, wood itself also have a function of carbon stock. However, it is difficult and costs much to collect, handle and convert the cellulosic biomass.

The present authors have paid attention to the indirectly heated biomass pyrolysis/gasification which enables the production of the high calorific value gas. Conventional pyrolysis/gasification processes tend to be complicated and large-scale, because they are composed of units of "Thermal cracking of organic carbon", "Tar separation from pyrolysis gas", "Gasification of tar", and "that of char". While the rotating cylinder reactors (rotary kilns) may be good for this process, the particles move at the lower part of the reactor along with its inclination, and the gas passes over the particle layer without gas-solid contact.

Kunii and Chisaki (2007) showed the possibilities of the use of horizontally rotating cylinder (HRC) with internal screw cylinders (ISCs) which enables the internal circulation of particles and gas seal between two chambers with different atmospheres [1]. Authors also have proposed and demonstrated the actual use of an indirectly heated HRC reactor with ISCs [2]. As a result, small pyrolysis/ gasification devices, which can be set up easily and moved to the vicinity of the biomass collection place, are designed. In such pyrolysis/ gasification reactors as above, the particles move back and forth through ISCs with screw partition. In the ISC, the reactant gas is forced to pass through the inside of the particle layer divided by the screw partition inside the ISC, leading to the accelerated gas solid contact.Hence both of the tar and char conversions are enhanced and high performance at low cost is expected in one small reactor with easy operation. Furthermore, the collection cost can be reduced because it can be set up near the source of the biomass.

However in the actual operation (e.g., [3]), the measurement of the particle behavior is difficult. Therefore, the particle behavior measurement using cold models is indispensable for the optimization of the device structure and the operating condition. In this paper the particle behavior was examined by using cold models made of transparent vinyl chloride.

Experimental 1: large-scale model

The cold model of the HRC with four ISCs (inner volume: 7.4 L) is shown in Figure 1. The spaces at the both ends of ISCs are used as particle storages. The right side is connected with a vacuum cleaner nozzle through tap #1. The left side is open to atmosphere through taps #2 and #3, orifice of 15 mm i.d. and tap #4. The pressure drop through the device was measured as the pressure difference of the water manometer connected to the taps #1 and #2 and the flow rate was measured from the correlation curve [4] and the pressure difference of the water manometer connected to the taps #3 and #4. The gas pipe was unfastened while rotating.

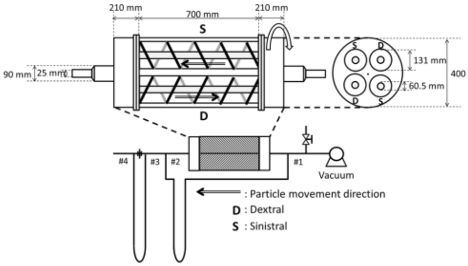

Figure 1. Schematic diagram of large scale experimental setup.

First of all, air was sent in the cold model without the particles by the vacuum cleaner And, the pressure drop through the device was measured. The flow rate of air was adjusted to 20 or 40 m^3/h. Columnar wood powder pellets (bulk density, 0.665 kg/L: length, 0.5 - 2.5 mm: diameter, 0.5 mm) were used as a feedstock. Eight L of pellets were put in the particle storages and the model was rotated for 30 min at 1.0 rpm while the steady state of particle packaging in the ISCs was attained within 10 min. After the rotation was stopped, the pressure drop was measured again. The procedures were iterated to 44 L loading while only the last charge was 4 L.

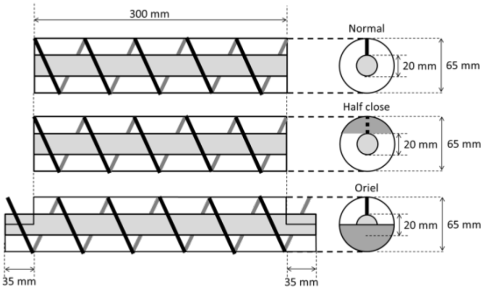

Figure 2. Schematic diagram of ISCs located at the bottom position of HRC small-scale mode).

Experimental 2: small-scale model

The small scale HRC with inner volume of one eighth of the large-scale model was used, while the length of the right particle storage is 235 mm, and the gas pipe is not connected or pressure drop through the ISC was not measured. Three kinds of ISCs shown in Figure 2 were used. Both ends of “Normal” and "Half close"d ISCs are opened and partly closed (rotation axis side) respectively and both are equipped with five winds of screw with 60 mm pitch. The cover of the "Half close"d ISC was set in order to prevent particle falling when the ISC was at the top position of the HRC. On the other hand the 35 mml of "Oriel" with closed side surface was attached in order to facilitate the intake of particles into the ISC inside. In the case of "Oriel" ISC, it is equipped with six winds of screw with 60 mm pitch and 5 mm clearances for both end. Only one ISC of "Normal”, "Half close" or "Oriel" was installed in the HRC.

Wood powder with bulk density of 0.260 kg/L was used as a feedstock. The photo of the powder is shown in Figure 3. The powder moves only from the right to the left with the rotation of HRC.

Figure 3. The photo of the wood powder and angle of repose.

Three L of wood powder was put in the right particle storage of the HRC leaving left storage open and the internal weight of powder was measured every 5 revolutions. As the weight was confirmed to be almost at the quasi-steady state after around 20 revolutions without significant change in the amount of powders in the right storage, the weight at 20 revolutions was used for further discussion. In the present paper the effect of the initial position of the screw (radial line in side view in Figure 2) inside each of the three types of ISCs is examined where the position shown in Figure 2 is denoted as 180°.by anticlockwise rotation.

Results 1: large-scale model

The relation between volume of particles in the storage and pressure drop through ISC at gas flow rate 20 and 40 m^3/h is shown in Figure 4 [4]. From Figure 4, it can be seen that the pressure drop is small and not changed up to 24 L where the gas did not pass through the particle bed of ISCs and the pressure drop was mainly caused at the piping parts at both ends of HRC. The pressure drop is seen to increase slightly at 32L of particles. When the gas passes through the entire particle bed in ISC, it causes big resistance. Hence, it is presumed that the pressure drop was not so large because of the short passing distance in the particle bed at 32 L loading. In addition, pressure drop is seen to increase exponentially at the particle amount of 40 L. It is thought that particles were filled enough in all of the ISCs to give high pressure drop. The measurements were iterated at 40 m^3/h by changing the position of the ISCs when the rotation was stopped. As a result, two sets of data around 1.2 kPa and those around 0.8 kPa were observed, which was explained as follows. Under the condition of 40 L of particles in the storage, the particles occupy almost half of its capacity. The entrance and the exit of one or two ISCs are below the surface level of particles and covered with those particles where the gas flow into the ISCs is blocked by the flow resistance by the particles in the storage. Hence the gas passes through only the other two or three ISCs, which give the two values of pressure drop with 1.5 times difference. The value of 1.2 kPa is thought to correspond to the case that gas passes through two ISCs and 0.8 kPa, three, respectively.

Then it is drastically increased at 44 L as shown in Figure 5 [4], where the piping parts at both ends of HRC were filled with particles so the main pressure drop is thought to originate there. The present results indicate the extremely narrow operational regime of this type of HRC.

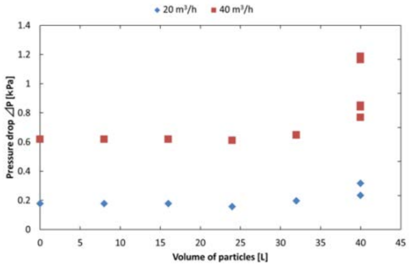

Figure 4. Relation between volume of particles (0 - 40 L) and pressure drop at gas flow rate 20 (◆) and 40 m^3/h (■).

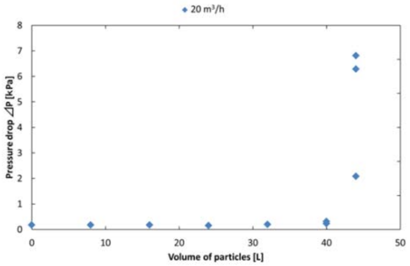

Figure 5. Relation between volume of feed particles (0 - 44 L) and pressure drop (⊿P [kPa]) at gas flow rate 20 m^3/h.

Results 2: Effect of entrance shape of ISC in small scale HRC

Effect of the initiation position of the screw inside ISC: “Normal”

Effect of the initiation position of the screw inside ISC without any modification (“Normal”) was examined using small scale HRC. The use of the small HRC enabled the examination of various effect of shape of ISC more easily.

Influence on powder loading in ISC of the starting position of the screw inside the “Normal” ISC is shown by ◆ in Figure 6. It is found that the packed amount is the largest around 45° or 90° of the initial position of screw, while the smallest around 270°. The present results may be well explained by the 45° of measured angle of repose of the wood powder. The wood powder is placed with the slope of heaped surface of 45° in the storage of HRC, and hence the ISC with the initial position of screw at 45° showed the highest value of powder loading in the ISC.

Effect of the initiation position of the screw inside ISC: “Half close”

In the case of “Half close”, effect of the initiation position of the screw on the powder loading in ISC is shown by ■ in Figure 6. The amount of powder loading in ISC was a little smaller than that in the case of “Normal” and hardly affected by the initial position of screw in the ISC. Thought in the previous paper [4] it was demonstrated that the modification of “Half close” increased the amount of powder loading in the large scale model of ISC/ HRC with powder pellets, the present experiment with small scale ISC/ HRC gave the different results. The present discrepancy might be explained by the difference in the friction with vessel surface between the wood powder and its pellets, which also indicates the easiness of movement in the ISC. In the case of wood pellets, they were easily filled down from the entrance of ISC, and halfly closed cover was effective to prevent the falling of the pellets, while in the case of wood powder, the prevention effect of falling was reduced and negative effect of closing the entrance area was increased.

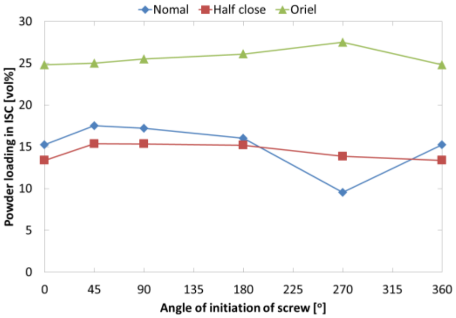

Figure 6. Influence of the initiation position of the screw inside the “Normal”, “Half close” and “Oriel” ISC.

Effect of the initiation position of the screw inside ISC: “Oriel”

Finally in the case of “Oriel”, effect of the initiation position of the screw on the powder loading inside ISC is shown by ▲ in Figure 6. It is demonstrated that the introduction of “Oriel” remarkably increases the powder loading inside ISC. The present results are suggested to be brought by the scooping effect of the oriel and hence the powders are effectively moved to the inside of ISC.

Conclusions

The relation between the powder loading of the particles and pressure drop of the gas stream through the HRC was measured and it was demonstrated that the pressure drop of steeply increased with increased load of the particles, which indicates all of the gas passes through the inside of the particle layer of ISC not over it. Under the present condition, the gas-solid contact is expected to be drastically improved. In addition, it was also demonstrated that the improvement of entrance shape of the ISC can also drastically increase the powder loading of the particles while the degree of the effect is also dependent on the particle properties and scale of the device. Especially the equipment of oriel drastically increased the powder loading in ISC.

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High-purity Pulp from Paper-grade Pulp by Enzymatic Treatment and Post-extraction in Caustic-borate Solution

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Abstract

High-purity cellulosic pulps with cellulose contents above 98% were produced from bleached softwood paper-grade pulp by applying an enzymatic treatment followed by caustic-borate extraction. In acetylation experiments, the extracted pulp samples having the lowest amounts of residual hemicelluloses resulted in very low yellowness, even as low as 0.18. However, those samples also showed a low transmittance of the triacetate dope, which is undesirable as regards the production of an acetate-grade pulp. This decrease in transmittance is believed to be due to the formation of Cellulose II and its hornification upon removing the water from the pulp.

Introduction

Dissolving pulps constitute a small but important share of the global pulp market. There, feasible production of high-purity cellulosic pulps suitable for e.g. acetate process is a continuous challenge since the availability of cotton pulp is diminished. [1] Conversion of bleached paper-grade pulp into acetate-grade dissolving pulp requires very extensive removal of wood hemicelluloses. Sodium borate ($Na_2B_4O_7$) used in a caustic post-extraction step (CCE/B) has demonstrated a potential of improving glucomannan extraction from pulps [2]. This effect can be explained by the complex formation with the adjacent hydroxyl groups of carbohydrate. High selectivity towards glucomannan is caused by the cis-position of the hydroxyl groups in the positions 2 and 3, while in xylan the trans-position of hydroxyl groups prevents the complex formation [3].

In the present work, the alkali-borate post-extraction of hemicelluloses from bleached pine kraft pulp is studied as a function of extraction temperature and sodium hydroxide and borate concentrations. In order to enhance the hemicellulose removal during the extraction, a series of enzymatic treatments with xylanase and mannanase prior to the CCE/B stage was designed. To evaluate the extraction efficiency, the yields and carbohydrate compositions of the solid residues were analyzed. Further, characterization of the extracted pulp samples as a potential raw material for an cellulose acetate process was performed.

Experimental

The raw material used in this study was bleached, non-dried Kraft pine pulp kindly provided by MetsäFibre, Rauma. In the first stage of the study, the optimum conditions for the alkali-borate extraction were determined. Both pure alkali extraction (CCE) and alkali-borate extraction (CCE/B) were performed under various temperatures and with different chemical concentrations: Temperature ranged from -10 to 80°C, sodium hydroxide concentration from 8 to 12 wt-%, and sodium borate concentration from 0 to 6 wt-% on solution. Total treatment time of each test point was 60 minutes and pulp consistency 5%. The experiments were performed in closed glass bottles in a water bath by adding 20g (OD) samples of pulp into alkali-borax solutions adjusted to reaction temperature. These suspensions were then mixed vigorously in every 10–15 minutes.

After the extraction, pulp samples were thoroughly washed by hot water and then rinsed several times with room temperature water. To avoid any residual alkali that could hinder the following acetylation, the washed samples were soaked overnight in 3% acetic acid solution (5% consistency) and then rinsed again with water several times the next day. Finally, the effects of each extraction were quantified by measuring the gravimetric yields, carbohydrate compositions of the residual pulps [NREL/TP-510-42618, 4], and their viscosities [SCAN-CM 15:99].

In the second stage of this study, an enzymatic treatment was performed prior to the alkali-borate extractions under selected conditions (30°C temperature, 3 wt-% of $Na_2B_4O_7$, and from 8 to 12 wt-% of NaOH). A commercial xylanase solution (Pulpzyme by Novozymes) and non-commercial thermomannanase (see Acknowledgements) in a powder form were used. Conditions during the enzymatic treatment were as follows: Temperature 70°C, consistency 3%, pH 5.5 (adjusted by NaH_2PO_4 and Na_2HPO_4 solution) and treatment time 120 minutes. The enzyme dosages were 2 000 AXU/g pulp and 200 AMU/g pulp. The non-dried pulp suspension was first diluted by the pH buffer solution close to the 3% consistency and then heated in a reactor with a stirrer to 70°C. A small portion of the buffer was used for the preparation of an enzyme solution with xylanase and mannanase, so that an even distribution of the enzymes during the treatment could be ensured. This solution was carefully poured into the reactor with a continuous stirring, the final concentration of the suspension being 3%. After two hours, the pulp suspension was collected and washed with hot water at 90°C. The sample was then rinsed with room temperature water, air dried, and weighted to measure the gravimetric yield.

The suitability of the enzyme-CCE/B -treated samples as a raw material for the cellulose acetate process was evaluated by performing acetylation experiments. In acetylation, air dried pulp samples were first disintegrated by stirring in acetic acid, then mixed with activation acid (acetic acid and a small amount of sulphuric acid) and, finally, acetylated in a jacketed beaker with a controlled temperature of 35°C by adding acetic anhydride. The used method is described in detail by Testova et al. [5] After the acetylation, the quality of each acetate dope was determined by measuring their yellowness, transmittance, and backscattering values using a Shimadzu UV-2550 spectrometer and Turbiscan MA 2000 device. In the acetylation experiments, high-quality commercial softwood acetate-grade pulp was used as a reference.

Results and discussion

The highest cellulose contents without an enzymatic treatment, about 97% on pulp, were achieved at a temperature range of 15–40°C with chemical concentrations of 3 or 6 wt-% of borate and 12 wt-% of sodium hydroxide (all the results not shown). Based on these results, the conditions chosen for the CCE/B stage used in the enzyme-CCE/B experiments were 30°C, 3 wt-% of borate and 8, 10, and 12 wt-% of sodium hydroxide. The carbohydrate compositions, yields, and viscosities of selected pulp samples exposed to CCE, CCE/B and enzyme-CCE/B treatments are shown in Table 1.

Table 1. Carbohydrate compositions, total pulp yields, and cellulose yields of the raw material, reference commercial acetate grade pulp, and the pulp samples after CCE, CCE/B, and enzyme-CCE/B treatments.

Treatment	NaOH, wt%	Cellulose, %	Xylan, %	GGM, %	Yield, tot, %	Cellulose yield, %
Raw material	-	81.9	9.4	8.7	-	-
Commercial	-	98.5	0.8	0.7	-	-
CCE	8	91.1	1.8	7.1	88.0	97.9
	10	93.9	1.0	5.1	85.6	98.1
	12	95.1	0.9	4.0	83.8	97.3
CCE/B	8	92.5	2.4	5.0	86.9	98.2
	10	96.0	1.2	2.8	84.1	98.5
	12	96.6	1.0	2.4	82.9	97.8
Enzyme-CCE/B	8	95.7	1.4	2.9	78.8	92.1
	10	98.0	0.6	1.4	78.1	93.4
	12	98.3	0.6	1.1	77.7	93.2

As the results show, after the CCE/B treatments the amount of residual glucomannan was clearly decreased compared to the pure CCE with similar alkali concentrations, while the amount of the xylan was not affected. These results can be explained by the sodium borate’s selectivity towards glucomannan. [3]

The addition of the enzymatic treatment prior to the extraction notably increased the final cellulose purity of the pulp. With a combined enzyme-CCE/B treatment, the highest cellulose content achieved was 98.3% on pulp, which is adequate for an acetate-grade pulp. It can be also seen that the high purity was achieved without major losses in cellulose yield, even though the selectivity of the extraction was decreased from above 97% to 92.1–93.4% when implementing the enzymatic stage, obviously due to non-selective enzymatic side reactions. The final viscosities of the enzyme-CCE/B -treated samples varied between 715 and 830 which is also at adequate level as regards the acetate-grade pulps.

The enzyme-CCE/B -treated samples were used in the acetylation experiments. The measured yellowness, transmittance, and backscattering values of the final triacetate dopes together with the reference sample are shown in Figure 1.

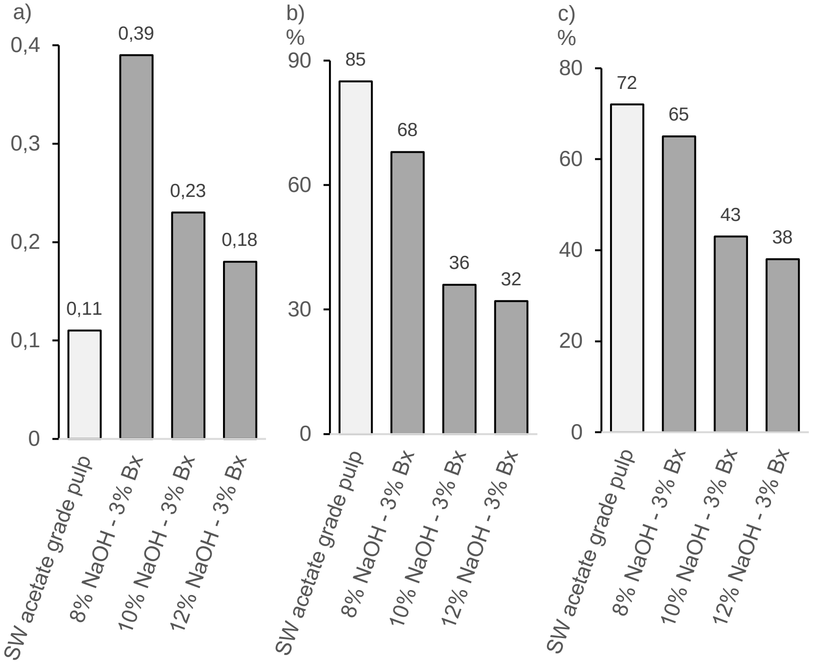

Figure 2. Properties of the cellulose triacetate solutions made of commercial acetate-grade softwood pulp and the enzyme-CCE/B -treated pulp samples. a) Yellowness, b) Transmittance, %, c) Backscattering, %.

Figure 1a shows the dependency of the triacetate solution yellowness on the residual hemicellulose content: as the amount of hemicelluloses decrease, so does the final yellowness. In the case of the pulp sample treated with 12 wt-% of NaOH and having the lowest amount of hemicelluloses, 1.7% on pulp in total, yellowness was as low as 0.18. This is very close to the yellowness of the triacetate made of high-quality commercial pulp, 0.11. However, the transmittance and backscattering results of the dopes, presented in Figures 1b and c, respectively, show an unexpected trend. It is known that the residual hemicelluloses cause yellowness and haze in the cellulose acetate solution [5], but the high-purity samples used in this study resulted in a reverse tendency. As the decreasing transmittance and backscattering values cannot be explained by the amount of residual hemicelluloses, other possible causes have to be considered.

One possible cause inducing the haze is the partial formation of Cellulose II and its enhanced tendency of hornification. As described in the Experimental section, pulp samples were air dried before the acetylation; because of the acetic anhydride used in the final stage of acetylation process, the water have to be completely removed. However, since the pulp samples are exposed to high alkali concentrations, 10 or even 12 wt-%, a notable share of the native Cellulose I is converted to Cellulose II. Further, Cellulose II has a tendency to hornify upon drying, which may reduce its reactivity. [6] Some indication of this was seen during the activation stage, as the samples treated with 10 or 12 wt-% of alkali were not fully disintegrated even after a vigorous stirring. Additionally, the activation acid mixture was not completely absorbed by the pulp sample. This behaviour may have hindered the final acetylation stage. During the next steps of this work, the cause of the increasing haze with increasing removal of hemicellulose will be studied. Parallel acetylation experiments with the enzyme-CCE/B -treated pulps are planned to be implemented by replacing the drying stage by a sequential solvent exchange in order to avoid the hornification. Thus, the effect of the hornification can be evaluated by comparing the final triactetate dope properties.

Conclusions

High-purity cellulosic pulps can be produced by implementing an enzymatic treatment followed by alkali-borate extraction as described in this study. Under optimized conditions, cellulose purity up to 98.3% is obtained without major losses in viscosity or in cellulose yield. The small amount of residual hemicelluloses in pulp results in a very low yellowness of the final cellulose triacetate dope. However, the appeared decrease in transmittances of the cellulose triacetate solutions produced from the high-purity samples is not acceptable as regards the production of commercial acetate-grade pulp. This phenomena, and the possible role of the Cellulose II formation in it, needs to be further investigated.

Acknowledgements

Many thanks to Yawei Wang and Hairong Xiong (Engineering Research Centre of Bioresources in Southern China, South-central University for Nationalities) and Ossi Turunen (Department of Biotechnology and Chemical Technology, Aalto University) for providing the thermomannanase used in the enzymatic stage. Special thanks to Annariikka Roselli for all the help with the practical issues regarding the enzymatic treatments. This study has been funded by WoodWisdom Network, Tekes, Andritz, MetsäFibre, and StoraEnso.

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Lignin Recovery with Acetic Acid

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Abstract

SLRP™ was developed to efficiently extract and purify lignin from pulp and paper black liquor. SLRP has the capability of using acetic acid as the strong acid, eliminating the use of sulfuric acid typically used in lignin recovery systems, and thereby eliminating that additional sulfur load on the host pulp mill. Additionally, this SLRP feature integrates seamlessly with a developmental process which produces an ultra-pure polymer-grade lignin with metal contents less than 100 ppm.

Why is Eliminating Sulfuric Acid Important?

Lignin recovery systems use carbon dioxide to reduce the pH to 9-10, precipitating the lignin from pulp mill black liquor. The carbonated lignin is then reacted with a strong acid to displace sodium and other cations from the carboxylic- and phenoxy-groups of the lignin. Sulfuric acid typically is used as the strong acid, creating a sulfate brine solution that is recycled to the host mill's chemical recovery cycle. This sulfate brine adds about 35 kg of sulfur per tonne of lignin recovered. Some mills can absorb this additional sulfur load, but other mills cannot, especially those located on inland rivers and lakes or those that have very efficient chemical recovery systems. For these mills, a lignin process that uses a strong acid other than sulfuric acid is needed.

SLRP's Acidification Reactor Allows Use of Acetic Acid

"SLRP" is the acronym for "Sequential Liquid-Lignin Recovery and Purification", a process developed using grants from the US Department of Energy. The SLRP process flow diagram is shown in Figure 1. Black liquor is fed into the SLRP process at the top of the Carbonation Column, while CO_2 is bubbled into the bottom. The temperature is kept elevated, >110°C. The temperature rises from the heat of reaction of black liquor and CO_2 so that the carbonated black liquor is returned to the host mill at a higher temperature than the black liquor received. As the black liquor cascades down the column, the pH drops to about 9-10, and lignin precipitates as a true liquid phase at elevated temperature. The liquid-lignin droplets naturally coalesce and separate by gravity in the Carbonation Settler as a dense liquid-lignin phase. This liquid-lignin phase is then pumped to the Acidification Reactor.

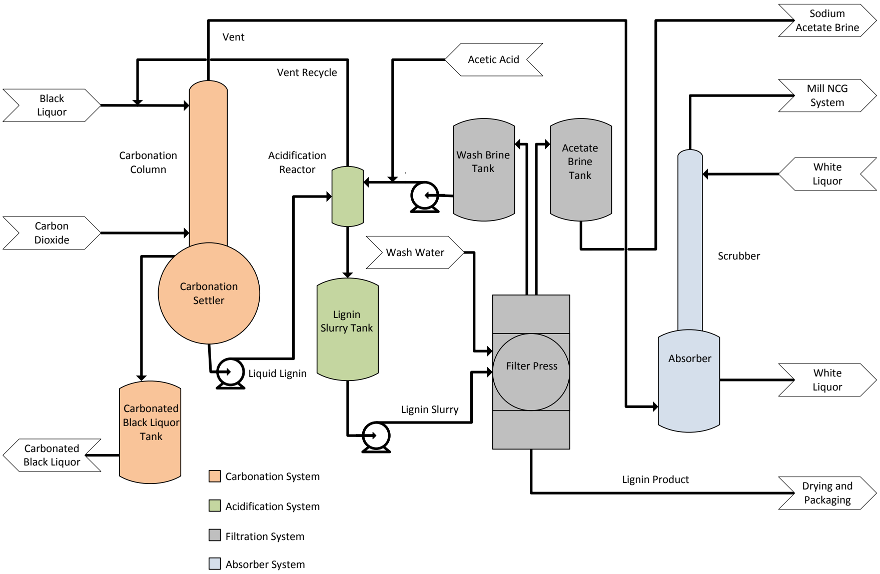

Figure 1. SLRP with Acetic Acid as the Strong Acid.

The reaction of liquid lignin with acetic acid in the Acidification Reactor is rapid. Other lignin recovery methods contact solid particles of carbonated lignin, so the reaction can be slow. In SLRP, liquid-lignin droplets contain dissolved bicarbonate anions which rapidly revert to gas-phase CO_2 as the droplets are contacted with the aqueous matrix of strong acid – in this case acetic acid – within the Acidification Reactor. The reaction is almost instantaneous, forming a solid, granular lignin that is separated easily by filtration.

In the filter operation, the initial filtrate is a solution of acetic acid and sodium acetate which is returned to the host mill recovery operation. The ensuing filtrate from the water wash, a weak solution, is recycled to the Acidification Reactor and used to dilute the glacial acetic acid feed. The strength of the acetic acid entering the Acidification Reactor is typically greater than 1.5N.

Since the Acidification Reactor operates at a higher pressure than the Carbonation Column, the liberated CO_2 exits through a pressure-reducing valve and is reacted with the incoming black liquor so that CO_2 losses from SLRP are minimal. SLRP uses less CO_2 than competitive processes because of this aspect. The exit gas from the top of the Carbonation Column, which is rich in H_2S and CO_2 but devoid of air, is bubbled through an absorber column filled with weak white liquor. Due to the absence of air which limits mass transfer, H_2S and CO_2 are scrubbed virtually quantitatively in the absorption column. In our pilot plant at

Clemson, H_2S concentrations are constantly monitored. The H_2S concentrations rarely reach 1 ppm and typically remain at the background zero level of the instrument. Another key feature of SLRP is the closed nature of the process which efficiently contains noxious gases.

SLRP Interfaces Well with Clemson's ALPHA Process

Working collaboratively with Lignin Enterprises, LLC, researchers within Clemson University's chemical engineering department are developing a process to produce a lignin containing less than 100 ppm ash that can be suitable for polymeric applications.[2] They have discovered that acetic acid-water mixtures can be used to extract the inorganic salts from lignin. They have named their process "ALPHA", the acronym for "Aqueous Lignin Purification with Hot Acids."

The formation of a liquid phase is important. Figure 2 shows the phase transition from a solid slurry to a liquid-lignin system for given composition of lignin, acetic acid, and water as a function of temperature. Each transition temperature was determined visually. The temperature of a given slurry was slowly increased until the lignin melted, a dense liquid-lignin phase formed and sank to the bottom of a stirred vessel. Analyses of the lignin-rich liquid-lignin phase and the supernatant acetic-water phase demonstrated that the inorganic salt preferentially partioned in the acetic-water phase. Molecular weight fractions of lignin also partitioned, with low MW lignin fractions more soluble in the supernatant phase.

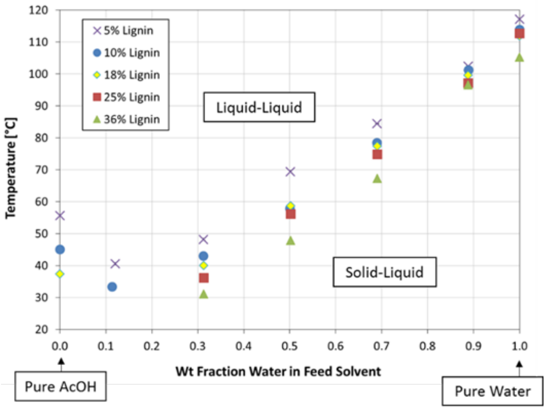

Figure 2. Phase Transitions of Solid Lignin Slurry to Liquid Lignin in Acetic Acid Water Mixtures.

This partitioning of sodium makes a multi-stage process feasible as shown in Figure 3. In Stage 1, lignin containing 1400 ppm sodium was mixed with a 50:50 mixutre of acetic acid:water in a batch reactor operating at 95°C. This elevated temperature was chosen to assure the formation of a dense liquid-lignin phase. A supernatant phase containing most of the sodium was withdrawn, and in Stage 2, the heavy liquid-lignin phase was contacted with a 70:30 ratio of acetic acid:water also at 95°C. The liquid-lignin phase from Stage 2 contained only 25 ppm sodium. This clearly demonstrates a multi-stage system extracting liquid lignin with acetic acid and water mixtures can effectively remove sodium salts and dramatically reduce the inorganic ash content of lignin.

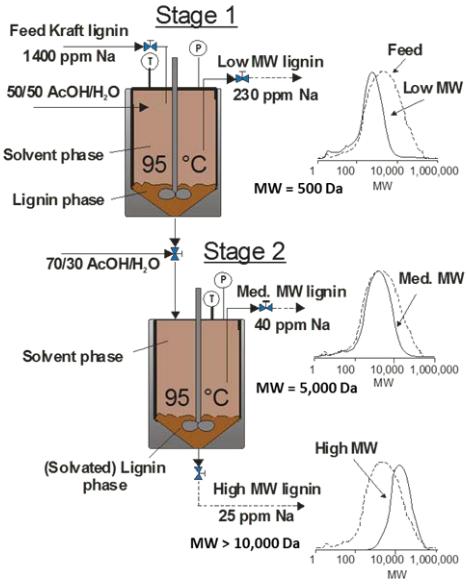

Figure 3. Two-Stage Extraction of Sodium from Liquid Lignin.

A provisional patent application has been filed.

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Lignin – Evaluation of Properties for Applications

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Abstract

Utilization of abundant lignin-rich natural resources will provide new revenue streams for today's kraft pulp mills. Owing to its phenol-rich structure, Lignin is very versatile and has much potential for application in many areas, for example: as a foundation for bulk chemical production, for conversion to fuel products, a binder material, a fertilizer, anti-oxidant, as a precursor for carbon fibres and nanofibres and for activated carbons.

The isolation of lignin - LignoBoost

Innventia, as co-founder of the LignoBoost process, has unique advantages and capabilities for the extraction of well-defined lignin's with high purity from kraft black liquors. In this process, we are afforded the ability to adapt the LignoBoost process and also integrate additional functionality so that we are able to tailor the lignin towards certain applications. The lignin can therefore be chemically or physically modified before, during or after isolation within the LignoBoost concept. Owing to the heterogeneous nature of lignin's macromolecular structure, tailoring the macromolecular and chemical properties towards specific applications – for example in carbon, fuel or chemical use – is a necessity. Innventia has therefore the capability to work at several scales to extract engineering lignins from black liquor; **from grams to tons**. This provides excellent opportunities to work with new lignin-rich streams, and together with our customers, maximise the potential for developing valuable lignin applications.

Lignin value development

One potential and highly valuable area of application for lignin is as a precursor for carbon fibres. Commercial carbon fibres are predominantly made from the petroleum based raw materials polyacrylonitrile (90%) and petroleum pitch (5 %). However, these precursors are too expensive for many potential applications, such as for mass reduction in transportation applications, and therefore there is a need for cost/performance-balanced raw materials for carbon fibre production. In order to provide such benefits, the precursor material should be bio-based, renewable and available in sufficient quantities. Lignin meets these criteria and may in the future be the best raw material for a "green" commodity carbon fibre. It has been calculated that current Swedish pulp mills could deploy the LignoBoost process and provide enough carbon fibre grade lignin to manufacture 1.8 million cars with a 25% weight reduction compared to the average car manufactured in Europe today. This in turn would provide annual savings of about 84 TWh of gasoline equivalent.

Innventia currently has several large projects directed towards producing lignin carbon fibres with tensile properties exceeding previously published data. These projects are all-inclusive so that each part of the supply chain is represented, from black liquor to carbon fibre composite, and all aspects are considered so that techno economic evaluation is performed. Several other carbon material projects using lignin precursors are also underway. Innventia leads globally in several additional lignin-based research areas for example in carbon nanofibres, activated carbons and activated carbon fibres; these are applications that present near-term commercial opportunities, where potential applications can be found in adsorbents, filters, electronics and so on.

Innventia offers our clients fully customized projects for evaluating and developing lignins towards high value products. Specialized equipment, instruments and laboratories are available for lignin separation, engineering property development, characterization and application are available.

Alkaline-catalyzed Modification of Organosolv Lignin: Optimization of Experimental Conditions

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Abstract

The structural changes of organosolv lignin from *E. globulus* processed with alkaline catalysts (NaOH and KOH) have been evaluated. The aim was to study the effect on lignin structure as well as to optimize conditions necessary for an increase in hydroxyl phenolic group content as a main response to base catalyzed depolymerization (BCD). A central composite factorial experimental design was used to optimize conditions, and total hydroxyl phenolic groups (from syringyl and guaiacyl units) were determined by ^{31}P-NMR as a response. The maximal yield of hydroxyl phenolic groups reached values of 5270 and 3970 μmol per gram of lignin^{-1} when NaOH and KOH, were used, respectively, while for the control lignin, the maximal yield of hydroxyl phenolic groups was 2830 μmol per gram of lignin^{-1}. The lignin obtained under these conditions was analyzed via SEC, DSC, and TGA. The results indicated that molecular weight (M_w) and glass transition temperature (T_g) for lignin-NaOH were lower compared to those of lignin-KOH and lignin-control. The weight loss showed that both lignin derivatives have greater thermal stability at high temperatures than does lignin-control after heating at 550 °C. Finally, in conclusion, the results show higher modifications in the structure of lignin as a result of the oxidation of lignin, mainly by cleavage of the β-O-4 ether bond and variations in thermochemical properties when NaOH is used as an alkaline catalyst.

Introduction

The use of renewable lignocellulosic biomass (LCB) has become a growing area of research in recent decades, and today, lignocellulosic materials have gained a special importance in product development because of their renewable nature [1]. From the main components of LCB, lignin has been considered a raw material with high potential because of its abundance of reactive sites, which offer possibilities for chemical and enzymatic modifications. Lignin could play a central role as a new chemical feedstock in a biorefinery concept [2]. Lignin can be used as a green alternative to many petroleum-derived products, such as oil-based resins, rubber additives, thermoplastic blends [3] carbon fibers [4,5] and activated carbon [6], as well as for generation of vanillin, vanillic acid, dispersing agents, polymer filters, DMSO, phenol, and ethylene, etc. [7]. The use of lignin as a wood adhesive has also been evaluated in several studies [8,9]. It has been suggested that the high content of phenolic hydroxyl groups in organosolv lignin from softwoods could be a potential source for the production of phenolic, epoxy, and isocyanate resins [10]. As is known, lignin macromolecules have multiple functional groups influencing the reactivity of lignin, such as methoxyl, phenolic and aliphatic hydroxyl, benzyl alcohol, noncyclic benzyl ether, and carbonyl groups [11]. The use of lignin as a substrate for chemical functionalization demands a precise knowledge of its content in functional groups [12] and could require some form of depolymerization or disintegration in order to generate smaller fragments or compounds more amenable to subsequent processing.

For this purpose, the aim was to study the effect of alkaline catalysts on lignin depolymerization and on the structure of newly generated compounds, with the goal of optimizing conditions to increase hydroxyl phenolic groups in organosolv lignin. Organosolv lignin from *Eucalyptus globulus* was used as a starting raw material because of its low condensation reactions in organic solvents and its structure, which is more similar to native lignin than that produced by other industrial processes. NaOH and KOH were used as alkaline catalysts at different conditions of time, temperature, and concentration. The conditions were optimized using chemometric tools, such as a central composite circumscribed design, and quadratic and cubic models. Finally, the phenolic compounds obtained from the optimal conditions' reaction, defined by the chemometrics model, were characterized, and different analyses, such as size exclusion chromatography (SEC), nuclear magnetic resonance (^{31}P-NMR), differential scanning calorimetry (DSC), and thermal gravimetric analysis (TGA), were performed.

Experimental

The organosolv lignin was recovered by acidic precipitation from ethanolic black liquor derived from organosov pulping of *E. globulus*, which was carried out in a batch reactor (4550 Parr). The study of influence of different variables was realized using a factorial design. The variables and ranges studied in the process were temperature (T: 150–170 ºC), time (t: 40–60 min), and concentration of the alkaline catalyst (C: 5–10% w/w). The model was subscribed to a factorial design central composite with star points. The experimental design was optimized to a response variable, defined as the free hydroxyl phenolic groups determined by phosphorous nuclear magnetic resonance (^{31}P-NMR), and the influence of each variable was determined using response surface methodology (RSM). The Modde software (Umetrics, Sweden) was used for data processing. Free hydroxyl phenolic groups was determined by ^{31}P-NMR [13] the molecular weight distribution of acetylated lignin was performed via SEC (size exclusion chromatography) [14]. Finally the thermal properties were determined by differential scanning calorimetry (DSC) and Thermogravimetric analyses (TGA)

Results

Optimal factorial design

The factorial design applied to optimize the response corresponding OH-Phe in modified lignin determined by ^{31}P-NMR were obtained, and the response polynomials for NaOH and KOH, respectively were obtained using multiple linear regressions, where Y_{pOH} represents the independent variable (response), defined as OH-Phe in the models, and the linear coefficient, quadratic coefficient, and interaction coefficient for dependent variables X_1 (temperature), X_2 (time), and X_3 (concentration of alkaline catalyst) are described in the following equations:

$$Y_{pOH(1)} = 5194.1(\pm 115.9) + 159.5[X_1](\pm 47.1) + 67.6[X_2](\pm 61.5) + 377.6[X_3](\pm 58.0) - 572.1[X_1]^2(\pm 61.5) - 340.0[X_3]^2(\pm 76.4) + 346.6[X_1X_3](\pm 61.5) - 90[X_2X_3](\pm 61.5)$$

$$Y_{pOH(2)} = 3848.0(\pm 88.5) + 94.1[X_1](\pm 36.6) - 1.9[X_2](\pm 36.6) + 88.8[X_3](\pm 36.6) - 126.6[X_1]^2(\pm 41.6) - 151.3[X_2]^2(\pm 41.6) - 200.8[X_3]^2(\pm 41.6) + 151.4[X_1X_2](\pm 50.1) - 211.4[X_1X_3](\pm 50.1)$$

When we evaluate the different coefficients indicated in the equations, all variables influenced the models, and interactions between them were also observed. The influence of temperature, time, and alkali concentration studied by analysis of variance (ANOVA) for a confidence level of 95% showed that both second-order polynomial models presented a high significance. The optimization of free hydroxyl phenolic group generation by alkaline catalysis were obtained and the contour diagrams describing the estimated response surface for free OH-Phe for both models are shown, with the reaction time fixed at 50 min. The results indicated that the maximal region of OH-Phe, found close to 5100 (μmol per gram of lignin), could be obtained using sodium hydroxide (Figure 1a) as an alkaline catalyst, while with potassium hydroxide, the maximal region reached lower values of approximately 3800 μmol per gram of lignin (Figure 1b).

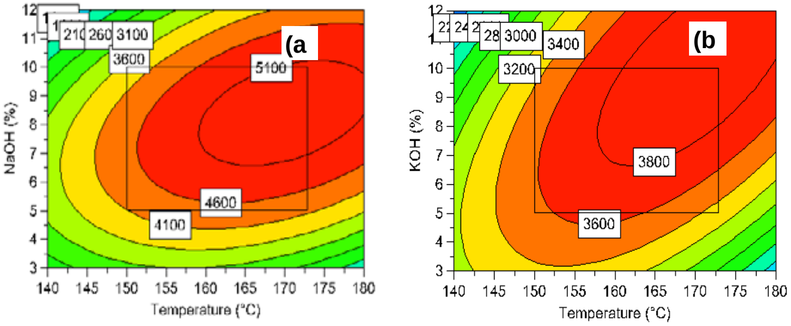


Figure. 1. Estimated response surface for free hydroxyl phenolic groups (*μ*mol/g of lignin) obtained as a result of the optimization of the experimental design using NaOH (a) and KOH (b) as catalysts at a fixed reaction time of 50 min.

The optimal conditions obtained showed that at similar reaction temperatures but different concentrations and reaction times, the maximal free OH-Phe predicted by the models are different, as can be seen in Table 1, where the optimal conditions found for each variable are described. Under these optimal conditions, the maximal free OH-Phe predicted by the models were 5383 and 4000 (*μ*mol per gram of lignin). Experimental values of 5270 and 3970 (*μ*mol per gram of lignin) were obtained when NaOH and KOH were used as catalysts, respectively, as can see in Table 1.

Table 1. Free OH-Phe groups estimated and obtained under optimized reaction conditions.

Variables/sample	Lignin-NaOH	Lignin-KOH
Alkali catalysts (%)	8.6	11.7
Temperature (ºC)	173	174
Time (min)	33	58
Free phenolic groups predicted (*μ*mol/g of lignin)	5383	4000
Free phenolic groups obtained (*μ*mol/g of lignin)	5270	3970

Determination of hydroxyl groups in lignin derivatives

The determination of hydroxyl groups (aliphatic, carboxyl, and phenol) by ^{31}P-NMR shown that an increase in the OH-Phe groups is mainly associated with an increase in OH-syringyl, condensed phenolic OH, and OH-guaiacyl when compared to the amount of hydroxyl groups obtained under alkaline catalyst modifications of organosolv lignin. The lignin-control and lignin-KOH show a total of 2830 and 3970 OH-Phe groups, while the lignin-NaOH presents a much higher value of 5270 *μ*mol per gram of lignin. The higher value obtained when NaOH was used as a catalyst can be explain by the different linkages in each sample of lignin, where the β-O-4 ether bond is the most common linkage in lignin from *E. globulus* and is mainly associated with syringyl units. Also, variations of aliphatic and carboxyl hydroxyl groups were also observed, indicating that different changes in the structure of lignin occur as a result of alkaline

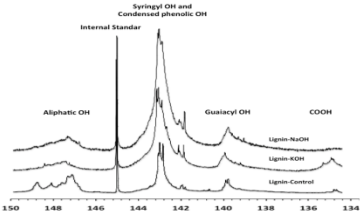
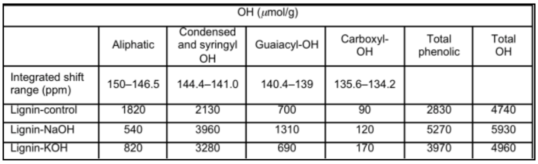


Figure 2. ^{31}P-NMR spectra of control lignin and lignin derivatives

Table 2. Hydroxyl groups in control and modified lignin determined by ^{31}P-NMR



	OH (μmol/g)					
	Aliphatic	Condensed and syringyl OH	Guaiacyl-OH	Carboxyl-OH	Total phenolic	Total OH
Integrated shift range (ppm)	150–146.5	144.4–141.0	140.4–139	135.6–134.2		
Lignin-control	1820	2130	700	90	2830	4740
Lignin-NaOH	540	3960	1310	120	5270	5930
Lignin-KOH	820	3280	690	170	3970	4960

Effect of alkaline depolymerization on the molar mass of organosolv derivative lignin

An important feature for the development of lignin-based products is the molecular weight and polydispersity of lignin derivatives. Thus, the determination of these characteristics in lignin is a useful tool to estimate chain lengths for future applications.

The results of molecular weight distribution obtained by GPC of acetylated lignin control and after modification are shown in Table 3. These results indicate that the M_w and M_n for lignin modified in optimal conditions with NaOH are lower compared to lignin-control and lignin-KOH, and small differences in the polydispersity index were found. Fragmentation under these conditions would be associated with the fact that during the reaction process, the formation of phenolate cation and carbenium ion derivatives generated the fragmentation of lignin in smaller lignin derivative fragments, and despite the fact that both catalysts are considered strong bases, it seems that NaOH could be more effective for the depolymerization of lignin despite small decreases in molecular weight obtained. This confirms the results shown before, that the repolymerization reactions could occur as a mechanism to stabilize the intermediate species formed during BCD or that KOH is less effective than NaOH in modifying lignin.

Table 3. Results of acetylated lignin of weight-average (M_w), number-average (M_n), and polydispersity (M_w/M_n).

Sample	M_w (g/mol)	M_n (g/mol)	M_w/M_n
Lignin-control	1855	815	2.3
Lignin-NaOH	1581	639	2.5
Lignin-KOH	2021	749	2.7

Thermal behavior properties of lignin and lignin-derivatives

Differential scanning calorimetric analysis

Usually, lignin has a very interesting thermal behavior and can act as a thermoplastic as well as a thermoset material. The T_g values of different underivated lignin samples have been reported to be between 90 and 180 ºC. The corresponding glass transition temperatures are presented in Table 4, where the T_g of lignin-KOH is higher in comparison with the control and with lignin-NaOH. This difference in T_g can be explained by the free volume concept as described by Mohamad *et al.* [15]

Table 4. Comparison of glass transition temperature (T_g), maximum of thermal decomposition temperature ($DTGA_{max}$).

Sample	T_g (ºC)	TGA 50% (ºC)	$DTGA_{max}$ (ºC)	Residue (% w/w) (550 ºC)
Lignin-control	135	398	374	35
Lignin-NaOH	131	500	362	46
Lignin-KOH	137	517	343	47

Thermogravimetric analysis

The thermal decomposition of different lignin derivatives (control, NaOH, and KOH) was investigated via thermogravimetric analysis. The results obtained in the experimental data, which includes the degradation temperature at 50% weight loss (TG 50%), the degradation temperature at maximal weight loss ($DTGA_{max}$), and the final residues (% w/w), can be seen in Table 4. The thermal degradation of lignin occurs over a wide temperature range (200–400 ºC) and can be explained by the fact that lignin presents a complex structure made up of phenolic hydroxyl, carbonyl groups, and benzylic hydroxyl, interlinked by various types of chemical linkages, which are connected by straight links. The temperature for 50% mass loss was higher for lignin derivative samples modified with alkaline catalysts, at 500 and 517 ºC for NaOH and KOH, respectively, whereas for the lignin control, the temperature was 398 ºC. The DTG with the maximum rate of weight loss for each lignin sample (control, NaOH, and KOH) appeared at 374.12 ºC, 362 ºC, and 342 ºC, respectively, as shown in Table 4. Finally, after heating at 550 ºC, the lignin NaOH and KOH samples that remained unvolatized were 46% and 47%, respectively, and 35% for the lignin control. These results reveal that both lignin samples modified by an alkaline catalyst have greater thermal stability at high temperatures than lignin that is not modified, which could be associated with a greater number of free hydroxyl phenolic groups for both types of lignin, and that the linkages between monomers are a preferment of C-C type rather than β-O-4 type as a consequence of repolymerization reactions.

Conclusions

The results show that under defined conditions, of base catalyzed depolymerization (BCD) process causes a variation in the content of the various functional groups, such as an increase of free OH-Phe, specifically OH-syringyl and carboxyl-OH groups, and a decrease of aliphatic-OH groups. As a catalyst, NaOH was more effective than KOH in modifying the lignin structure, demonstrated by a change in chemical characteristics. Also, the use of NaOH generated a decrease in the molecular weight distribution compared with unmodified lignin or treatment with KOH, confirming that despite the fact that both are considered strong bases, NaOH would seem more appropriate for BCD. Variations in thermal behavior properties were observed generated by possible structural changes occurring as a product of BCD, principally an increase in free OH-Phe groups for cleavage of the β-O-4 ether bond and repolymerization reactions. Finally, the possibility of defining optimal conditions for the generation of derivatives of lignin with different chemical and thermal properties than original lignin could be an alternative method of valorizing lignin as waste to produce new chemical compounds and materials.

Acknowledgments

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Upgrading Birch Kraft Pulp to Dissolving Pulp and Xylo-oligosaccharides by Water Post-hydrolysis

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Abstract

Water post-hydrolysis of birch Kraft pulps in a flow-through reactor allows their conversion to viscose-grade pulps while recoverying the extracted sugars as xylo-oligosaccharides (XOS). Up to 240 ºC, increasing extraction temperature favors the removal of xylan over the degradation of cellulose. Beyond 240 ºC, increasing temperature has negligible effects on the selectivity of xylan removal. The recovery of XOS from the hydrolysates increases with flow rate due to limited formation of sugar degradation products.

Introduction

In the last decade, the demand for dissolving-grade pulps has more than doubled; the total world consumption has increased from 2.8 million tons in 2004 to 5.7 million tons in 2013 [1,2]. Dissolving pulps, with high cellulose content (>90% wt) and low amounts of impurities, are utilized in the manufacture of cellulose specialty products for textiles, films, lacquers, food, drugs, etc. The high demand for dissolving pulps, mostly for the production of textile fibers (e.g. viscose), is partly related to the growing world population and the increasing purchasing power in developing markets, and thus is expected to continue increasing in the future [3].

Recently, we have suggested that hot water extractions in a flow-through reactor may be applied to paper-grade pulps to convert them into dissolving-grade pulps [4]. At 240 ºC, water extraction (post-hydrolysis) of unbleached birch Kraft pulp lowered the xylan content down to 5-7% without losses in cellulose yield. Moreover, the extracted xylan was recovered almost quantitatively from the hydrolysates as XOS. The recovery of XOS is of interest because of their potential use as prebiotics. Mäkeläinen et al. have shown that, in colon simulation studies, XOS with degree of polymerization (DP) between 2-10 enhance the growth of bifidobacteria [5]. In addition to removing the xylan, water post-hydrolysis of unbleached pulp reduced the lignin content by 50%, which may facilitate the subsequent bleaching of the pulp [4]. Interestingly, increasing temperature from 200 °C to 240 °C lowered the xylan content at which cellulose started to degrade. Here, we have investigated the effect of extraction temperatures higher than

240 °C on the pulp composition. The effect of flow rate under selected post-hydrolysis conditions on the recovery of sugars from the hydrolysates has also been investigated.

Experimental

Pulp material and hot water extractions

Unbleached birch Kraft pulp, taken from the production line before the oxygen delignification stage, was delivered by a pulp mill in Finland. The identified chemical composition of the pulp was 72.3% glucose, 25.7% xylose, 0.1% mannose, 2.1 acid-insoluble (Klason) lignin and 1.3% acid-soluble lignin (ASL).

About 15 g (oven-dry mass) of pulp were placed in a 190 mL flow-through reactor (Unipress Equipment, Poland), equipped with a high-pressure pump, preheater and auxiliary heaters, heat exchanger, and back-pressure regulator. Water at room temperature was initially pumped through the reactor to wet the pulp and to set the back-pressure regulator to the operating pressure. The preheater was then turned on, and once the water reached the desired setup temperature, the hot water was circulated through the reactor for a predetermined amount of time. The extraction temperatures used in this study were 200, 240, 260 and 280 ºC, and the flow rate was 100 mL/min. Under selected conditions of temperature and time, flow rates of 50, 200 and 400 mL/min were also used. Upon exiting the reactor, the hydrolysate was cooled by passing through the heat-exchanger and collected in a sampling container. Once the reaction time was completed, the pulp was cooled by circulating cold tap water and recovered for subsequent analyses.

Analytical determinations

The carbohydrates and lignin composition of the pulp was determined after a two-stage hydrolysis, according to the analytical method NREL/TP-510-42618 issued by the US National Renewable Laboratory (NREL). The amount of Klason lignin was quantified gravimetrically, and the amount of ASL was determined in a Shimadzu UV-2550 spectrophotometer at a wavelength of 205 nm. Monosaccharides were determined by high-performance anion exchange chromatography with pulse amperometric detection (HPAEC-PAD) in a Dionex ICS-3000 (Sunnyvale, CA) system. Based on the amount of neutral monosaccharides, the cellulose and xylan fractions were calculated using the formulas given by Janson [6]. With these formulas, cellulose is defined as the content of anhydroglucose in the sample after subtracting the contribution of glucose to glucomannan, and xylan is defined as the content of anhydroxylose including uronic acid constituents. The kappa number and the intrinsic viscosity of the pulps were determined according to the SCAN-C 1:100 and SCAN-CM 15:99, respectively.

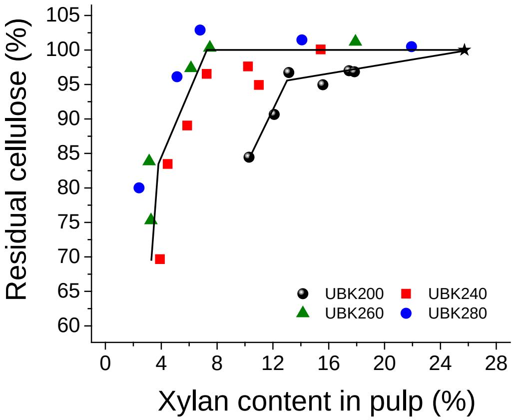

Figure 1. Residual cellulose as a function of xylose content after water post-hydrolysis of unbleached birch Kraft pulp at temperatures between 200-280 ºC and 100 mL/min flow rate.

Results and discussion

The effect of water-posthydrolysis on the removal of carbohydrates (xylan and cellulose) from pulp is shown in Fig. 1. At any extraction temperature, the amount of residual cellulose remained fairly constant until a particular xylan content in pulp was reached, and thereafter a further reduction in xylan content was accompanied by a reduction in cellulose yield. In those extractions at 200 ºC, the cellulose yield decreased abruptly at a xylan content of about 13%, higher than in those extractions at 240-280 ºC, in which xylan contents of 5-7% were reached before cellulose yield started to decrease. Moreover, given a xylan content, the degree of polymerization of the pulp extracted at 200 ºC was notably lower than that of pulps extracted at 240-280 ºC (Fig. 2). These results support our previous observation that increasing extraction temperature from 200 to 240 ºC favored the removal of xylan over the degradation of cellulose [4]. Between 240 and 280 ºC, increasing temperature appeared to result in a somewhat better preservation of cellulose yield (Fig. 1), but no clear differences were observed in terms of degree of polymerization of the pulp (Fig. 2). In addition to the removal of carbohydrates, some of the residual lignin in the pulp was also removed by water post-hydrolysis. The initial lignin content (3.3%) was reduced to about 1.9±0.4 % for all pulps, but a clear trend in decreasing lignin content with increasing extraction temperature and time was not found (results not shown).

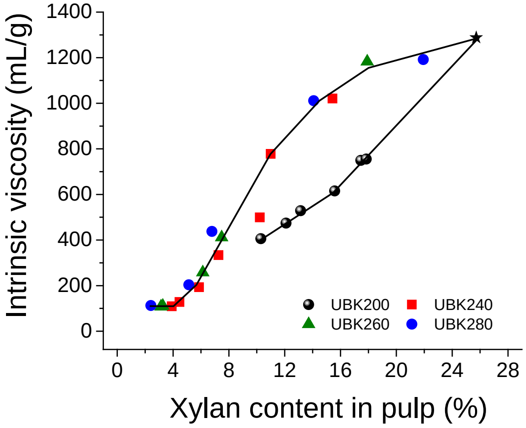

Figure 2. Intrinsic viscosity as a function of xylose content after post-hydrolysis of unbleached birch Kraft pulp at temperatures between 200-280 ºC and 100 mL/min flow rate.

According to Figs. 1 and 2, some of the extracted pulps with xylan contents between 5-7% and intrinsic viscosity around 400 ml/g may be suitable for the manufacture of viscose fibers. These pulps could also be utilized for the production of IONCELL-F textile fibers by means of dry-jet wet spinning [7]. Acetate-grade pulps, with xylan content below 2%, may only be achieved after severe losses in cellulose yield and intrinsic viscosity, which hinders their production at industrial scale. From a practical point of view, the use of extraction temperatures higher than 240 ºC would not be recommended because of the negligible effects on cellulose preservation and the increased costs associated to higher energy requirements.

The effect of flow rate on the pulp and hydrolysate composition was investigated on a selected water post-hydrolysis experiment at 240 ºC and 10 min extraction time. The flow rate had little effect on the pulp composition. However, the composition of the hydrolysate was very much dependent on the flow rate (Table 1). Most of the xylan-based sugars were recovered as XOS, with only small amounts being recovered as xylose monomers. Increasing the flow rate from 50 to 400 mL/min doubled the recovery of XOS, from 10 to 20% of the initial pulp. The mass balances from Table 1 also indicate that formation of sugar-degradation products increased with decreasing flow rate. At 400 mL/min, the extracted xylan was recovered quantitatively, but the concentration of the XOS in the hydrolysates was the lowest. Therefore, the selection of a flow rate for water post-hydrolysis of pulp should take into account not only the potential recovery of sugar-based products, but also their concentration in the hydrolysate.

Table 1. Xylan in pulp and XOS and xylose monomers in the hydrolysate after water post-hydrolysis at 240 ºC for 10 min and various flow rates. All values are based on % on initial pulp. Standard deviation in parentheses.

Flow rate (mL/min)	Xylan (%)	XOS (%)	Xylose (%)	n.d[*] (%)
50	6.2 (2.1)	10.0 (1.7)	0.6 (0.3)	9.1
100	5.0 (0.8)	14.8 (1.6)	0.4 (0.1)	5.7
200	5.9 (0.5)	17.1 (0.5)	0.1 (0.0)	2.9
400	5.4 (0.1)	20.3 (2.6)	0.0 (0.0)	0.2

[*] Not determined. This amount is calculated by subtracting the total recovered xylan-based fractions from the initial amount of xylan (25.7%) in pulp.

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Acid Precipitation Lignin Removal Processes Integrated into a Kraft Mill

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Abstract

The objective for this work is to review and compile the differences and possibilities with the different acid precipitation lignin removal processes LignoBoost, LignoForce and Sequential Liquid-Lignin Recovery and Purification process (SLRP). The three processes are rather similar but they have some certain strengths and weaknesses. However as mill size operating data is still unavailable for the processes, it is still difficult to make a correct comparison

Introduction

During kraft pulping, several lignin reactions occur and the dissolved lignin in the black liquor differs from the native wood lignin. Lignin in black liquor have rather high degree of polydispersity, meaning presence of low molecular mass phenols as well as high molecular mass lignin attached to carbohydrate residue [1]. Lignin in kraft black liquor also contains sulphur and sodium, but these elements are not present in the native lignin [2]. The lignin is normally burnt in the recovery boiler to generate process energy, but the lignin could also be extracted from the black liquor and used as a raw material for production of renewable composites, chemicals and fuels.

Already in the 1940s Tomlinson and Tomlinson applied for a patent regarding lignin removal from black liquor [3]. There are today several techniques for extraction of lignin, e.g. acid precipitation, electrolysis and ultrafiltration, where acid precipitation is the most developed and implemented technique [4]. The study in this paper is focusing on acid precipitation lignin removal integrated in a kraft pulp mill, see schematic process integration in Figure 1.

Lignin removal according to the LignoBoost process is today marketed by Valmet. Domtar pulp mill in Plymouth NC in USA installed a full scale production plant in 2012-2013. A second full scale plant at Stora Enso Sunila in Finland started in early 2015 and is now in operation. In June 2014 an announcement were made regarding a first commercial-scale LignoForce plant, marketed by NORAM, at the West Fraser´s pulp mill in Hinton Alberta in Canada.

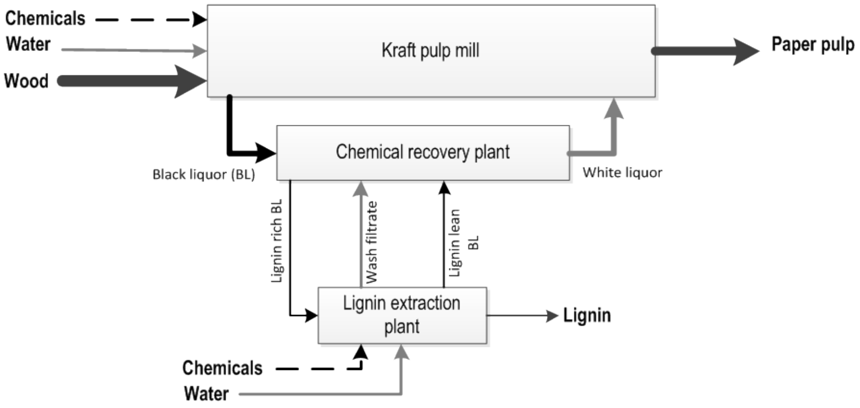

Figure 1. Acid precipitation lignin removal process integrated with a kraft pulp mill.

Method

This literature review of acid precipitation lignin removal processes in pulp mills is focusing on LignoBoost, LignoForce and SLRP. Available data from the literature were used for a comparison of the three processes. Data on the LignoBoost and LignoForce processes are readily described in available literature, but the published research and data regarding the SLRP-processes is yet limited. Although there are no data from real operating lines available, some key performance indicators, based on pilot plant trials, can be found in the literature.

Short summary of acid precipitation lignin removal processes

LignoBoost

Innventia in Sweden has together with Chalmers University of Technology, Sweden, developed a method for lignin extraction under the trade name LignoBoost. The LignoBoost process is a result of R&D carried out within the framework of the KAM- (the Ecocyclic Pulp Mill), FRAM- (the Future Resource-adapted Pulp Mill) and FRAM 2- (the Future Resource-adapted Pulp Mill, part 2) programs. In 2008 Valmet acquired the IPR rights and started to commercialize the LignoBoost process. [5]

In the LignoBoost-process black liquor of approximately 40% dry solids (ds) concentration is withdrawn from the evaporator train and acidified with CO_2 to pH 10 thereby precipitating approximately 70% of the lignin. The precipitation temperature is normally 55-70°C, depending on type of black liquor [6]. In the filtration and dewatering step the lignin-lean black liquor is separated from the lignin phase and sent back to the evaporation plant. The precipitated lignin is re-dispersed in sulphuric acid at pH 2-3. Residual sodium carbonate and sodium hydrosulfide are converted to gaseous CO_2 and H_2S. These gases could be recycled and mixed with the original black liquor. By recycling the gases, the consumption of fresh CO_2 could be reduced [7]. After a short residence time, the lignin is separated, washed with sulphuric acid and water at a pH of 2-3 and dewatered in the second filter press. The wash filtrate could be sent back to the evaporation [1]. In Figure 2 is a schematic view of the LignoBoost process.

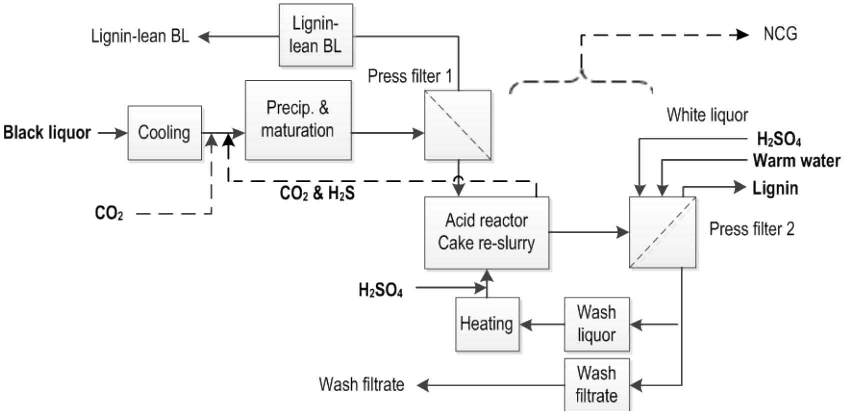

Figure 2. Schematic view of the LignoBoost process.

LignoForce

FPInnovations in Canada has developed a process for lignin extraction under the trade name LignoForce. The process has been demonstrated in a pilot plant built at a kraft pulp mill in Thunder Bay Ontario, Canada. The technology is marketed by NORAM and the first commercial full-scale plant was announced in June 2014. The plant has a capacity of 30 ton lignin/d and is located at West Fraser's plant in Hinton Alberta Canada.

The LignoForce process is a three-stage operation. In the first oxidation step, the black liquor is oxidized by adding O_2. Oxidation of the black liquor improves the filterability of the acid-precipitated lignin by providing suitable conditions (e.g. lower pH and higher temperature) for lignin colloid agglomeration [8]. The oxidation step (exothermic reactions) also involves oxidizing the TRS compounds to non-volatile compounds such as sulphuric acid, methane sulphonic acid and dimethyl sulphone. This will lead to reduction in the emissions of volatile TRS compounds and odour. Also carbohydrates will be transformed to saccharinic acid and/or simpler organic acids. These compounds together with the oxidized compounds will consume some of the residual effective alkali (sodium hydroxide) in the black liquor, which will reduce the amount of needed CO_2 in the acidification step [9] [8]. According to [8] the oxidation of the black liquor has no major impact on the lignin molecular weight and no major differences could be seen regarding main functional groups of the produced lignin.

In the next step, the oxidized black liquor is acidified with CO_2 to pH 9,5-10, at a temperature between 70-75°C. After precipitation, in the third step, the lignin slurry is filtered using a filter press. During the filtration step, the lignin filter cake is washed with sulphuric acid [8] and water, and then pressed for removal of the acid wash liquor. The wash filtrate and the lignin-lean black liquor can be sent back to the pulp mill and the evaporation plant, Figure 3.

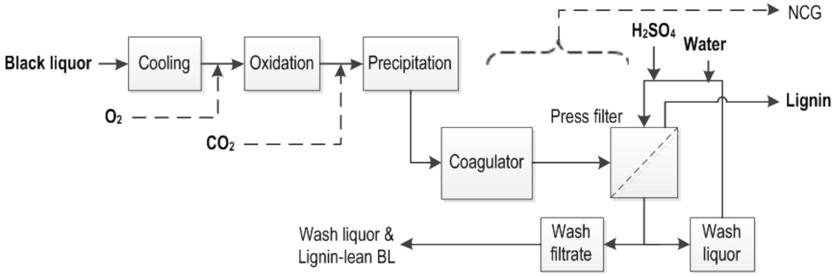

Figure 3. Schematic view of the LignoForce System process.

SLRP

The Liquid Lignin Company in South Carolina USA has developed a process for lignin extraction under the trade name Sequential Liquid-Lignin Recovery and Purification (SLRP). The process has been demonstrated in a continuous pilot plant at Clemson University, SC USA, but the process is not yet industrially implemented. The SLRP-process is based on technology developed by Tomlinson and Tomlinson [3]. They introduced a lignin removal process where the first precipitation step was done under high temperature and pressure. A dense liquid-lignin phase was formed and separated by decantation [10].

The SLRP-process is a continuously four-stage operation, Figure 4. The black liquor at approximately 40% ds concentration is withdrawn from the evaporator train and pumped to the carbonation column. The black liquor temperature could, depending on the actual mill conditions, be increased before the carbonation column. The black liquor is injected at the top of a carbonation column and CO_2 is injected in the bottom part of the column. The pressure in the carbonation column should be sufficient to prevent boiling (less than 4 bar(g)). The pH is reduced to 9-10 and the lignin precipitates as small molten liquid droplets. According to [10] the countercurrent gas-liquid reaction between the CO_2 and lignin is very efficient, resulting in a low CO_2 loss into the vent (less than 5% of the total CO_2 feed). The liquid lignin droplets coalescence to form a dense liquid lignin phase at the bottom of the carbonation settler. The dense liquid lignin phase is separated from the lignin lean black liquor by gravity in the carbonation settler. The interface between the two liquid phases is distinct which enables a rather easy separation [10]. The lignin-lean black liquor is returned to the evaporation plant. Due to heating before the carbonation column and the exothermic reactions in the carbonation column, lignin lean black liquor is returned at a higher temperature compared to the withdrawn black liquor (minimum 5-10°C higher). The liquid lignin phase is pumped to the acidification reactor, operating under higher pressure (less than 6 bar(g)) compared to the carbonation column. In the acidification reactor the pH is lowered to 2-3 by adding sulphuric acid. By lowering the pH the lignin is converted to a solid state. Residual sodium carbonate and sodium hydrosulfide are also converted to gaseous CO_2 and H_2S. These gases, devoid of air, are recycled to the carbonation column. By recycling the gases, the consumption of fresh CO_2 could be reduced by approx. 30% [10].

The temperature of the lignin slurry is reduced to approx. 70°C, to achieve good filtration conditions and high lignin yield [11]. In the filtration step the lignin is separated, washed and dewatered in a filter press. The wash filtrate could be sent back to the evaporation.

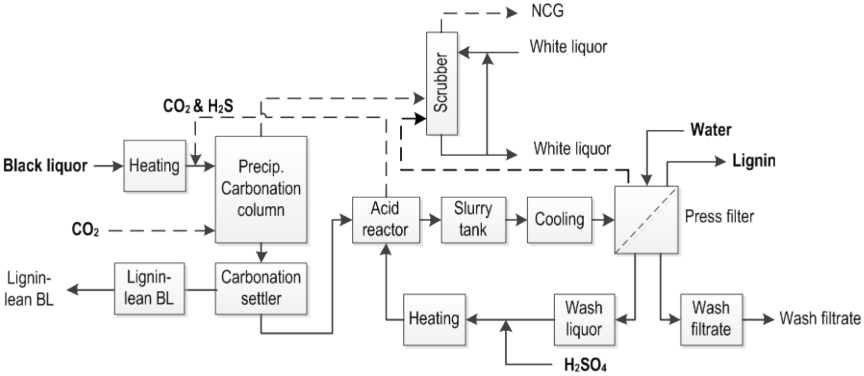

Figure 4. Schematic view of the SLRP-process.

Results and discussion

The three reviewed acid precipitation processes are rather similar. However there are some differences that distinguish the processes. In the LignoBoost process two filter presses are used, but the LignoForce and the SLRP processes are designed with only one filter press. The filter press is often mentioned as the equipment with the biggest impact on the investment cost. In the early acid precipitation processes only one filter press was used and severe problems were obtained related to plugging of the filter cake. The plugging resulted in low flow of wash liquor through the filter cake, leading to high levels of impurities in the solid lignin phase [12]. These effects have been shown to be caused by changes in the surroundings of the lignin, caused by the pH and ionic gradient. This gradient will affect the lignin solubility during the washing process and can result in restructuring the lignin particles, e.g. returning to a colloidal state or re-precipitation of the dissolved lignin [13]. To solve these plugging problems the LignoBoost process is designed with two filter presses, where washing occurs in the second filter press. Before the second filter press, the lignin filter cake is re-dispersed and acidified. The conditions in the cake re-slurry step are similar to those of the final washing step, meaning that the concentration gradients during the washing step will be low. Therefore any changes in lignin solubility will take place during the cake re-slurry step and not during the final washing step [5].

Compared to the LignoBoost process, the LignoForce process doesn´t include the first filter press and the acidifying step prior to the final washing step. In the LignoForce process the incoming black liquor is oxidized to improve the lignin filtration properties. Experiments made by Kouisni [8] showed a significant increase in filtration rate when the black liquor was oxidized. Compared to un-oxidized black liquor the filtration rate could be up to 2 times higher [8]. Using a scanning electron microscopy it was also seen that the oxidized black liquor slurry, after acidification, composed of larger lignin particles, which could generate a higher filtration rate [8]. In the SLRP process the precipitated lignin phase is separated from the lignin-lean black liquor by gravity. This separation step is comparable to the first filter press in the LignoBoost process.

CO_2 consumption is the main operating cost for acid precipitation of kraft lignin [9] and it is of importance to reduce the amount of fresh CO_2 added. According to experiments made by Kouisni [8] the CO_2 consumption could be reduced by approximately 50%, compared to the conventional process, if the black liquor is oxidized prior the acidification step. Available CO_2 consumption figures for the LignoForce process is however in the same range as the LignoBoost and SLRP-process, Table 1. The LignoBoost and SLRP-process are designed with system for re-circulation of generated gases, reducing the amount of fresh CO_2 needed.

The wash filtrate from the washing step is normally sent to the evaporation plant, resulting in an increased evaporation load. The evaporator load is also affected by the temperature of the returned lignin-lean black liquor and the recirculation points of the filtrates. Based on available data in the literature, the wash water amount needed differs between the different acid precipitation processes. The wash water consumption for the LignoForce-process, Table 1, is rather high compared to the other processes. This could perhaps be explained due to that the entire black liquor flow is fed to the washing step. In the LignoBoost and SLRP-process the lignin-lean black liquor has already been separated before the washing step.

In the SLRP-process the pressurized system keeps the precipitated lignin as a liquid and this has according to the Liquid Lignin Company a positive impact on the chemical consumptions. As the precipitated lignin is kept as a liquid, it is possible to keep the ds content in the acidification reactor at a relatively high level. By keeping a high ds the wash water demand will be reduced compared to the other processes. The higher ds is also expected to have a positive impact on the required amount of sulphuric acid (lower amount of carry over which needs to be neutralized).

It is still difficult to find exact consumption figures for the different lignin removal processes before data from real operating lines are available. Influence of process parameters, e.g. wood raw material, residual alkali in the black liquor etc, also affects the consumptions figures. This should be kept in mind when comparing the figures. In Table 1 comparative data from the literature are compiled for the different processes.

Table 1. Comparative consumption figures from literature.

Comparative data	LignoBoost	LignoForce	SLRP
CO_2 consumption	0,20-0,25 t/t lignin [6] 0,15-0,25 t/t lignin [1]	0,25 t/t lignin [14] 0,20-0,40 t/t lignin [15]	0,14-0,18 t/t lignin [16][10]
H_2SO_4 consumption	0,15-0,25 t/t lignin [6] 0,15-0,25 t/t lignin [1]	0,35 t/t lignin [14] 0,10-0,20 t/t lignin [15]	0,09 t/t lignin [16]
O_2 consumption	-	Not published.	-
Water requirements	2,2-2,5 m^3/t lignin [5]	12,5 t/t lignin [14] 4-5 m^3/t lignin [15]	1,2 t/t lignin [16]
Temperature 1st precip. step	65-70°C (SW) 55-60°C (HW) [6]	70-75°C [8]	105-125°C [16]
Pressure 1st precip. step	Atmospheric	Atmospheric	< 4 atm [10]
Pressure 2nd precip. step	Atmospheric	Atmospheric	< 6 atm [10]
pH 1st precip.step	10 [1]	9-10[9]	9-10 [10]
pH wash step	~2,5 [1]		2-3 [10]
Ash content	Median value 1%[5] 0,02-1% [1]	0,2% [9] 0,1-0,7% [15]	1% [10] 1-2% [17]
Sulphur content	1,3-3,4% [6] 2-3% [1]	1,63% [9]	2-3% [17]

Conclusions

All three reviewed processes have strengths and weaknesses but as mill size operating data is still unavailable for the processes, it is difficult to make a correct comparison. However, it can be expected that there are some differences regarding investment cost and operating cost between the processes.

Published consumption figures for the SLRP-process are limited and no deeper analysis has been made for the SLRP-process integration with a pulp mill. Based on the available published information, the SLRP-process seems to have some energy and chemical consumption benefits compared to the other two processes. It should therefore be of interest to investigate the SLRP-process and evaluate the process in a mill wide perspective.

Acknowledgements

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Deep Eutectic Solvents for Biomass Fractionation

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Abstract

Deep eutectic solvents (DES) have emerged as new promising tools for conversion and separation of biomass. In this study we have developed a new, economically and industrially feasible DES-composition for the separation of lignin in high quantity and purity directly from wood-based biomass without any chemical pre-treatment. By changing the parameters, it is also possible to convert hemicellulose into useful platform chemicals such as 5-hydroxymethylfurfural and furfural.

Introduction

Deep eutectic solvents (DESs) are generally regarded as a sub-class of ionic liquids prepared from low-cost, biodegradable and non-toxic substances by mixing of them at room or lightly elevated temperatures. From a physicochemical point of view DESs are low-volatile eutectic mixtures of two or more components with significantly decreased freezing points than that of each individual component (Figure 1). The large decline in freezing point is usually explained through non-symmetric complexation of substances via hydrogen bond interactions. Recently DESs have emerged as a new potential breakthrough technology for the conversion of biomass into valuable platform chemicals and polysaccharide components. Here we present a new DES composition based on a specific hydrogen bond donating species and choline chloride and demonstrate its efficiency in the fractionation and chemical conversion of softwood materials.

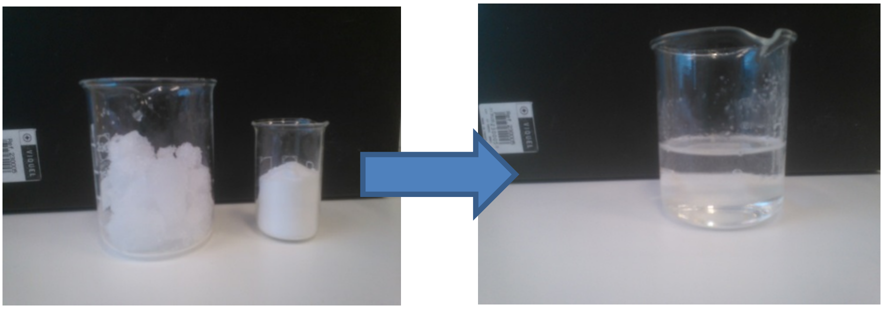

Figure 1. DES can be formed by mixing two appropriate solid substances.

Experimental

Raw materials

Softwood saw dust and thermo mechanical pulp (TMP) were used in fractionation experiments. Softwood saw dust ("SW coarse") was collected from a Finnish saw mill and had an average particle size of 1–2 mm. A portion of the coarse material was ground using Wiley-mill equipped with a 1.0 mm sieve ("SW fine"). TMP was also ground with Wiley-mill using 0.25 mm sieve. A portion of the SW fine was also dried at the oven at 140 °C for 4 hours prior to fractionation experiments.

All the used chemicals to form deep eutectic solvents were purchased from Sigma (St. Louis, MO, USA). Sodium hydroxide and hydrochloric acid were purchased from Merck.

DES preparation and fractionation

The experiments were carried out using Tornado Plus Overhead Stirring System with six seat reactor carousel made by Radleys (Radleys Discovery Technologies, UK). DESs consisting of choline chloride and hydrogen bond donor (HBD) in molar ratio of 5:3 were first prepared by mixing components at 60 °C. The water content was subsequently fixed with distilled water (0, 5 and 10 wt% of total weight).

DES extractions for lignicellulosic materials were carried out for 16 hours at different temperatures (75 °C, 95 °C and 110 °C). The amount of lignocellulosic material was 5 wt% of the total DES weight. Dry wood material was added slowly under mechanical stirring to ensure good mixing of solution and wood.

After extractions the mixtures were diluted with excess of boiling water and immediately conducted through metallic sieves (1 mm, 0.3 mm and 0.15 mm) under vacuum suction. The obtained fractions were carefully washed with water and oven-dried (60 °C, 24 hours).

Analyses

Lignin and saccharide compositions of fractions: samples were hydrolyzed with sulphuric acid and monosaccharides were analysed with HPAEC/PAD with pulse amperometric detection (Dionex ICS 3000LC) equipped with CarboPac PA1 column. Unsolubilized lignin concentration was determined gravimetrically and solubilized lignin was quantized by UV-visible spectrophotometry.

The 5-hydroxymethyl furfural (5-HMF) and furfural as well as formic acid, acetic acid and levulinic acid contents in DES solutions were analyzed with a P/ACE MDQ capillary electrophoresis instrument equipped with a photodiode array UV/Vis detector (PDA) (Beckman-Coulter, Inc., Fullerton, CA, USA). Prior to the acid analyses, chloride was removed with OnGuard II Ba/Ag/H cartridges (Dionex Ltd.).

^{31}P NMR was used to determine the functional groups of lignin in “lignin fraction”. ^{31}P NMR measurement is based on the method developed by Granata et al.

Results

Fractionation of softwood with eutectic solvent

Gravimetric fraction distribution in percentage of the fractionated wood samples at 95 °C is presented in Figure 1. The better the fractionation ability, the better the wood meal settle to smaller fractions. The influence of refining the samples can be seen in case of TMP at 95 °C. Comparison of the samples SW coarse and SW fine shows clearly the effect of the particle size, while finer particle size fractionate more easily to smaller cuts. Addition of water in DES increases agglomeration of saw dust which can be seen in the increase of >1 mm and 300 µm fractions when compared to the SW fine sample.

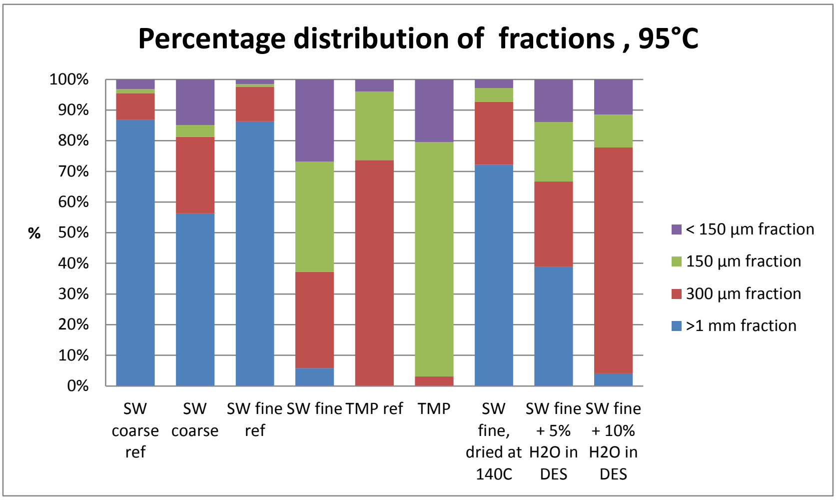

Figure 1. Fraction distribution in percentage of the whole mass in DES screening tests at 95 °C.

According to the fractionation tests, the highest reaction temperature of 110 °C was more effective than 95 °C in general, although in some experiments showed nearly similar yields (Table 1). In addition, particle size has clear effect on fractionation. Smaller particles are more susceptible due to the bigger surface area. The fractionation of SW coarse at 110 °C was most efficient resulting 28.5 wt% yield of finest solid fraction. Also the fine saw dust and especially TMP were good substrates accordingly to the fractionation test. The behaviour of TMP regarding temperature is totally different compared to the others. The precipitates become smaller when the temperature increased. The dried fine softwood was the worst substrate accordingly to the results. The reason for this is probably the detrimental effect of heating on wood meal, since wood's macrostructure close due the elevated temperature like in the thermo-treated wood and thus penetration of DES solvent to wood structure become more difficult.

Table 1. The fractionation yields of smallest fraction (particle size < 150µm) in the experiments of softwood using DES solution. As a reference, the fractionation tests of saw dusts were done only in water, gave for coarse 3.4%, fine 2.0% and TMP 4.1% as finest precipitates.

Substrate	75 °C	95 °C	110 °C
	Precipitate (particle size < 150µm) relative amount (%)		
SW coarse	12.3	13.9	28.5
SW fine	10.2	25.0	26.2
TMP	19.9	18.5	8.6
SW fine, dried at 140 °C	2.6	2.6	1.9
SW fine + 5% H_2O in DES	5.0	12.5	15.0
SW fine + 10% H_2O in DES	8.8	12.5	14.8

Changes in hemicellulose contents

Used fractionation procedure decreased hemicellulose content in all fractions. UV-VIS measurements of the DES liquors revealed the presence of the 5-hydroxymethylfurfural (5-HMF) and furfural in liquids (Figure 2). The UV/Vis spectroscopy is good tool to estimate 5-HMF and furfural concentrations in different DES experiments, but it does not separate compounds from each other due to the overlapping absorption maxima. It is obvious that high acidity of DESs promotes the formation of 5-HMF from hexoses and in smaller extent the formation of furfural from pentoses of hemicelluloses. The yield of 5-HMF was highest 29.1 mg/g of dry wood with 10% water content and 5% water content gave almost equal 5-HMF conversion. This is not yet economically reasonable amount to collect, but by optimizing fractionation conditions and by applying biphase collection system there, the extraction of furans can be improved. Most probably, water enhances solubility of furans and on the other hand simultaneous affect slightly on pH of DES liquor. If more than 10% water was added, the furan formation diminishes due to the increased pH. The degradation reactions of both 5-HMF and furfural produce formic, acetic and levulinic acids. The concentration of levulinic acid at 95 °C experiments is rather low, but as excepted, increased temperature, 110 °C, accelerates degradation of furans and increases the amount on levulinic acid. The oven drying pretreatment gave lowest furan and degradation product yields indicating that this pretreatment cause wood meal which is resistant to DES treatment at any temperature tested.

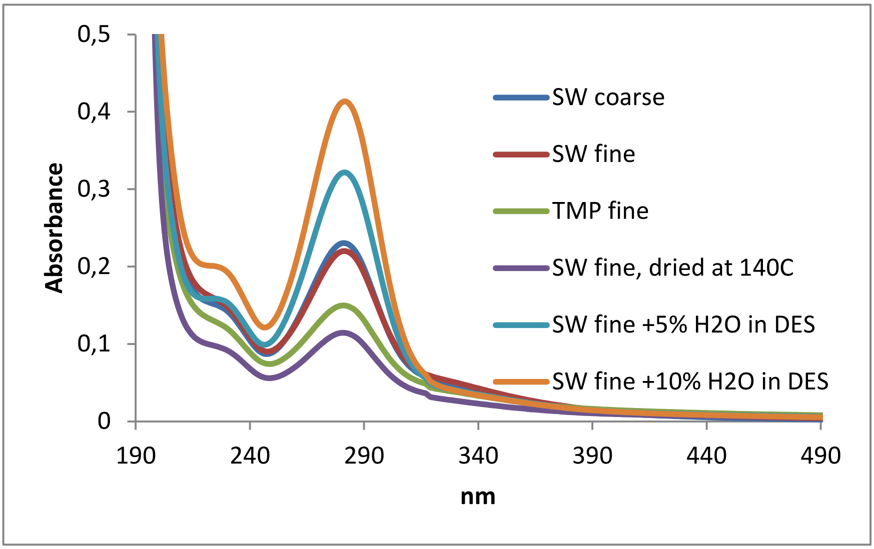

Figure 2. UV-VIS spectra of six different sample solutions obtained in the treatment at 95 °C. The signal at 283 nm indicates the presence of furans (5-HMF, furfural).

Lignin analysis and properties of precipitated lignin

Significant lignin enrichment was found in smallest fraction. Lignin analysis of lignin rich portion of <150 µm fraction was performed to study the nature of lignin obtained with DES. Two samples form 95 °C experiments were studied using quantitative ^{31}P NMR analysis to determine the content of aliphatic, phenolic and carboxylic acid based OH groups. The results shows that in both samples condensed OH units are missing which are typical for kraft lignin. In addition, amount of guaiacyl related OH units are relative low indicating some reactivity of lignin in DES treatment. Mw of the samples were between 2500–3500 (GPC).

Conclusions

This DES mixture was able to fractionate lignin directly from wood in high purities while simultaneously preventing degradation and condensation reactions. Futhermore, dissolved hemicelluloses were efficiently converted to valuable biochemical such a 5-hydroxymethyl furfural (5-HMF), furfural and levulinic acid.

Conventional methods for biomass deconstruction into cellulose, hemicellulose and lignin often require high temperatures and pressures and cause chemically undesired side reactions. DESs in general may be promising future alternatives foor selective wood fractionations. We anticipate that the development of new DES compositions will continue to bring new alternatives and enchance the use for such wood components that have previously been used only for production of energy.

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Biorefinery Concepts Integrated to Alkaline Pulping

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Introduction

Recently, there has been renewed interest in the conversion of biomass into green chemicals [1]. One of the most attractive possibilities is more effective and versatile utilization of existing and novel by-products of chemical pulping. The most common and effective approach is to introduce an acidic or alkaline pretreatment stage of chips into the alkaline pulping process [2]. The main by-products formed under acidic conditions are carbohydrates and volatile acids, whereas under alkaline conditions lignin, extractives and carbohydrates-derived aliphatic acids are obtained (Fig. 1). In addition, the partial recovery of these fragments is possible from the cooking liquor ("black liquor", BL) after delignification. Recovery of the feedstock degradation products is an attractive alternative to using them as fuel and this strategy improves directly the profitability of producing cellulosic fibre from wood by traditional pulping. In this paper, the delignification of hardwood and softwood feedstock chips was studied by the sulphur-free process including the acidic or alkaline pretreatment stage followed by soda-AQ pulping.

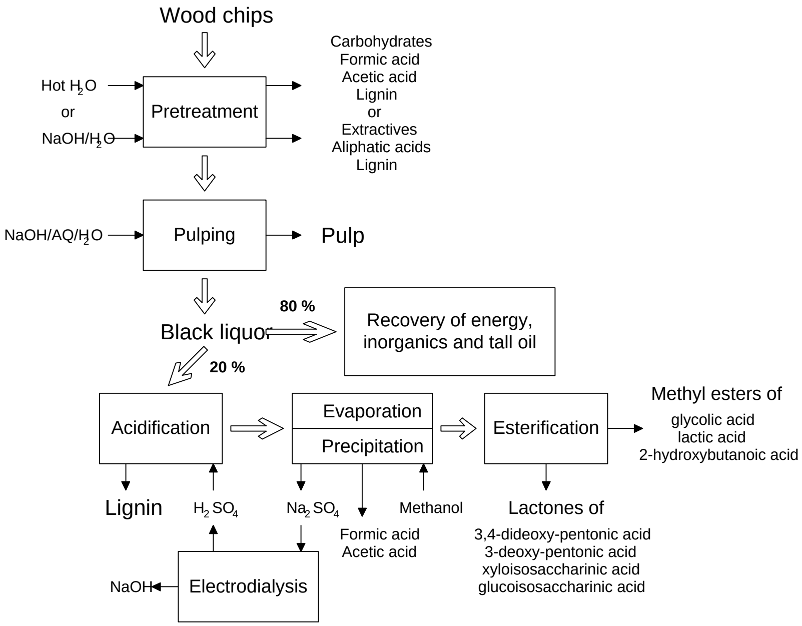

Figure 1. Schematic presentation of an integrated biorefinery process of alkaline pulping.

Experimental

Pretreatment stages

Acidic: 150 °C, 90 min and liquor-to-wood ratio 5 L/kg.

Alkaline: 150 °C, 90 min, NaOH charge 8 % on o.d. wood and liquor-to-wood ratio 5 L/kg.

Soda-AQ cooking

Hardwood: 170 °C, 120 min, NaOH charge 18 % on o.d. wood, AQ charge 0.1 % on o.d. wood, liquor-to-wood ratio 5 L/kg and cooking yield 53.5 %.

Softwood: 170 °C, 120 min, NaOH charge 22 % on o.d. wood, AQ charge 0.1 % on o.d. wood, liquor-to-wood ratio 5 L/kg and cooking yield 54.7 %.

Lignin separation from BL and liberation of acids: pH to ~2 with 2M H_2SO_4.

Separation of volatile acids (formic and acetic acids) by evaporation.

Precipitation of Na_2SO_4 from the acidified BL with methanol (1:1 v/v) followed by esterification of the LMM hydroxy acids [3]: 70 °C, 4, 8, 12 and 16 h with an acid catalyst Amberlite 15 (0.2 wt%).

Electrodialysis (ED) experiments [4]: flow rate of 10 L/h for 5 h at a constant rate of 20 V.

Analytical determinations

Volatile acids by GC/FID [5], hydroxy carboxylic acids by GC/FID [6] and sodium by ICP/OES.

Main findings

- The material removed in the acidic pretreatments: 16.1 (hardwood) and 9.1 (softwood) % of the initial wood d.s.
- The material removed in the alkaline pretreatments: 16.1 (hardwood) and 12.5 (softwood) % of the initial wood d.s.
- Pulp yields in the soda-AQ pulping of the pretreated (acidic) chips: 44.9 (hardwood) and 49.7 (softwood) % of the initial wood d.s.
- Lignin yield in the acidification of BL: ~75 % of the initial.
- Sodium recovery in the precipitated Na_2SO_4: ~90 % of the initial.
- Hardwood BL: Volatile 41, LMM (glycolic, lactic and 2-hydroxybutanoic acids) 24, HMM (mainly 3,4-dideoxy and 3-deoxy-pentonic and xylo- and glucoisosaccharinic acids) 30 and other acids 5 % of the total acids.
- Softwood BL: Volatile 17, LMM 24, HMM 35 and other acids 24 % of the total acids.
- In a mill with an acidic pretreatment (1,000,000 ton hardwood feedstock, a BL withdrawal of 20 % for the separation process): pulp 450,000, carbohydrates 120,000, volatile acids 30,000, LMM hydroxy acids 9,000, HMM hydroxy acids 11,000, alkaline lignin 31,000, extractives 35,000 and other material 38,000 ton.
- In a mill with an acidic pretreatment (1,000,000 ton softwood feedstock, a BL withdrawal of 20 % for the separation process): pulp 500,000, carbohydrates 74,000, volatile acids 9,000, LMM hydroxy acids 7,000, HMM hydroxy acids 10,000, alkaline lignin 40,000, extractives 45,000 and other material 33,000 ton.
- ED overall average energy consumption ~0.40 kWh/mol Na.

Acknowledgements

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Supercritical Fluid Chromatography of Lignin-Derived Phenols from Alkaline CuO Oxidation

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Abstract

A supercritical fluid chromatography method for analysis of 11 major lignin-derived phenols produced by alkaline cupric oxide (CuO) oxidation was developed. The monomeric lignin phenols released were clearly separated within 6 minutes with excellent peak shape. The optimized and validated method was applied to qualitative and quantitative study of lignin-derived phenols obtained upon alkaline CuO oxidation of a commercial humic acid. The result showed for the first time that supercritical fluid chromatography is a fast, sensitive and reliable method for analysis of lignin-derived phenols in complex environmental samples.

Introduction

Catalytic alkaline oxidation is an important method for both lignin biorefinery and characterization.[1-3] Application of copper in catalytic oxidation of lignin to release small molecules is well known.[4] Alkaline CuO oxidation is one of the mostly adopted methods for characterization of lignin.[5] Methods reported for analysis of the 11 major phenols (Figure 1) generated by CuO oxidation are gas chromatography (GC), high-performance liquid chromatography (HPLC) and capillary electrophoresis (CE).[6-8] These methods suffer either from a need for derivatization, long analysis time or poor precision of identification. The present work reports a simple, reliable and fast supercritical fluid chromatography (SFC) method for separation and quantification of lignin-derived phenols.

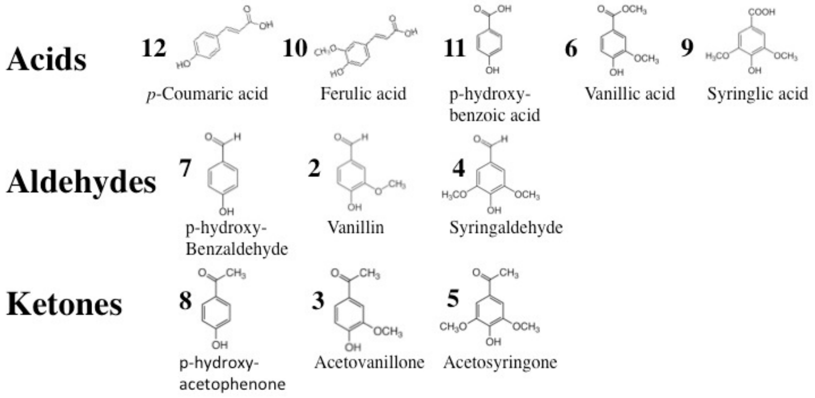

Figure 1. Structures of major CuO-reaction products of lignin.

Experimental

The analysis was performed on a Waters UltraPerformance Convergence Chromatography System with a Diode Array Detector. Optimization of the method was done with a standard mixture of the 11 phenols. The CuO oxidation of a commercial humic acid was carried out in a Biotage Initiator Microwave Reactor. After acidification, extraction, solvent evaporation and re-dissolution, the samples were analyzed with the method developed.

Results and discussion

It can be clearly observed in Figure 1 that the 12 phenolic compounds (11 lignin phenols and ethyl vanillin as internal standard) were well separated in 6 min with all peaks being highly symmetrical. The resolution factors of each pair of adjacent two peaks varied between 1.38 and 10.93. The limit of detection (LOD) for each phenol ranges from 0.5 to 2.5 μM and limit of quantification (LOQ) 2.0 to 5 μM. The applicability of the method developed was tested by analysis of phenol content in a humic acid sample. The lignin-derived phenols were identified with both elution times and characteristics of absorption spectra from external standard runs. No interfering peaks were found that co-elute with the lignin phenols of interest. The quantitative analysis results of a humic acid were in good agreement with those previously published.[8]

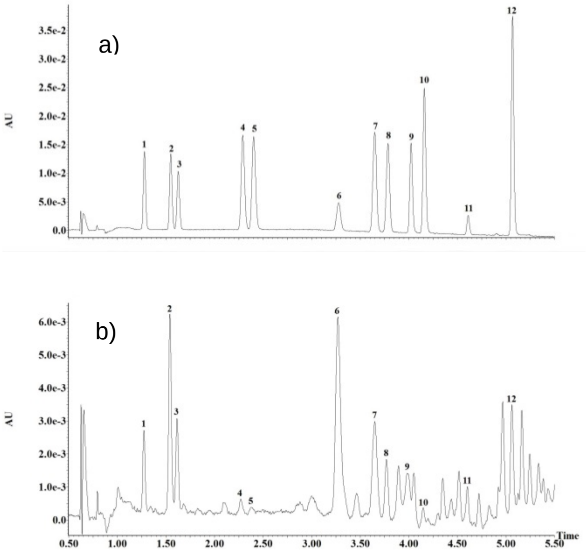

Figure 2. SFC chromatograms of a) standard mixture (0.1 mM) and b) humic acid sample. See Figure 1 for peak indentification.

Conclusions

The supercritical fluid chromatography method described gave rapid and clear separation of the 11 major lignin-derived phenols from cupric oxide oxidation with good selectivity and resolution. Using this SFC method, derivatization step is not needed as it is for GC/MS determination and the analysis time is shortened to less than 6 minutes. Application of this method in the quantitative study of humic acid sample proves its great suitability and potential in the analysis of complex environmental samples.

Acknowledgement

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Increasing Pulp Reactivity and Thermoformability by Combined Ionic Liquid and Enzyme Treatments: Screening of Optimal Ionic Liquid – Enzyme Combinations

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Abstract

In order to allow the preparation of new fibre-based products, it is a key challenge to find methods that increase the reactivity of fibre materials, while still maintaining their mechanical properties. In our current work, we have been looking into a new processing concept, which involves the swelling of fibre surfaces by treatment in ionic liquids (ILs), with a subsequent enzymatic modification step. ILs dissolve cellulose, but adding water to them in a suitable proportion will instead lead to cellulose swelling. While the IL treatment increases the fibre surface accessibility for enzymes, the use of hydrolytic enzymes (glycosyl hydrolases, GHs), e.g. endoglucanases, is anticipated to increase the fibre surface "hairiness" and thus fibre reactivity. Xylanases similarly affect the xylan components of the fibres. Cellulose-swelling ILs inactivate GHs, why the first step in our research was to screen for suitable combinations of GHs and cellulose-swelling ILs. A screening protocol was set up for this task, and nearly 20 endoglucanases and xylanases were screened in two rounds with 15 and 40 % (w/w) solutions of seven different ILs. In this study, several potential GH+IL combinations were found, in which > 60 % of relative enzyme activity was retained in 40 % IL.

Introduction

Replacing products made from fossil raw materials by biobased products is a current megatrend and the utilization of fibre materials in new applications is expected to grow steadily in the future. Increasing pulp reactivity for further chemical modifications or for better properties regarding physical attachment to other material components in e.g. new cellulose-based composite materials, or further to increase the thermoplasticity of cellulosic fibres, are all enabling technologies that need further studying. One of the most interesting developments in cellulose chemistry during the last decades is the discovery, reported in 2002, that cellulose can be dissolved in certain ionic liquids (ILs).[1] ILs are salts with low melting points (< 100 °C). They have especially beneficial solvent properties as the constituent ions can be chosen out of a large repertoire meaning that the solvent can be tailor-made for each application. The combination of organic and ionic character make ILs excellent solvents for many reactions, and the negligible vapour pressure of ILs reduces all emissions of volatile organic compounds and reduces explosion hazards typically related to organic solvents.

ILs have successfully been used together with enzymes in various reactions. Typically many enzymes remain active in hydrophobic ILs, whereas hydrophilic ILs are inactivating. Of the cellulose-dissolving ILs reported to date, most are hydrophilic which clearly limits their use together with enzymes. The use of GHs together with cellulose-dissolving ILs has been studied rather intensively, mostly in enzymatic total hydrolysis of lignocellulose with IL pretreatment. Mostly, very difficult compatibility issues have been reported for the combination of ILs and GHs.[2] Enzyme thermostability has been reported to correlate with IL tolerance.

Using ILs as activating or swelling solvents for fibres prior to enzymatic treatments has scarcely been reported in the literature. Enzymatic treatments have been reported to increase cellulose reactivity in e.g. the rayon process or in cellulose derivatization.[3] In this study, our aim has been to activate fibres with aqueous ILs and to enzymatically treat the fibres in this activated state. The hypothesis is that the GHs would create new cellulose chain ends on the fibre surface, and in that way increase the fibre reactivity in a synergistic way. Because of the earlier described poor enzyme-IL compatibility a screening experiment, of which the results are reported here, was done to find the best combinations of GHs and ILs. The aim was also to study enzymes from different GH families to inspect the impact of GH family on IL tolerance and on the enzymatic activation step.

Experimental

Materials

Seven different ILs, known to dissolve or swell cellulose, were synthesized in collaboration with Helsinki University, with the exception of [DMIM]DMP, which was bought from IoLiTec (Heidelberg, Germany) (**Figure 1**). The tested endoglucanases were *Aspergillus niger* GH12 (AnGH12), *Bacillus amyloliquefaciens* GH5 (BaGH5), *Talaromyces emersonii* GH5 (TeGH5), *Termotoga maritima* GH5 (TmGH5), *Clostridum thermocellum* GHX (CtGHX), *Dictyoglomus turgidum* GHX (DtGHX), *Trichoderma reesei* Cel5A (TrGH5) and Cel7B (TrGH7), VTT metagenomic endoglucanase KP7 GH12 (KP7GH12) and an GH5 EG from *Pyrococcus horikoshii* (PhGH5). From ROAL two GH45 EGs (ROALGH45_1 and ROALGH45_2), of which the other one is linked to a carbohydrate-binding module (GH45_1+CBM), a GH5 EG (ROALGH5) and a GH7

EG (ROALGH7), were acquired. The tested xylanases were GH10 xylanase from *Thermopolyspora flexuosa* (TfXYN10A), GH10 xylanase from *Thermotoga maritima* MSB8 (TmXYN10B) and GH11 xylanase from *Dictyoglomus thermophilum* (DtXYNB), and two commercial GH10 and GH11 xylanases from ROAL.

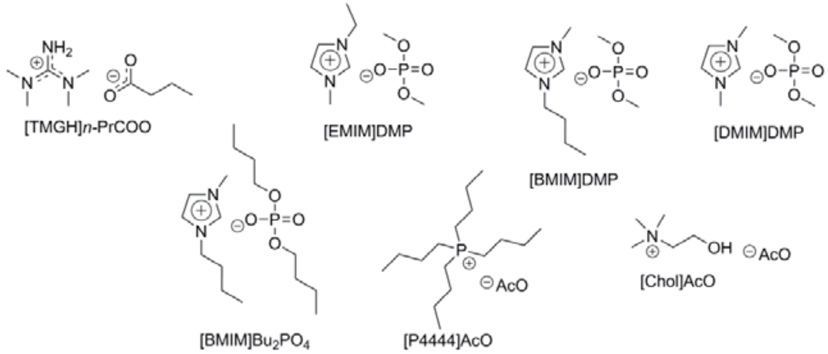

Figure 1. Ionic liquids used in this study.

Methods

The enzymatic screening reactions were performed in a miniaturized assay on 500 µL 96-well microplates. All activity assays were performed in 200 µL volume followed by an assay of reducing sugars to detect substrate degradation. The DNS assay [4] was used with all ILs except [P4444]AcO with which the PAHBAH assay [5] was used. The activity of endoglucanases was measured using 1 % (w/v) CMC as substrate in 0.050 M Na-citrate (pH 5.0) containing 0, 15 or 40 % (w/w) of IL, 0.1 mg/mL bovine serum albumin (BSA) and 2 h incubation time with no agitation. An assay temperature of 50 °C was used for all enzymes except for PhGH5 for which 70 °C was selected. After 2 h incubation, DNS or PAHBAH reagent mixtures were added and the substrate degradation was evaluated with the respective colorimetric assay. For xylanases, the reaction conditions were similar but the temperatures were 60 °C (TfXYN10A, ROAL GH10 and ROAL GH11) or 70 °C (TmXYN10B and DtXYNB) with 2 % (w/w) birchwood xylan as substrate and pH 7.

Results and discussion

In this work, the aim was to identify suitable combinations of cellulose-dissolving or -swelling ILs and endoglucanase or xylanase enzymes, with the goal to use these IL-enzyme combinations for pulp treatments to increase the pulp's reactivity. The used enzymes were chosen from as many as possible different GH structural families. Especially thermostable enzymes were prioritized due to the reported correlation between thermostability and IL-tolerance.[6]

The work began with the setup of the protocol assay and method development. The rather long assay time of 2 h was chosen to reflect factors related to both enzyme activity and stability in IL solution. The screening was done in two rounds, the first in 15 % (w/w) of IL, and the second in 40 % (w/w) of IL. In some cases, it was noticed that the IL compatibility with the colorimetric reagent solution (DNS or PAHBAH) was low, why both assays had to be used according to compatibility with the different ILs.

In the results, it can be seen that clear differences exist between the IL-tolerance of the different endoglucanases (**Figure 2**). CtGHX, TmGH5 and DTGHX had the lowest IL-tolerance, whereas those EGs acquired from ROAL generally had a high performance in 15 % (w/w) IL. Some enzymes, such as KP7GH12 showed large differences in their tolerance to different ILs. Generally it can be said that [BMIM]DMP and [DMIM]DMP appear to be the least inactivating ILs, suggesting the dimethylphosphonate anion to be an enzyme-compatible one. [P4444]AcO was clearly the most inhibiting of the tested ILs. By comparing ROAL GH45_1 and its variant carrying a CBM, it is very interesting to notice that the presence of the CBM appears to induce a significant tolerance to IL. In the 40 % (w/w) screening reactions several candidate combinations of EG and IL were found, in which >60 % of the reference activity was retained in the screening assay. These combinations were [DMIM]DMP with AnGH12, ROALGH45_1+CBM and PhGH5, [EMIM]DMP with ROALGH45_1+CBM and PhGH5, [Chol]AcO with ROALGH45 + and w/o CBM, and [TMGH]*n*-PrCOO with PhGH5. PhGH5 performed well in the 40 % (w/w) assay and at 70 °C, strengthening the hypothesis of correlation between thermostability and IL-tolerance.

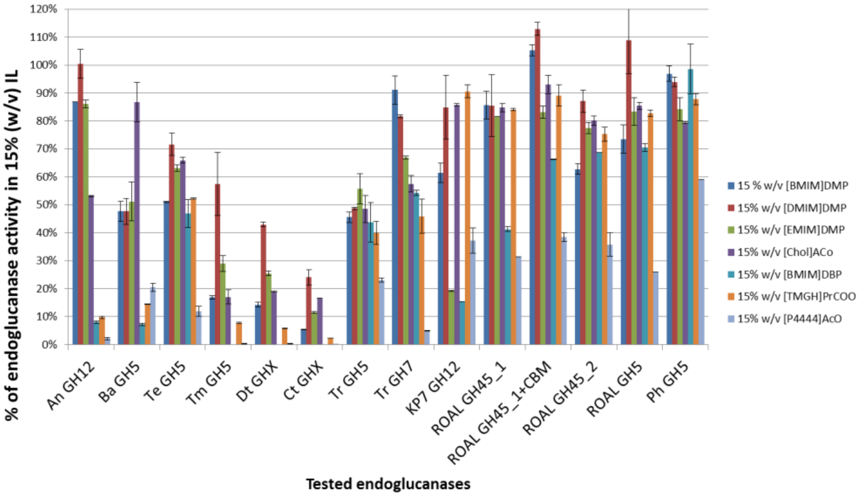

Figure 2. Results from screening endoglucanases in 15 % (w/w) IL solutions. The buffer result is used as reference 100 %.

The activity of GH10 and GH11 xylanases in the presence of ILs was tested in 15% and 40% solutions (w/v) at temperatures at least 20 °C below the optimum temperature, since ILs typically decrease the temperature optimum. The xylanase tolerance to ILs varied greatly (**Figure 3**). Typically, GH10 xylanases showed higher IL tolerance than GH11 xylanases. An exception was 15% [Cho]AcO that was tolerated second best by DtXYNB belonging to GH11 family. The results showed that TfXYN10A belonging to GH10 xylanase family was the most active xylanase in ILs. It tolerated best almost every IL in 15% and 40% concentrations. The best tolerated ILs in 40% concentration were [Cho]AcO, [DMIM]DMP, [EMIM]DMP and [EMIM]AcO. Among GH10 xylanases, the general tolerance order was TfXYN10A > ROAL GH10 > TmXYN10B. Like for the endoglucanases, [P4444]AcO was very inhibiting for xylanases. Surprisingly, TfXYN10A was 100% active in 15% [P4444]AcO, Although TmXYN10B is the most thermostable xylanase in this group of enzymes, it was not the most IL-tolerant. This supports the earlier findings with [EMIM]AcO that resistance to competitive inhibition by IL is a dominating factor for enzyme's IL tolerance [7,8]. Nevertheless, thermostability probably protects against unfolding effect of ILs also in xylanases.

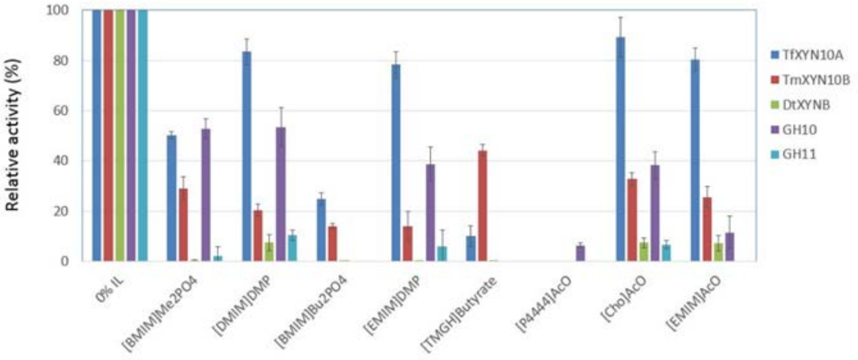

Figure 3. Results from screening GH10 and GH11 xylanases in 40% (w/w) IL solutions. The buffer result is used as reference 100%.

Conclusions

The ultimate goal of this work was to find methods for combined IL and enzymatic modification of pulp fibres to increase their reactivity and thermoplasticity. In this first part of the work, IL and enzyme combinations were screened. Several strong candidate combinations were found, in which endoglucanases retained >60 % of their buffer reference activity in 40 % IL. Among the studied xylanases, one enzyme (TfXYN10A) was found to show even 80% activity in several 40% ILs. Several interesting trends for explaining the deeper mechanisms guiding enzyme activity and stability in IL solutions were also observed.

Acknowledgements

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Estimation of the Deprotonation Degree of Phenolic Groups on Kraft Lignin

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Abstract

Lignin is an abundant biomaterial, with potential as raw material feed stock for production of solid- and liquid fuels as well as phenolic components and carbon fibres. Lignin may be separated from various process streams in an integrated pulp production and wood-based biorefinery. Separation of Kraft lignin from black liquor can be made by the LignoBoost technology; it starts with precipitation of lignin by acidification of the black liquor and consequently protonation of the phenolic groups on lignin, in equilibrium with the surrounding liquid. The protonation degree of phenolic groups on kraft lignin has been identified as a key-property in controlling the precipitation yield. It has been investigated if the protonation degree of lignin in a black liquor system can be modelled using a modified Poisson-Boltzmann cell model which has been combined with the Pitzer method. It was found that the model gave reasonable results. Furthermore, the model indicated that the protonation degree is strongly dependent on the pH and temperature of the black liquor, however, the molecular weight of lignin has a minor influence and at the high ionic strength in black liquor a small change in ionic strength has only a very small influence on the protonation. Additionally, the predicted deprotonation degrees were compared with previously measured precipitation degrees at industrially relevant conditions.

Introduction

Separating lignin form black liquor is a step towards the conversion of the conventional pulp mill to a wood-based biorefinery. This can be achieved by the LignoBoost technology. The precipitation of lignin in the LignoBoost process consists of two main steps; the first step being acidification of the black liquor, which lowers the pH and consequently, the solubility is decreased due to the protonation of negatively charged phenolic groups; the second step is agglomeration of lignin macromolecules, which leads to precipitation. However, knowledge regarding the equilibrium of dissolved and precipitated lignin, for a given condition, is scarce. It is therefore of crucial importance to further investigate the phenomena that influence the equilibrium (i.e the solubility equilibrium) in black liquor; which is relevant for *e.g* the precipitation of lignin in the LignoBoost process. During the past years some work has been done regarding this; *e.g* Alén et al (1979) [1], Norgren et al (2001) [2] and Zhu & Theliander (2015) [3]. However, the fundamental mechanisms are far from fully understood.

In order to increase the understanding of the fundamental mechanisms that determine the equilibrium state of lignin in black liquor, a study of the deprotonation degree of the phenolic groups on softwood kraft lignin in black liquor has been carried out. In this work an attempt to mathematically model the ion concentration distributions around lignin fragments in black liquor has been made by investigating the possibility to use a modified Poisson-Boltzmann cell model and extend the validity of the cell model by extrapolating the valid ionic concentration range using the Pitzer method. The model has been used to predict the pH dependent deprotonation degree, under various conditions relevant in the LignoBoost process.

Moreover, it is of great importance to investigate the relationship between the deprotonation degree and the precipitation degree. Such information will serve as an indication on how to optimize the process conditions for a given precipitation yield in the precipitation stage as well as how to tune the molecular properties of the precipitated lignin.

Theory

Behaviour of kraft lignin in black liquor

Black liquor is a complex, highly concentrated and alkaline mixture of inorganic ionic species and organic fragments (macromolecules) of wood constituents from the cooking process stage in kraft pulp production. Lignin is the most abundant organic component in black liquor, however also other components are present in relatively high concentrations: such as residues of xylan and glucomannan as well as sugar acids. The Lignin macromolecules are dispersed in the black liquor due to the repulsive forces that appear between lignin molecules themselves and between lignin molecules and other macromolecules in the mixture. Acidification of the black liquor, the addition of salt and decreased temperature (at conserved pH) have shown to increase the precipitation of lignin [3]. Thus, it is suggested that the mechanisms responsible for the electrostatic repulsive forces, which are typically dependent on those parameters, are of importance for the solubility. The protonation/deprotonation of acidic groups on the lignin macromolecule surface in equilibrium with the surrounding liquid has been identified as a key mechanism; phenolic groups being the most abundant ionized group at alkaline conditions, thus contributing the most to a charged surface. Due to charged surfaces in an electrolytic environment, electrostatic repulsive forces are assumed to act between like-charged macromolecules in the black liquor. If the electrostatic double layer repulsion overcomes the attractive van der Waal forces the solution will be stable, according to the DLVO theory. Thus, this theory may be applicable to this system especially since previous observations regarding the stability of kraft lignin in solution exhibit a dependence on pH, ionic strength, temperature and molecular weight. However, it should be mentioned that non-DLVO phenomena may also affect the solubility of kraft lignin in black liquor.

The Modified Poisson-Boltzmann cell model

The black liquor system is complicated and in order to describe it in a simplified but realistic way several assumptions have to be made, which are listed below:

- The dissolved lignin macromolecules are repelled from each other in order to maximize the distance from each other (i.e. minimize its free energy). Thus, the system resemble, an average state of a periodic structure of packed cells. The packed cells are described as somewhat overlapping spherical cells (based on the total system volume and the number of dissolve lignin fragments) containing a concentric spherical lignin macromolecule. Thus the description of the system is reduced to the single cell.
- The polydispersity of the dissolved lignin is assumed to have negligible influence on the homogeneity of the dispersion.
- The maximum surface charge density, at fully deprotonated phenolic groups, is approximately the same for all lignin molecules and the phenolic groups are evenly distributed on the surface.
- The dielectric property of water in the solution is assumed to be identical to that of pure water.
- The precipitated lignin is assumed to have minor influence on the remaining dissolved lignin and its distribution in the available liquid volume.

One general problem is that the ionic strength is often very high at industrial conditions and models, such as the classical Poisson-Boltzmann model, describing physical/chemical phenomena of charged macromolecules and colloids in an electrolytic solution are often only strictly valid for very dilute solutions. This is also the case for our problem: black liquor has a very high ionic strength and the Poisson-Boltzmann cell model is, thus, not valid since it is based on an electrochemical potential of the ions having ideal entropies, namely the ideal-gas approximation, and thus do not account for interionic interactions. In an attempt to overcome this problem we have assumed that it is possible to adjust the entropy of the ions with their specific activity coefficients. This adjustment is in analogy with earlier work done on e.g. boiling point elevation of electrolytes having a high ionic strength [4].

This approach yields a modification of the Boltzmann distribution of the ions around the lignin macromolecules, and a modified Poisson-Boltzmann cell model is obtained [5]: presented in Eq. 1:

$$\nabla^2\Phi(r) = -\frac{F}{\varepsilon_0\varepsilon_r}\sum_i z_i \frac{\gamma_i(\mathrm{R}_{cell})}{\gamma_i(r)} c_i(\mathrm{R}_{cell}) \exp\left(-\frac{z_i F\Phi(r)}{RT}\right) \qquad \text{Eq. 1}$$

$$Boundary\ conditions\colon \left.\frac{d\Phi}{dr}\right|_{r=R_{lig}} = -\frac{\alpha\sigma_0}{\varepsilon_0\varepsilon_r} \quad , \quad \left.\frac{d\Phi}{dr}\right|_{r=R_{cell}} = 0$$

Φ (V) is the electrostatic potential; F (C mole^{-1}) is the Faraday's constant; ε_0 (C V^{-1} m^{-1}) and ε_r (-) are the electric permittivity in vacuum and relative permittivity of water, respectively; z_i (-), γ_i (-) and c_i (mole m^{-3}) are the valency, activity coefficient and concentration of an ion i, respectively; r (m) is a radial coordinate in the cell; R_{lig} (m) and R_{cell} (m) are the radii of a lignin macromolecule and the cell, respectively; R (J mole^{-1} K^{-1}) is the gas constant; and T is the temperature (K). The inner boundary condition is the electric field at the surface of the lignin macromolecule and is linearly dependent on the surface charge density at totally ionized phenolic groups σ_0 (C m^{-2}) and the deprotonation degree (i.e. the fraction of ionized phenolic groups), α (-). Consequently, it is coupled to the protonation/deprotonation equilibrium condition given in Eq. 2:

$$K_a = \frac{\gamma_{phO^-}\gamma_{H^+}}{\gamma_{phOH}}\frac{\alpha}{\alpha-1}c_{H^+} \qquad \text{Eq. 2}$$

The Pitzer method [6] was used to estimate the specific activity coefficients of the ions, due to the highly concentrated electrolyte solution of the black liquor, implying significant specific interionic interactions in the solution.

Experimental

Most of the characterisation of the black liquor and fractionated black liquor has been used from previous studies [3]. Complementary characterisation was made by measuring the concentration of Cl^-, SO_4^{2-}, SO_3^{2-} and $\mathrm{S}_2\mathrm{O}_4^{2-}$ using ion chromatography. The instrument used was a 850 Professional IC, Metrohm with Metrosep A Supp7 columns. Samples were filtered through 0.45 µm PVDF membrane syringe filters prior to injection, and the experiments was run at a flow rate of 0.8 mL min-1 with sodium carbonate (3.6 mM) as the eluent. The concentration of each anion was calculated based on a standard calibration. Three different concentration points for each anion were chosen: Cl^- with 10-50 mg L-1, SO_4^{2-} with 50-150 mg L-1, SO_3^{2-} with 10-50 mg L-1 and $\mathrm{S}_2\mathrm{O}_3^{2-}$ with 56-140 mg L-1. The standard deviation was ±1.5% based on the calibration curves of standard solutions.

Results and discussion

Characterisation of Black Liquor

The results of the complementary concentration measurements of ion species is given in Table 1. The carbonate (CO_3^{2-}) concentration was estimated based on similar systems of black liquors in literature. An average, 50 g kg^{-1} total dry solids were used based on three softwood black liquor characterisations from the literature [4]. The remaining characteristics of the system was, as previously mentioned, taken from previous studies [3]. By summing up the concentrations of the relevant ions in the system, based on previous measurements, the measurements in this work and literature based estimates, a lack of anions was observed in order to close the charge balance. This is due to that black liquors contain negatively charged organic carboxylic acids that have not been measured.

Table 1. Complementary concentration measurements of some anions for the unfractionated black liquor, S0, and for the fractionations, F1, F2, and F4.

Black liquors		S0	F1*	F2	F4
$[Cl^-]$	Mole kg^{-1} liquid	0.021	0.013	0.029	0.030
$[SO_4^{2-}]$		0.173	0.948	0.132	0.149
$[SO_3^{2-}]$		0.166	0.049	0.135	0.155
$[S_2O_3^{2-}]$		0.107	0.053	0.170	0.191

* After fractionation of S0, F1 was first diluted and later Na_2SO_4 (160.5 g kg^{-1} black liquor) was added to it [3].

Deprotonation degree of phenolic groups

The deprotonation degree was estimated for several industrially relevant precipitation conditions based on experimental data from previous studies, both for unfractionated and fractionated softwood black liquor [3]. In Figure 1 the temperature dependence of α for the unfractionated lignin, S0 and the fractionated lignin F1, F2 and F4 is displayed. In the plot on the right-hand-side the predictions of α indicate that it is strongly dependent on the pOH (or pH) and temperature, however, the influence of an increase of the ionic strength by up to 20% is very small. In the plot on the left-hand-side the predictions of α for different fractions, having different average molecular weight indicate that the molecular weight, or size, of the lignin macromolecules has a negligible influence on α. Due to the highly screened electrostatic potential around the lignin molecules, the difference between the bulk pH and the pH at the surface of the lignin molecules is very small: less than 1%. Further analysis revealed that the strong temperature dependency of α for a given pOH is explained by the temperature dependency of the protonation/deprotonation equilibrium constant K_a of the phenolic groups and the water ionization constant K_w given by the van't hoff equation; the latter being dominant due to the larger value of the ionization enthalpy of water (51.6 kJ/mole) in comparison to the acidification enthalpy of the phenolic groups (20.0 kJ/mole).

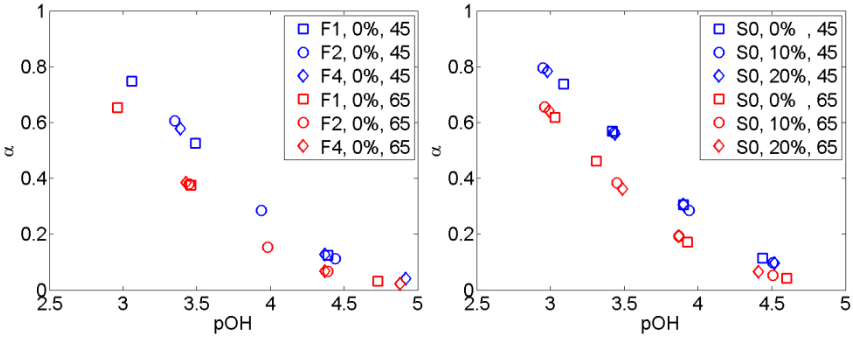

Figure 1. Predictions of α for given pOH, Temperature (ºC) and addition of ionic strength (%), for unfractionated lignin S0, and fractionated lignin (F1, F2 and F4).

The dependency of the precipitation degree on the deprotonation degree

The precipitation degree was compared with the predictions the deprotonation degree for several conditions and in Figure 2 the result is display for two fractions: F1, having the largest mass-averaged molecular weight (MW), and F4, having the smallest MW. Figure 2 indicates a strong dependency of the precipitation degree on α. It strengthen the explanation that the precipitation/solubility of kraft lignin is dependent on the electrostatic repulsive forces, induced by a negatively charged surface of the lignin. For a given α, also the molecular weight of the lignin molecules have a strong influence on the precipitation degree which has also been observed in previous studies [3]. This may be related to the ability of the lignin molecules to stick to each other upon contact when the lignin becomes unstable in the black liquor, i.e. when the attractive interactions of lignin molecules overcome the repulsive interactions. Furthermore, an increase of the temperature is shown to favour solubility and the effect increases with increasing α. This could be explained by strong temperature dependencies of the electrostatic repulsive forces, as the precipitation is less pronounced at higher deprotonation degrees of phenolic groups, which render higher surface charge densities. It should be mentioned that the temperature often affects many types of interactions, both repelling and attractive, however despite this fact, the trend previously mentions yet indicates a strong temperature dependency of the electrostatic repulsive interactions.

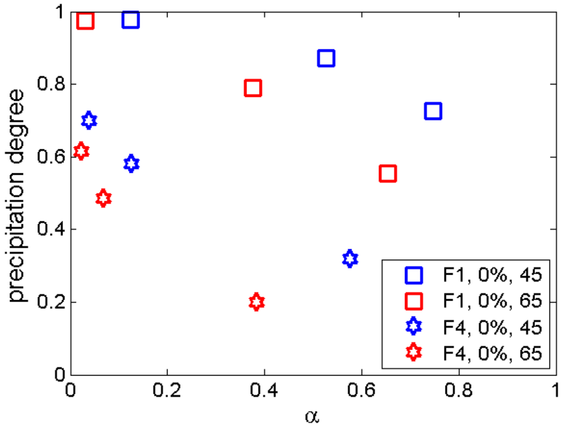

Figure 2. Precipitation degrees of fractionated lignin (F1 and F4) from previous studies compared to the predictions of α, at several conditions.

Conclusions

The following conclusions were made from this study:

- The pH and temperature are predicted to strongly influence the deprotonation degree of phenolic groups on kraft lignin.
- The influence of the molecular weight of lignin and a small increase in ionic strength on the deprotonation degree is predicted to be very small, in black liquor systems of high ionic strength.
- The pH at the surface of lignin macromolecules is predicted to be approximately the same in black liquor systems of high ionic strength.

Acknowledgements

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Nano-scale Ceramic Membranes in Separation of Lignin and Monosaccharides from Biorefinery Process Streams

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Introduction

Pressure-driven membrane processes are one of the feasible methods for the separation of lignin from carbohydrates in future biorefineries. One advantage of the membrane processes is that they can be applied both to recover the wanted dissolved wood compounds from the extraction liquors or process waters, and to concentrate and purify them prior to further processing [1].

The choice of a suitable membrane is in a key role in designing of a membrane process, because it determines the selectivity and filtration capacity of the process. An optimal membrane enables high filtration capacity without severe fouling problems. When a biorefinery stream is treated to separate lignin from monosaccharides, the membrane should retain most of the lignin and permeate most of the monosaccharides. The challenge is, however, that these compounds together with other substances found in these streams (e.g. wood extractives, chemicals, additives used in production process) may foul the membranes severely [2] thereby decreasing the filtration capacity and causing process inefficiency as well as increasing operational costs [3]. These drawbacks can be reduced e.g. by adopting a suitable pre-treatment [3] or by selecting a membrane that is less prone to fouling-induced problems, for example by having a longer lifespan and tolerance to the harsh operating conditions and frequent cleaning [4]. These properties can be addressed to nano-scale ceramic membranes which have recently been successfully upscaled to larger unit sizes (length up to 120 cm, having a filtration area of 1.3 m^2/membrane unit), and which thereby could be a viable option to the treatment of biorefinery streams already in the near future.

In this study, the applicability of the ceramic nanofiltration membranes were tested in separation of lignin from monosaccharides. The used membranes were of similar structure and cut-off than the novel upscaled modules, thus giving a good reference point to the industrial use of such membranes. The usability evaluation was based on membrane capacity, fouling and separation efficiency.

Experimental

Materials

The hydrolysate used as the feed solution was received from a Finnish biorefinery. It was a mixture containing lignin and mainly hexoses (glucose content 81%, rest being hemicellulosic sugar units such as xyloses), and it was pre-filtered with the RC70PP ultrafiltration membrane at 1 bar and 65 °C by using a CR250 high shear rate filtration unit. The pH of the hydrolysate was 4.9 and conductivity was 5.9 mS/cm. It contained ca. 2.9 g/L of lignin and appr. 100 g/L of monosaccharides. The content of total organic carbon (TOC) was ca. 40 g/L.

The TiO_2-based ceramic membranes used in the experiments were developed as a part of the CeraWater project in the European Union 7th Framework programme. Both unmodified 19-channel membrane element (referred to as 'Native') and a similar membrane modified to have a low fouling tendency ('Grafted') [5] were tested in the experiments (see Table 1). Both membranes were of 0.5 m in length, had a molecular weight cut-off of 600-650 Da and a filtration area of 0.1 m^2. The Grafted membrane was functionalized by grafting methyl and phenyl groups onto the membranes with a Grignard method (by using organometallic reagents), as described by Mustafa et al. [5].

Table 1. Key properties of the membranes tested given by the suppliers.

	Native	Grafted
Supplier	RKV/Fraunhofer IKTS	Base from RKV/Fraunhofer IKTS, anti-fouling modification by VITO N.V.
pH range	3-13	3-10
Max. temperature, °C	350 °C (dry conditions)[a)]	<80 °C at low/high pH (wet conditions)
Contact angle [5], °	20	60

[a)] Membrane stability in wet conditions at temperatures above 100 °C not yet known (dependent of solution properties such as pH, chemical composition etc.)

Process description

The experiments were performed with a laboratory-scale filtration unit. The cross-flow velocity was 2.7 m/s and hydrostatic pressure 5 bar. Each membrane was tested individually.

Pure water flux (PWF) for the membrane was first measured at 70 °C. The hydrolysate was then concentrated at 77 °C to a volume reduction factor (VRF) of 2. Samples were collected from the initial feed, final permeate and concentrate. To determine the capacity of the membranes, the permeate flux was monitored during the filtration. After concentration filtration the membrane was rinsed thoroughly and PWF was measured again in similar conditions as in the beginning in order to determine membrane fouling.

To enable the evaluation of the applicability of these membranes for the separation task at issue, the collected samples were analysed for the lignin retention (Jasco V-670 Spectrophotometer, determined as UV absorbance at 205 nm and with a correlation factor of 0.110 L/(mg·cm)). The monosaccharide content and its retention was evaluated based on degrees Brix (VWR International Digit-020 ATC refractometer, estimated as degrees Brix at room temperature) which determines the sugar content of an aqueous solution, or, in the case of mixtures, approximates the content of dissolved solids. It was used in this study to estimate the monosaccharides as the majority of the dissolved solids (appr. 97%) derived from carbohydrates.

Results and discussion

The results show that both of the tested novel ceramic membranes separated lignin partly from carbohydrates, by retaining more than 60% of lignin and only 7-9% of the monosaccharides (Table 1), thereby producing a permeate containing over 90 g/L of monosaccharides and less than 1.2 g/L of lignin. This equals to a monosaccharide content of ca. 99% of dissolved solids. Whether this level of purity is adequate depends on the process using the produced fractions.

The moderate lignin retention implies that during the production of monomeric sugar units also some lignin has been fragmented to a rather small molecular size which is then permeated through the membrane. The purity of the produced monosaccharide fraction might be possible to increase further by using a two-pass nanofiltration process (permeate filtered again).

Table 2. Separation efficiency of the membranes.

	Native	Grafted
Lignin retention, %	63	61
Monosacch. retention, %	7	9

The filtration capacities of the ceramic membranes were higher, 6-7 kg/(m^{2}h·bar on average, compared to what has been measured with the polymeric nanofiltration membranes used with similar solutions (e.g. Desal-5 DL from GE Osmonics 1 kg/(m^{2}h·bar) and NFW from Synder 3 kg/(m^{2}h·bar)). Also, no significant fouling (determined as the decrease in the pure water fluxes) was observed with either of the membranes, although the permeate flux decreased by 46 and 68 % during concentration filtration (for the Grafted and Native membranes, respectively) (see Figure 1).

The observed decrease in permeate flux could result, for instance, from the increased osmotic pressure, increased viscosity, or from a change of molar mass distribution in the concentrated feed stream. In addition, high molar mass compounds might have been forming a secondary layer on membrane surface thereby decreasing the permeate flux. By taking the change in osmotic pressure into account (estimated using van't Hoff equation [6] and assuming average molecular weights of 180 g/mol and 800 g/mol for the dissolved monosaccharides and lignin) it was found that the capacity of the Grafted membrane did not change during the concentration: the membrane permeability remained stable and the decrease in the permeate flux derived from the increase in the osmotic pressure. However, the capacity (i.e. membrane permeability) of the Native membrane decreased by 40% during the filtration when considering the effect of the change in osmotic pressure. The viscosity of the feed stream was not likely to increase notably, as the solids content and temperature of the solution do not markedly change during the concentration to the VRF -value of 2 [7]. Thus, the formation of a secondary layer on the membrane surface might have been the reason for the capacity decline in this case.

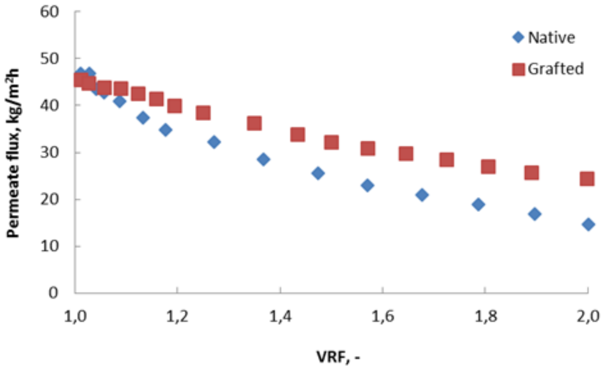

Figure 1. Permeate fluxes during concentration filtration.

Based on the low fouling tendency and good permeate flux compared to polymeric membranes, it can be concluded that the tested novel ceramic membranes are a viable option for the separation of lignin and carbohydrates in biorefinery process streams.

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Thermodynamic Analysis of Ionic Liquid Recycling

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Abstract

Spinning of cellulose fibers from a solution in ionic liquid [DBNH][OAc] (IL) into water can be considered as feasible and eco-friendly processing route for textile fibers production in future. The conventional production of man-made cellulose fibers (viscose and Lyocell process) involve consumption of hazardous chemicals and byproducts formation. To replace commercial direct solvents by IL, efficient and cost-effective recycling of IL from spin bath solution is obligatory.

In this work, the possibility of thermal recycling of IL from IL+water is explored. Measurements and modelling of vapor pressures of IL as a temperature function and vapor liquid equilibrium (VLE) of IL+water systems are carried out. The test runs of IL-recycling are performed on pilot scale of thin-film evaporation system. A sufficient purity of the IL product suitable for re-dissolving cellulose was achieved in one of the nine tests performed at different temperature and pressure conditions. Therefore, the thin-film evaporation system was demonstrated to have the capability of recycling IL from IL+water mixture.

Introduction

Ionic liquids have shown potential for replacing industrial solvents due to their low vapor pressures, better thermal stability, non-corrosive nature and safe handling. Some ionic liquids are able to dissolve cellulose and regenerate it after the addition of an anti-solvent [1][2]. A successful dry jet-wet spinning of cellulosic fibers from IL solution was demonstrated earlier in the lab scale [3]. Currently, this IL based fiber spinning process is considered as a potential competitor for the conventional Viscose process (production by derivatization to cellulose xanthate) and the Lyocell process (direct cellulose dissolution to N-methylmorpholine N-oxide (NMMO)). These aforementioned conventional processes for man-made fiber production have environmental and operational issues due to consumption of hazardous chemicals and the formation of undesired byproducts. The increase in demand of man-made cellulose fibers is expected due to growing population and insufficient increase in supply of cotton. However, an adequate and economical recycling of IL from spin bath solution is vital for replacing commercial direct cellulose solvents (e.g. NMMO in Lyocell process). The spin bath solution contains large fractions of IL and water (anti-solvent) and minute factions of side products (hydrolyzed IL and decomposed carbohydrates from pulp feed). The desired purity of the recycled IL for dissolving cellulose pulp is ≥ 95 w%. Due to continuously growing interest in the field of ionic liquids and their potential applications, measurements and modelling of several ionic liquid systems have been carried out during the last one and half decade [4][5][6]. Recycling of different ionic liquids in other applications has been investigated earlier [7][8].

In this study, the vapor pressure measurements of IL ([DBNH][OAc]) at various temperatures and VLE measurements of IL+water mixture are performed. The experimental data is further utilized in modeling of thermal separation of IL. In the second task, test-runs for recycling of IL from spin bath solution (approx. 80 w% water and 20 w% IL) were conducted on a pilot scale of a thin-film evaporation at UIC GmbH, Germany. Several conditions for feed flowrates, temperatures and pressures were tested for purifying IL by evaporation of water. Results from the test-runs on thin-film evaporator are further compared to single stage separation of two components (IL+water) predicted by preliminary VLE model.

Experimental

Vapor pressure and vapor liquid equilibrium measurements were performed in this study. The vapor pressures of IL at several temperatures were measured using a vacuum distillation method. The distillation experiments were performed at 355-480 K temperature and 5-150 kPa pressure ranges. The VLE measurements of IL+water were performed using a static total pressure method. Four equilibrium cells were used simultaneously in the measurements. The measured temperature region was 303-353 K. The measurements were started at 303 K temperature which was increased by approximately 10K after each measured equilibrium point. Therefore, six points were measured for each system.

For the test runs of IL recycling using the thin-film evaporator, IL was diluted with water to make 20 w% solution in order to mimic the actual spin bath solution that will be recycled in the actual process. The solution was preheated and fed to the jacketed thin-film evaporator. IL-rich product from evaporator was collected as a residue and almost pure water product was collected as a distillate. The distillate was condensed in a water-cooled condenser. The pressure within the system was maintained using a vacuum system connected to the distillate line. The experiments were performed at 16-31 mbar pressure range. The temperatures of all heating units were kept below 100°C to avoid thermal degradation of IL. Several sets of temperature, pressure and feed rates were tested. Feed and products samples were collected from all sets of conditions and analyzed for composition.

Results

The measured vapor pressure values were used to regress the Antoine vapor pressure equation parameters for the pure IL assuming that IL evaporates as a single component. In addition, the heat of vaporization value 74.28 kJ/mol was calculated from the vapor pressure data. The Antoine parameters were used in the calculation of the VLE results.

The results of the VLE measurements were used to optimize the interaction parameters of the Non-random two liquid (NRTL) activity coefficient model. Activity coefficient models take into account the physical interactions between the molecules. The VLE measurements of IL+water systems showed a negative deviation from the ideal behavior (Raoult's law). The activity coefficient model is useful in prediction of the thermal separation behavior. Figure 1. demonstrates the experimental results (points) and model predictions (lines) by the optimized model parameters. These experimental measurements are important at the initial phase of equipment selection and process design. Modeling of vapor pressure and VLE data was utilized in development of a preliminary model for single stage evaporator.

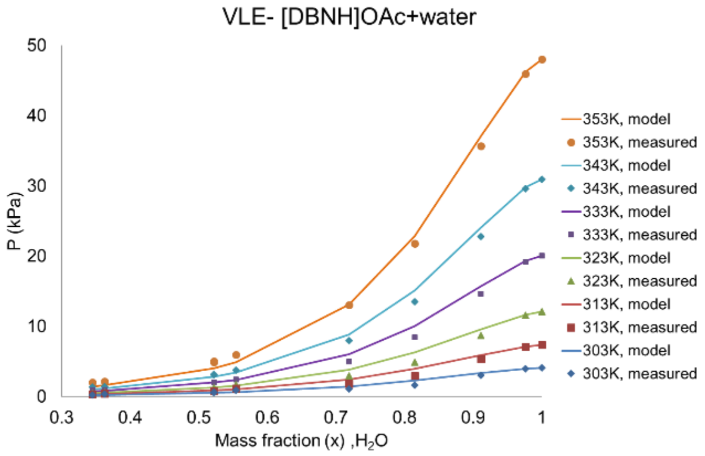

Figure 1. VLE measurements (i.e. vapor pressures of IL+water mixtures) and NRTL model predictions for IL+water at T = 303, 313, 323, 333, 343, and 353 K

The challenges faced in thermal recycling of IL are: 1) hydrolysis product formation at high temperature, 2) thermal degradation of IL above 100°C. This temperature sensitivity means that thermal separation should be performed at lower temperatures and consequently at lower pressures.

The performance of thermal recycling on pilot scale thin-film evaporator was inspected at different feed flowrates, temperatures and pressures. The composition analysis of residue samples showed that IL product with 5-11w%

residual water was achieved. The distillate contained 98.5-99.8 w% water. A comparison between a single experiment from test-run and a preliminary single stage evaporation model is illustrated in Figure 2. This comparison predicted that evaporation temperature is close to residue temperature which was not true for all experiments. In experiments with increased jacket temperature or lower system pressure, the evaporation temperature was close to heating jacket temperature. The evaporation temperature was predicted by analysis of water contents in residue and distillate.

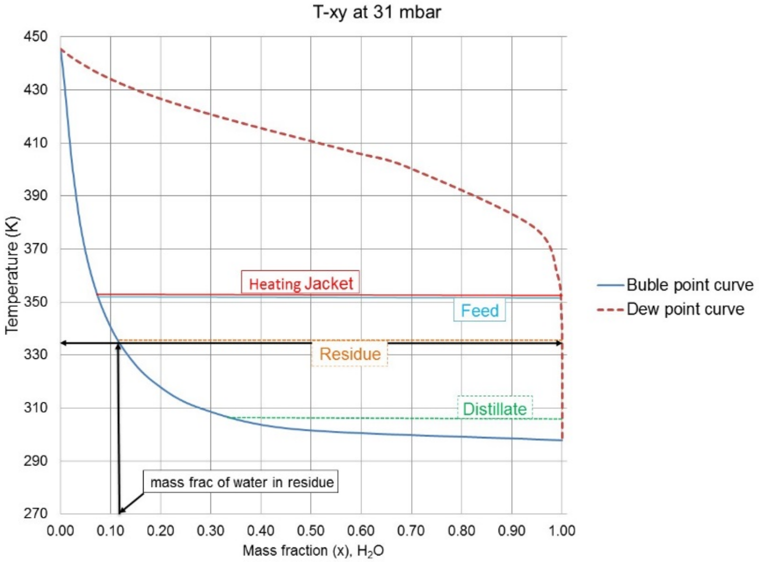

Figure 2. Comparison of test-run results (single experiment) with single stage evaporator model.

In the modeling, it is challenging to pre-define the evaporation temperature when the thin-film evaporator is considered as a single stage due to several temperature levels at different parts of the equipment. To accurately model the thin-film evaporation, the actual number of stages need further investigation at different pressure levels. In the future, more experimental measurements of important physical properties (heat capacity, density of mixtures, viscosity, etc.), VLE measurements and tests of IL recycling will be employed in the development of a comprehensive model for an IL recycling scheme. Additional tests on the pilot scale will develop understanding about the separation stages in thin-film evaporator system and optimizing the operating conditions for better product quality and reduced utility costs. The successful recovery of IL on pilot scale will lead to the industrial scale cellulose fiber production using IL as a direct solvent.

Conclusions

The results from measurements and modelling for vapor pressure and VLE were used to evaluate the possibility of thermal separation of IL from spin bath solution. According to the initial test-run results, thin-film evaporation system seems promising for recycling IL at low temperatures without thermal degradation or significant hydrolysis product formation. The experimental measurements and modelling work along with the pilot scale experiments will effectively contribute in development of the industrial scale recycling scheme for IL.

Acknowledgements

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Europe's First Pilot Facility for Crystalline Nano Cellulose (CNC)

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Abstract/Introduction

Europe's first pilot facility for crystalline nano cellulose (CNC) will be in operations in 2016 thanks to a collaboration between industrial partners together with SP and with regional funding to support the initiative.

Crystalline nano cellulose – an promising biobased material

Crystalline Nano Cellulose (CNC) is a versatile and interesting material with many potential future applications in such various fields as construction materials, biobased composites, optical and electronics and additives for paints, coatings, food and hygienic applications. Most research and development efforts within the field of CNC have so far been carried out at laboratory scale. The lack of availability of larger amounts of CNC is an obstacle for the development and testing of CNC in new application. To address this issue a pilot plant facility for production of CNC will be built. The pilot facility will be located in Örnsköldsvik (Sweden) and integrated within the existing R&D&I infrastructure. The pilot plant will be an open R&D&I facility for companies, universities, and research institutes. The CNC pilot is a joint effort of SP Technical Research Institute of Sweden, MoRe Research, Melodea, and Holmen and supported by regional funds. The pilot will be based on the technology that is developed by Melodea and will be an important tool in the development and commercialization of new CNC-based products. The facility is expected to be up and running during the first half year of 2016.

More details on plans and possible process- and application oriented examples will be communicated at the NWBC conference. It has been research for decades, e.g. by Canadian researcher Prof Derek Gray who received the Marcus Wallenberg prize in 2013 for his achievements. Scaling up to pilot scale now will enable suitable and needed quantities and qualities to be tested in prototypes and demonstrators.

Figure 1. (Left) Overview of the industrial and pilot facilities in Örnsköldsvik, Sweden at which the new CNC pilot facility will be erected. (Right) A sample of CNC nanocellulose shown by one of the co-authors.

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Low-cost Ionic Liquids for Wood Fractionation

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Abstract/Introduction

Pretreatment of lignocellulosic biomass is the first step in the production of chemicals and fuels from woody biomass. It is also of the most expensive steps and has many implications on down-stream processes. Hence pretreatment technologies must be developed that are have low cost and provide high-quality substrates for subsequent chemical and biological transformations. To optimise cost, valorisation of all components contained in the lignocellulosic feedstock is required, including the hemicellulose and the lignin. A novel pretreatment technology is the application of low-cost ionic liquid water mixtures.

Advantages of wood fractionation at the pretreatment stage

The Ionosolv process is a novel solvent based technology that separates lignin from cellulose during the pretreatment.[1] It uses inexpensive ionic liquid solutions to extract and dissolve hemicellulose and lignin, leaving the cellulose as a solid. The lignin is subsequently precipitated by reversible addition of water. Separating lignin from the cellulose at the pretreatment stage has a number of advantages, especially when dealing with high lignin content biomass and when down-stream applications are sensitive to side-products of lignin and hemicellulose hydrolysis, such as phenolic compounds and aldehydes. Advantages are, in addition to the (1) reduction of inhibitors, (2) a purer cellulose potentially suitable for material applications, (3) reduced size of downstream equipment as 50% of the material taken out, (4) reduced loading of cellulase/hydrolytic enzymes, resulting in higher product titres. Another advantage is the higher quality of the isolated lignin, which can be channelled into chemical and material applications.

Low-cost ionic liquids

We have developed ionic liquid solvent solutions based on the hydrogen sulfate, $[HSO_4]^-$, anion that can cost as little as \$1.24/kg, which is in the range of common organic solvents such as acetone and toluene.[2] This overcomes justified concerns about the economic viability of ionic liquid based pretreatment pretreatment processes due to the high cost of many ionic liquids (> \$50/kg).[3] The ionic liquids are protic, yet non-volatile and thermally and chemically very stable (even towards harsh oxidation conditions [4]). This makes this class of ionic liquids very attractive for bulk applications such as lignocellulose pretreatment and fractionation.

Ionosolv fractionation procedure

The ionosolv process employs acidic low-cost organic salts, for example triethylammonium hydrogen sulfate. Some water is added to avoid sulfation of the hydroxyl groups in the biomass and to reduce viscosity. We then employ elevated temperature (120 °C - 170 °C) to dissolve the lignin and the hemicellulose from a wide variety of biomass, including hardwood and softwood. After separating the ionic liquid from the cellulose, the lignin is precipitated by adding water as an antisolvent. Preliminary models have shown that reducing the amount of antisolvent used will reduce energy demand of the process and reduce operating cost.

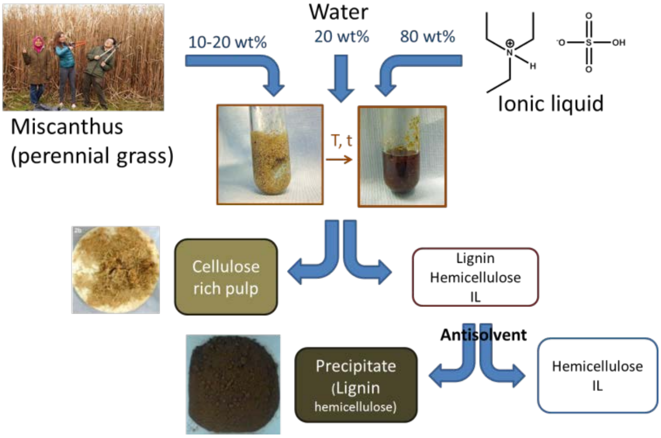

Figure 1. Fractionation procedure.

Lignin

Lignin can be precipitated by adding water as an antisolvent. The lignins have interesting properties, they have a low sulfur content, are odourless and characteristics, such as the molecular weight, the linkages and degree of condensation can be tuned widely (**Table 1**). Lignin with very high phenolic content can be isolated, which is interesting for antioxidant applications.[5]

Table 1. Summary of lignin properties isolated from a grass biomas using ionic liquid. [5]

Impact	Experimental evidence	Technique
Carbohydrate free	No carbohydrates detected in NMR and mass spectrometry (arabinose and xylose at very short treatment times)	HSQC NMR, Py-GC-MS
Hydrolysis of ether and ester linkages	Disappearance of β-O-4 ether linkages Disappearance of p-coumaric and ferulic acid from lignin Decreased molecular weight	HSQC NMR, Py-TMAH-GC-MS, GPC
Changes in subunit composition	More H and G units Fewer PCA, FA and S units	Py-TMAH-GC-MS, ^{13}C-NMR, HSQC NMR
Condensation	Increased C-C aromatic bond content Increased phenolic hydroxyl content Molecular weight increased after 8 h Increased carbon content	^{13}C-NMR, GPC, HSQC NMR, ^{31}P-NMR, EA

HSQC NMR spectra illustrate the extensive changes in lignin isolated using Ionosolv processing with increasing process severity (**Figure 2**).

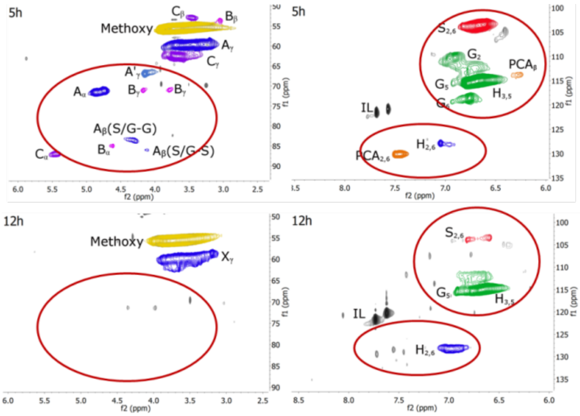

Figure 2. ^{1}H-^{13}C HSQC NMR of lignin isolated using Ionosolv ionic liquids.

Cellulose

The undissolved solid is rich in cellulose (**Figure 3**). Hemicellulose can be completely removed, depending on treatment conditions, and lignin content reduced to below 10% of what it was in the original biomass.

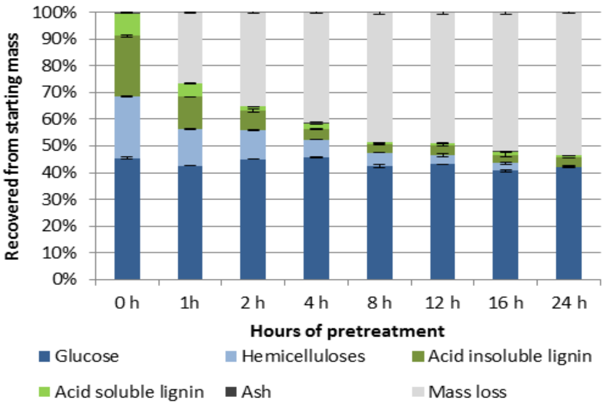

Figure 3. Pulp composition after pretreatment with a triethylammonium hydrogen sulfate solution at 120 °C.

Unlike pretreatment with the cellulose dissolving ionic liquid 1-ethyl-3-methylimidazolium acetate, [Emim][OAc],[6] cellulose after ionosolv treatment retains it's crystalline structure (**Figure 4**), making the pulp fraction an interesting raw material for cellulose materials applications.

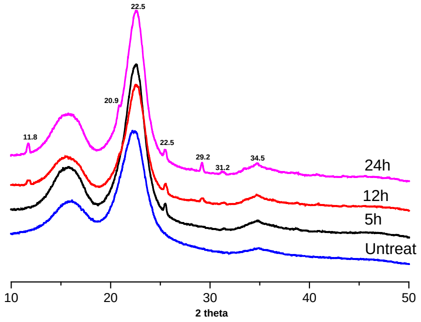

Figure 4. Cellulose crystallinity.

Conclusions

Fractionation of woody biomass using low cost ionic liquid water mixtures has significant promise. It results in efficient separation wood into a crystalline cellulose fraction and a pure, low sulfur content, odour-free lignin without premium cost of the solvent. The application of ionic liquids in a wood fractionation process will result in a number of process benefits such as reduced abrasion due to the liquid’s lubrication properties and early removal of the lignin,[7] in reduced solvent losses and a low pressure process due to non-volatility of the solvent.

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Composites on The Basis of Renewable Raw Materials

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Abstract

The work is devoted to investigation of the composites obtained on the basis of fine dispersive dry leaves and some organic and inorganic binders (phenylethoxysilane, polyethylene, colophony, wood glue and liquid glass). There were investigated the strength at bending, impact viscosity, softening dependence on temperature, water absorption of composites formed by method of hot pressing. It is shown, that the measured physical parameters of these materials essentially depend on their composition - type, concentration and number of binder ingredient. It must be noted that the amount of each binder in the composites is very low (mainly 3-5 wt%, in the separate cases 10 wt %). The numerical data of the measured parameters show that they depend on the composition of the materials differently.

Introduction

Hybrid organic–inorganic nanomaterials with remarkable improvement in properties such as mechanical, thermal, electrical, and magnetic compared to pure organic polymers, are promising systems for a variety of applications due to their extraordinary properties based on the combination of the different building and thus attract a lot of attention during the last years. The most commonly employed preparation procedures for these materials are the use of the sol–gel process for the formation of interpenetrating networks between inorganic and organic moieties [1,2]. The conception on development of the composites based on wood materials leads to idea about application of such materials as wood leaves in composites containing different organic and inorganic binders, as in this case appears the possibility of obtaining of the light and cheap construction material of new generation.

It is known that the leaves mainly contain sufficient amounts of starch, cellulose, hemi-cellulose, and pectin substances, lignin, poly-phenols. All these mentioned above compounds may react with proposed binders. For example phenylethoxysilane (PhES-50 and PhES-80) contains ethoxyl groups. The noted groups participate to the etherification reaction with a leaves through the macro-molecular and intra-molecular reactions.

Processes that occur during the curing are complex and varied. A modern look at an overview of the curing liquid glass itself and in the various homogeneous and heterogeneous systems, the most widely encountered in practice, is presented in a number of works [3-7].

Our work is devoted to obtaining and investigation of the properties and structure of composites based on different woods leaves and some organic and inorganic binders.

Results and discussion

a) Physical-mechanical properties

On the table1 there are presented the numerical data of strength on bending and impact viscosity for composites obtained by us.

Table 1. Physical-mechanical characteristics of the composites based on dry leaves high-dispersive powders with different binders (the composites are obtained at 150 kg/cm^2 and 130 °C).

#	Binder in composite (wt,%)	Strength on bending, kg/cm^2	Impact Viscosity, kJ/M^2
1	LG (3)	12.6	21.2
2	LG (5)	20.9	21.3
3	LG (10)	21.5	20.5
4	LG (15)	14.4	22.4
5	PhES-50 (3)	15.5	22.9
6	PhES-50 (5)	16.3	22.7
7	PhES-50 (10)	11.2	17.7
8	PhES-50 (15)	12.0	17.5
9	PhES-80 (3)	16.7	17.9
10	PhES-80 (5)	17.9	21.0
11	PhES-80 (10)	9.6	22.4
12	PhES-80 (15)	11.9	20.6
13	PE (10)	16.7	23.5
14	PE (15)	17.8	24.5
15	colophony (10)	19.0	18.6
16	colophony (15)	17.0	14.7
17	wood glue (10)	16.9	16.3
18	wood glue (15)	15.9	18.0
19	PhES-80 (3) + LG (3)	13.0	18.0
20	PhES-80 (5) + LG (5)	17.0	21.0
21	PhES-50 (3) + PE (3)	15.0	23.5
22	PhES-50 (5) + PE (5)	16.0	25.0
23	PhES-50 (5) + PE (10)	13.4	21.0
24	PhES-80 (3) + PE (3)	9.0	18.0
25	PhES-80 (5) + PE (5)	16.7	23.0
26	LG (5) +PE(5)	17.0	27.0

#	Binder in composite (wt,%)	Strength on bending, kg/cm^2	Impact Viscosity, kJ/M^2
27	PhES-50 (5) + LG (5)+ PE(5)	13.6	21.0
28	PhES-80 (3) + LG (3)+ PE(3)	14.0	23.0
29	PhES-80 (5) + LG (5) + PE(5)	13.0	21.0

The data of the Table 1 show that the dependences of mechanical properties of the composites containing one binder (liquid glass, PhES-50 and PhES-80) have extreme character - at increasing of the binder concentration the mechanical parameters increase till definite value of them. At more high concentrations the value of these parameters decreases. One of the possible reasons of this phenomenon is the peculiarity of the microstructure of these composites-compatibility of ingredients, which is decreased at relatively high concentrations of the filler. In the last case filler particles create associates (clusters) in polymer matrix and therefore reduce the mechanical properties of materials. Composites, containing the polyethylene (PE) as a binder, are characterized with high to some extent mechanical properties. Such properties of this composite is due to homogenization of the composite blends because of melting of PE at formation of the composite material with followed by the introduction of macromolecules PE empty of leaves structure (physical adhesion). We attempt to increase the mechanical properties of composites by introduction additionally several binders to blend. In accordance with Table 1 data only in some cases this attempt gave the positive results. So, with high impact viscosity (in kJ/M^2) are distinguished composites containing two types of binders 1) PhES-80(5%) and LG (5%) impact viscosity is about 21.0; 2) PhES-80(5%) and PE(5%) - 23.0; 3) PhES-50 (3%) and PE(3%) - 23.5; 4) PhES-50(5%) and PE(5%) - 25.0. With the same values are characterized composites with three types of binders (for example, the impact strength for composite PhES-50(3%) + LG (3%) + PE (3%) is 23 kJ/M^2.

b) Thermal stability. Thermal stability of the obtained composites is reflected on the plots of the Figures 1-3. Analyses of these plots allows us make the following conclusions:

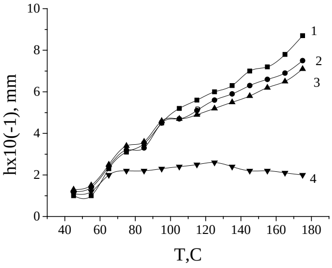

Figure 1. Dependence of the softening (deepening of indentor in the sample) of composites based on leaves and LG (3%) -1, LG(5%) -2, LG (15%) - 3, LG(10) -4 on the temperature.

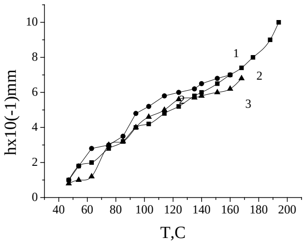

Figure 2. Dependence of the softening (deepening of indentor in the sample) of composites based on leaves and PhES50 (3%) -1, PhES-80 (3%) -2 and PhES80 (5%) - 3 on the temperature.

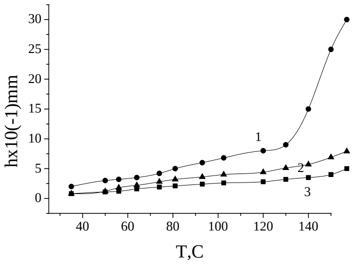

Figure 3. Dependence of the softening of composites based on leaves and wood glue (10%) - 1, wood glue (15%) -2, colophony (10%) -3 on the temperature.

1. The softening of composites based on leaves and liquid glass (LG) increases monotonic at increasing of temperature, but with different rate - the higher binder concentration the lower is this rate (Figure 1). Although this rule breaks the composite containing 10% of LG - the noted dependence essential changes it form, transfers to horizontal line, i.e. saturates. Apparently at this concentration of LG creates the optimal conditions for obtaining of more monolith structure based on leaves particles and LG.
2. Thermal stable properties of the composites with two modification of PhES (Figure 2) little differ one from other, although this property of composite containing PhES-80(5%) is better to some extent.
3. Composites with wood glue and colophony are characterized with good thermal stable properties, at relatively low temperatures (Figure 3). Composite with colophony exhibits better thermal stability in comparison with wood glue, because of it more high compatibility with biopolymer.
4. Skill selection of binder type and it concentration would be right way to achieve the more high thermal stable composites.

c) Water absorption. On the Table 2 there are presented the numerical data of water absorption for composites based on leaves.

Table 2. Water absorption of the composites based on the leaves and different organic and inorganic binders

#	Binder in composite (wt%)	mass, g	density, g/cm^3	Mass after 24 h exposition in water, g	water absorption, %
1	LG (3)	4.8	1.36	5.8	20.4
2	LG (5)	4.9	1.39	6.7	36,8
3	LG (10)	4.7	1.47	7.8	68.1
4	LG (15)	4.8	1.34	5.4	13.9
5	PhES-50 (3)	4.8	1.35	6.9	44.7
6	PhES-50 (5)	4.5	1.35	9.0	99.1
7	PhES-50 (10)	4.8	1.35	8.1	71.0
8	PhES-50 (15)	4.5	1.35	6.9	52.8
9	PhES-80 (3)	4.8	1.36	6.9	44.5
10	PhES-80 (5)	4.6	1.38	7.7	66.6
11	PhES-80 (10)	4.6	1.44	5.7	23.4
12	PhES-80 (15)	4.5	1.41	8.1	80.0
13	PE (10)	4.4	1.32	4.8	7.9
14	PE (15)	4.6	1.31	4.9	27.5
15	Colophony (5)	3.4	1.22	4.8	39.2
16	Colophony (10)	4.7	1.41	5.2	10.8
17	Colophony (15)	4.6	1.43	6.5	41.5
18	Wood glue (10)	4.8	1.49	8.4	77.5
19	Wood glue (15)	4.8	1.43	6.9	43.7
20	PhES-80 (3) + LG(3)	4.6	1.41	5.1	11.3
21	PhES-80 (5) + LG(5)	4.8	142	5.5	13.3
22	PhES-50 (3) + PE(3)	4.3	1.35	4.8	11.9
23	PhES-50 (5) + PE(5)	3.9	1.36	4.6	18.4
24	PhES-50 (5) + PE(10)	4.8	1.28	5.1	7.8
25	PhES-80 (3) + PE(3)	4.8	1.35	5.5	14.5
26	PhES-80 (5) + PE(5)	4.5	1.26	4.7	5.6
27	LG(5) + PE (5)	4.2	1.33	4.5	14.4
28	PhES-50 (5) + LG(5) +PE (5)	4.6	1.38	5.5	17.5
29	PhES-80 (3) + LG(3) +PE (3)	4.5	1.34	4.8	7.6

On the basis of these data it may be made the following conclusions:

1) Water absorption of the systems contained one binder is characterized with display of the extreme dependence of this parameter on the concentration of the binder and are characterized with maximums, the value of which depends on the type of binder. So, if in case of composites, containing 10% of the liquid glass (LG) maximal absorption of water (after 24 h exposition in water) corresponds to near 70% this parameter for composites containing PhES-50, as binder, maximal water absorption reaches to even 99%, but at 5% of this binder. In the case of composites with PhES-80 the

maximal water absorption (80%) appears in composite with 15% of the binder. These results indicate on the creation of porous system (with connected each to other pores) with maximums at definite for the each system concentrations of binder;

2) The obtained results allow establish the best results (minimal water absorption) for considered composites. Such result (14%) are observed in the system leaves+LG at concentration of binder about 15%, while for the system leaves +PhES-50 minimal water absorption (near 20%) corresponds to composite with 20% of binder and for system with PhES-80 (near 24%) to 10% of the binder. Better results were obtained in case of the composites containing the binders with following concentrations : 1) PE(10%), water absorption 8%; 2) PhES-80(3%)+LG(3%)+PE(3%) - 8%; 3) PhES-50 (5%) +PE(10%) - 8%; 4) PhES-80(5%)+PE(5%) - 6%; 5) PhES-80 (5%) + PE (10%) - 8%;
3) Polyethylene in all composites effectively improves the hydrophobic properties of our composites, which is, naturally, must be ascribed to high water resistant properties of PE.

Conclusion

The composites on the basis of leaves and liquid glass, phenethoxysiloxane - PhES-50, 80, wood glue, polyolefin’s, colophony as the binders, have been obtained and their physical-mechanical, thermal stable and hydrophobic properties have been determined. Experimental results indicate the optimal concentrations of ingredients, at which the best results may be obtained. It was shown that from polyolefin’s better properties of composites reach at using of PE.

Acknowledgements

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Development of Enzyme Production Technology for Biorefineries in *Trichoderma Reesei*

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Abstract

Trichoderma reesei is a mesophilic filamentous fungus originally isolated from the Solomon Islands. Soon after discovery it was found to be efficient in the degradation of cellulose and hemicellulose due to its capacity to secrete large amounts of lignocellulolytic enzymes, cellulases and hemicellulases. The enzyme cocktail produced by *T. reesei* is able to degrade polymeric cellulose and hemicellulose into monomeric sugars such as glucose and xylose. *T. reesei* is an important biotechnological workhorse for the industry producing enzymes for various applications such as the production of second generation biofuels from lignocellulosic materials.

The original isolate, QM6a, has been improved by a series of strain development with the emphasis on increased protein production. Mutagenesis followed by screening has led to the isolation of carbon catabolite derepressed strains producing at least 20 times more protein than the original isolate. The whole genome sequence of *T. reesei* and new modern genetic engineering tools such as targeted deletion have led to the generation of a new set of improved production strains for the industry.

Strain development at VTT

The recent work done at VTT has led to the identification of novel genes involved in protein production and this has opened many novel targets for strain improvement. As an example we show here how a series of deletions of proteases identified from the culture media (Landowski et al., 2015) has led to increase in the production of the native cellulases. For production of foreign (hemi)cellulases the reduction of the protease load is even more important than for the native cellulases. Analysis of the *T. reesei* transcriptome with arrays has led to the identification of a novel cellulase gene major regulator, *ace3*, that when overexpressed leads to 3 to 6 fold increase in cellulase production (Häkkinen et al., 2014). Modification of another known transcriptional regulator, Xyr1, with strong activation domains has also led to improvement in cellulase production.

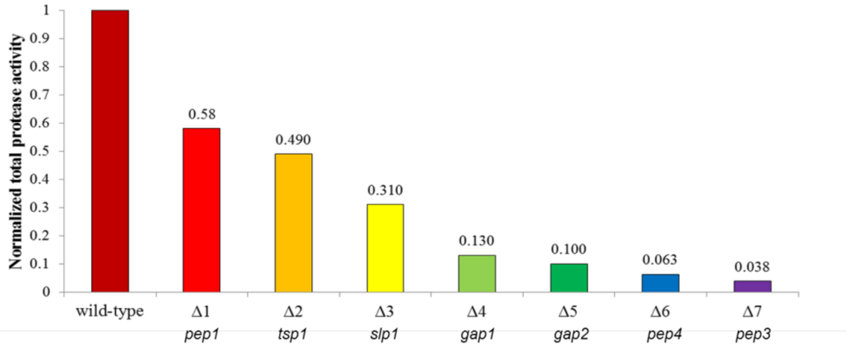

Figure 1. Sequential protease deletions leads to reduce protease activity in culture supernatant. Total protease activity against fluorescent casein substrate was measured from small-scale cultures

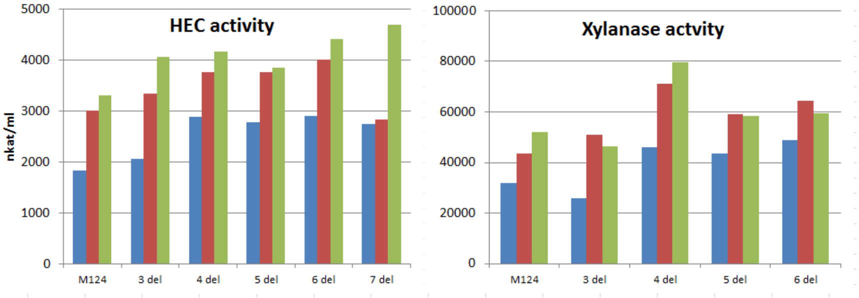

Figure 2. Deletion of protease genes from *T. reesei* strain M124 leads to increase in the production of endoglucanase (measured as HEC activity) and xylanase activities.

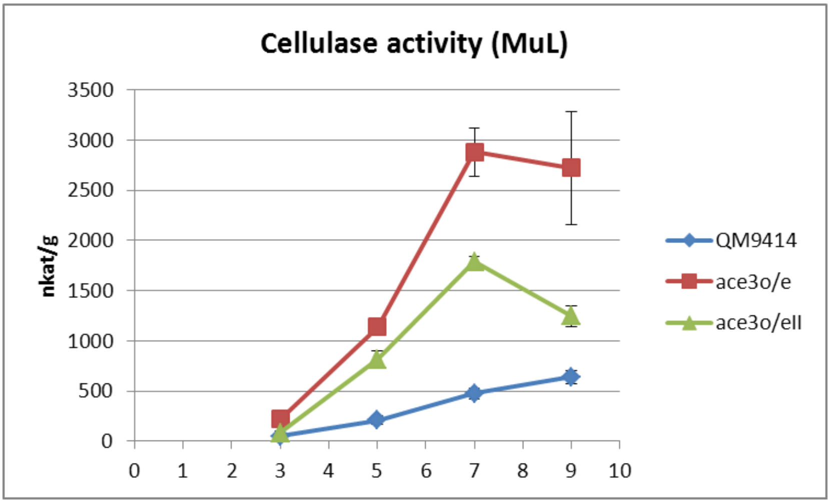

Figure 3. Enzyme production in a shake flask cultivation with a control strain (QM9414) and two transformants over-expresing regulatory factor *ace3* (ace3 o/e).

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Series title and number

VTT Technology 233

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Abstract	These proceedings highlight the latest advances in the wood-based biorefining related R&D&I and form a "snapshot" of the state of the art today. The most discussed topics include lignin based products and sugars; wood fractionation, enzymatic hydrolysis, filtration, and extraction processes; Kraft pulping process integration; and lignin separation from spent cooking liquors.
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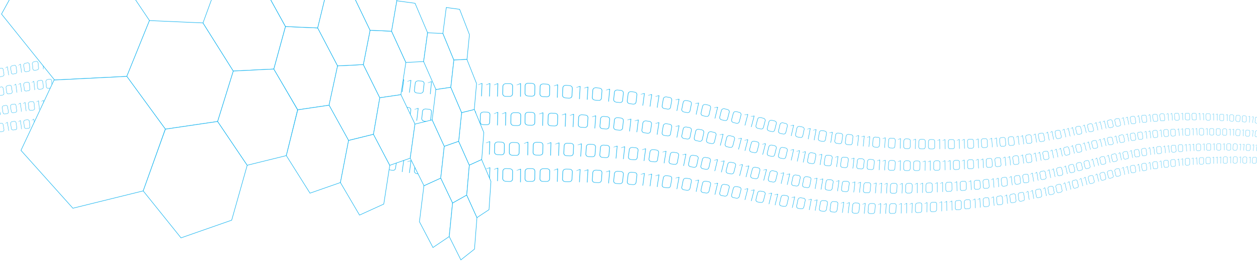

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