Department of Chemical and Metallurgical Engineering

Design and evaluation of biorefinery concepts

Kristian Melin

Aalto University

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Aalto University
School of Chemical Engineering
Department of Chemical and Metallurgical Engineering
Research Group of Plant Design

Supervising professor
Professor Pekka Oinas

Thesis advisor
Docent Markku Hurme

Preliminary examiners
Professor Jukka Konttinen, Tampere University of Technology
Professor Per Alvfors, KTH

Opponents
Doctor Gonzalo Guillén Gosálbez, Centre for Process Systems Engineering, Imperial College of Science, Technology and Medicine, UK and Professor Jukka Konttinen, Tampere University of Technology

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Abstract

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Kristian Melin

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Abstract

When new biorefinery processes are developed, certain challenges are encountered during the research and development stage. There are multiple possible production routes to select from but due to limited information available at this stage it is difficult to assess the reasoning of the selected route especially when it concerns environmental and economic issues.
In this thesis, a new modelling approach for this problem was developed. This new method can be used to design, evaluate and select process alternatives in research and process development, thus enhancing process development by enabling making more informed decisions earlier.
Firstly, multiple lignocellulosic raw materials, for example those based on wood biomass or straw, and processes were evaluated based on the maximum product yield of the main product for each raw material. Secondly, the best processes were selected for analysis of main and side product energy yields, greenhouse gas (GHG) emission reductions and net present values (NPV), using simplified flowsheet models based on maximum heat recovery. Thirdly, the previous calculations were repeated for the selected processes employing rigorous flowsheet models.
At the first modelling level, calculated energy yield of main product was employed as the preliminary indicator, and showed satisfactory accuracy. At the second and third modelling levels the differences of the indicators in main and side product energy yields, differences in GHG emission reductions and NPV are relatively small. The indicators based on second level models can in most cases be used in the early phase of process development.

New process concepts that utilise separate lignin and carbohydrate fraction processing, including enhanced methanol and synthetic natural gas and hydrocarbon production, were developed by employing the modelling approach described. They were compared with conventional processes, such as methanol and synthetic natural gas (SNG) production, including combined biochemical ethanol and methanol production via lignin residue. Among the novel processes, hydrocarbon production utilising external low-temperature heat gave the highest product yield, 72.5 %, the highest GHG reduction per year and the lowest costs of GHG reduction when the produced biofuel substitutes fossil fuel. Integration to pulp and paper plants or stand-alone pulp mills was found advantageous since the processes could utilise unused heat, unused bark and the separated lignin from chemical recovery from the pulp mill. The novel processes could be run in two modes: either using external heat and power available in summer from solar economy sources, or self-sufficiently in winter. The processes studied are at an early development stage. Therefore, the performance of the novel processes should be verified with a larger scale experimental study.

Keywords Biorefineries, lignocellulosic biofuel production, techno-economic evalution, process modelling

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Tiivistelmä

Kun uusia biojalostusprosesseja kehitetään, tutkimusvaiheessa on haasteena mahdollisten tuotantoreittien suuri lukumäärä. Tuotantoreitin järkevyyttä kustannusten ja ympäristön kannalta on kuitenkin silloin vaikea arvioida, koska arviointiin tarvittavia tietoja on rajallisesti saatavilla. Työssä kehitettiin monivaiheinen mallinnus- ja arviointimenetelmä, jonka avulla voidaan valita prosessivaihtoehtoja. Tämä tehostaa prosessikehitystä, koska tällöin tietoon perustuvia päätöksiä voidaan tehdä jo tutkimus- ja kehitysprosessin aikana. Ensiksi, useita lignoselluloosapohjaisia raaka-aineita, esimerkiksi puu ja peltobiomassaa, ja prosesseja arvioitiin maksimituotesaannon perusteella. Toiseksi, maksimituotesaannoltaan parhaat prosessivaihtoehdot valittiin jatkotarkasteluun perustuen yksinkertaistettuihin flowsheet-malleihin, joilla laskettiin prosessin maksimaaliseen lämmön talteenottoon perustuen pää- ja sivutuotteiden energiasaannot, kasvihuonekaasupäästövähenemät ja nettonykyarvot. Kolmanneksi, parhaat vaihtoehdot edellisestä vaiheesta valittiin jatkotarkasteluun, jossa edellisen vaiheen laskelmat toistettiin käyttämällä tarkempia flowsheet-malleja. Ensimmäisellä mallinnustasolla käytetyllä prosessin suorituskykykriteerillä, päätuotteen energiasaannolla, tarkkuus oli tyydyttävä. Ero toisella ja kolmannella mallinnustasolla laskettujen tulosten välillä, joita olivat pää- ja sivutuotteiden energiasaannot, kasvihuonekaasupäästövähenemät ja nettonykyarvot, oli suhteellisen pieni, jolloin toisen mallinnustason arvojen tarkkuus oli useimmissa tapauksissa riittävä prosessikehityksen alkuvaiheen arviointitarpeisiin.

Työssä kehitettiin myös uusia prosessikonsepteja käyttäen kehitettyä mallinnus- ja arviointitapaa. Nämä prosessikonseptit olivat parannettu metanolin, synteettisen maakaasun sekä hiilivetyjen tuotanto ja ne perustuivat ligniinin ja hiilihydraattien erilliskäsittelyyn. Uusia prosesseja verrattiin tunnettuihin prosesseihin, esimerkiksi metanolin ja synteettisen maakaasun tuotantoon sekä yhdistettyyn etanolin ja metanolin tuotantoon ligniinijäänteestä. Uudessa hiilivetyjen tuotantoprosessissa hyödynnettiin ulkopuolista lämpöä ja siinä saavutettiin korkein energiahyötysuhde alemman lämpöarvon suhteen, 72,5 %, alhaisimmat tuotantokustannukset, suurimmat kasvihuonekaasupäästövähenemät sekä matalimmat kasvihuonekaasupäästövähennyskustannukset. Prosessien integrointi yhdistettyyn paperi- ja sellutehtaaseen tai erilliseen sellutehtaaseen havaittiin ihanteelliseksi, koska tällöin prosesseissa oli mahdollista hyödyntää sellutehtaasta saatavaa hyödyntämätöntä lämpöä, puunkuorta ja kemikaalikierrosta erotettua ligniiniä. Uusia prosesseja voidaan operoida kahdella tavalla, joko talvella energiaomavaraisesti tai kesällä käyttämällä saatavilla olevaa ylimääräistä energiaa, esimerkiksi aurinkoenergiaperäistä lämpöä ja sähköä. Kehitetyt prosessit ovat varhaisella kehitysasteella, joten prosessien tehokkuutta tulisikin verifioida suuremman mittakaavan kokeissa.

Avainsanat Biojalostamot, lignoselluloosapohjaiset biopolttoaineet, teknis-taloudellinen arviointi, prosessimallinnus

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Sammandrag

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Författare
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Sammandrag

När nya bioraffinaderikonsept utvecklas är ett problem att det finns ett stort antal möjliga processalternativ och mängden tillgänglig information för evaluering av processrutter från ekonomisk och miljösynpunkt är begränsad.

I detta arbete utvecklades en modelleringsmetod och bedömningsmetod, som effektiverar processutvecking eftersom mera informerade beslut kan göras redan i processutvecklingskedet. Först granskades flera lignocellulosa-baserade råmaterial som härstammar från skog eller åkermark och processer på basen av maximalt utbyte för huvudprodukten. Bästa processalternativen valdes för vidare beräkning med förenklade flowsheet modeller baserade på maximal värmeintegrering. I beräkningarna ingick beräkning av energiutbyten av huvudprodukter och biprodukter, reduktion av växthusgaser och nettonuvärde (NPV). De valda processerna analyserades igen med noggrannare processmodeller. På första modelleringsnivån användes huvudproduktens energiutbyte som en preliminär indikator för processens prestation med nöjaktig noggrannhet. Skillnaderna mellan beräknade värdena för andra och tredje modelleringsnivån i indikatorerna som beskrev processen prestation d.v.s. utbyte av huvud och biprodukter, reducering av växthusgaser och nettonuvärde (NPV) var relativt små. Därför kunde prestationsindikatorerna räknade med andra modelleringsnivån processmodeller i de flesta fall användas i ett tidigt skede inom processutveckling.

Genom att använda den utvecklade modelleringsmetoden utvecklades också nya process koncept optimerad produktion av metanol, syntetisk naturgas eller kolväte, som grundade sig på separat konvertering av lignin och kolhydrater. Dessa jämfördes med konventionella processer för metanol, syntetisk naturgas produktion och kombinerad etanol och metanol produktion från lignin resten. Bland de nya processerna som studerades, hade kolväteproduktionsprocessen som utnyttjade inmatad värme från omgivningen, det högsta utbytet av 72,5 % högsta minskning av växthusgaser and lägsta kostnad av minskning av växthusgaser. Integrering till kombinerade eller enastående massa -och pappersbruk visade sig vara gynnsam eftersom processerna kunde använda tillgänglig värme, bark och avskild lignin från återvinningen av kemikalier vid cellulosafabriker. De nya processerna kunde opereras i två tillstånd, antingen utan inmatad energi från omgivningen på vintern eller på sommaren med inmatning av t.ex. solbaserad värme eller el.

Processerna är i ett tidigt utveckligsskede och därför borde resultaten verifieras med experiment i större skala.

Nyckelord Bioraffinaderier, tekno-ekonomiska beräkningar, lignocellulosa-baserade biobränslen, processmodellering

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Contents

This thesis consists of articles I-V and some original material

List of publications

I Melin K., Hurme M. Biorefining Route Assessment by Multilevel Modeling, *20th European Symposium on Computer Aided Process Engineering: Computer-Aided Chemical Engineering,* **28,** Pierucci S., Ferraris G. B., Elsevier, Ischia, Naples, Italy (2010) 1745-1750, ISBN(CD): 978-0-444-53718-8.

II Melin K., Hurme M. Evaluation of Lignocellulosic Biomass Upgrading Routes to Fuels and Chemicals, *Cellulose Chem. Technol,* **44** (2010) 117-137.

III Melin K., Hurme M., Parviainen K. Efficient Integration of Biofuel and Chemical Production Processes with Pulp Mills and Energy Production, *Chemical Engineering Transactions,* **25** (2011) 977-982., http://www.aidic.it/cet/11/25/163.pdf

IV Melin K., Kohl T., Koskinen J., Hurme M., Performance of Biofuel Processes Utilising Separate Lignin and Carbohydrate Processing, *Bioresource Technology*, **192** (2015) 397–409.

V Melin K., Kohl T., Koskinen J., Hurme M., Enhanced Biofuel Processes Utilizing Separate Lignin and Carbohydrate Processing of Lignocellulose Biofuels, *Biofuels,* 7 (2016) 21-36.

Author’s contribution

Paper I.	The author created the simulation models, made all the calculations and wrote the paper together with M. Hurme.
Paper II.	The author created the simulation model, made all the calculations and wrote the paper. The draft of the paper was first written by the author and then edited under the supervision of M. Hurme.
Paper III.	The author created the simulation model, calculated the mass and energy balances including the power production and wrote the draft of the paper. The paper was then edited under the supervision of M. Hurme, and K. Parviainen commented the paper.
Paper IV.	The author invented the novel processes concepts, created the simulation models, calculated the mass and energy balances including the power production and calculated the process key performance criteria. The author wrote the draft of the paper while the editing of the paper was done under the supervision of M. Hurme, and T. Kohl commented the paper.
Paper V.	The author created all the simulation models, calculated the mass and energy balances and the process key performance criteria. T. Kohl contributed to the power production calculations and commented the paper. The author wrote the paper and the editing of the paper was done under the supervision of M. Hurme.

List of abbreviations

ABE	Acetone butanol ethanol
AFEX	Ammonia fibre expansion
APR	Aqueous phase reforming
ASU	Atmospheric separation of oxygen
CHP	Combined heat and power
DME	Dimethyl ether
ENHHC	Enhanced hydrocarbon production by APR
ENHMEOH	Enhanced methanol process
ENHSNG	Enhanced synthetic natural gas production
ETBE	Ethyl tert-butyl ether
ETOH	Ethanol
FAME	Fatty acid methyl ester
FCI	Fixed capital investment
FT	Fisher-Tropsch
GHG	Greenhouse gas emissions
GHSV	Gas hourly space velocity
GWP	Global warming potential
HHV	Higher heating value or gross heating value
HMF	Hydroxymethylfurfural
HP	High pressure
IRR	Internal rate of return
ISI	Inherent safety index
LCA	Life cycle analysis
L&G	Liquid and gas
LHV	Lower heating value or net heating value
LNG	Liquefied natural gas
MEOH	Methanol
MTG	Methanol to gasoline
MTHF	Methyl tetrahydrofuran
MTO	Methanol to olefins
NOx	Nitrogen oxides NO and NO2
NPV	Net present value
NREL	USA’s national renewable energy laboratory
P&P	Paper and pulp
ROI	Return on investment
RWGSR	Reverse water gas shift reaction

SHE	Safety health environment
SNG	Synthetic natural gas
SSF	Simultaneous saccharification and fermentation
STDAV	Standard deviation of absolute values
TEG	Tetra ethylene glycol
WGSR	Water gas shift reaction
ZSM	Zeolite

Symbols

a	case a subcase
b	case b subcase
a_f	Annuity factor
A_v	Average value of the absolute values of differences
C_i	Cost of a item
C_{cost}	Production cost of a product
C_m	maintenance cost
D	Difference
FCI	Fixed capital investment
GHG_{sav}	GHG emission savings
i	internal rate
E_i	Produced amount of biofuel or other product by energy
fs	una cost present value factor
n	Capacity exponent of plant
p	primary energy factor
S_i	Plant capacity
t_{op}	Annual operation time of plant
α	chain growth probability or the probability in Fischer-Tropsch reaction
η	Energy fraction in production compared with raw material
η_p	Primary energy efficiency

1. Introduction

The use of biofuels such as ethanol for car engines and chemicals is not new. As early as 1820, Samuel Morey, who created the world's first combustion engine and the German inventor Nicholas Otto in 1860, both used ethanol as fuel in their engines (Anon, 2017). Also, many chemicals were produced from lignocellulosic biomass such as acetone, acetic acid and butanol. There was a whole chemicals industry based on wood. Many of the old processes were inefficient in terms of process yield and energy consumption. Later, when new processes from cheap oil or natural gas feedstock were developed, the wood chemical industry could not compete (Haynes 1947).

Recently, there has been a strong interest in using renewable energy and biofuels. Firstly, the world population is growing and oil reserves are limited. Global energy consumption will increase significantly. At the same time, the recovery of oil is becoming more costly as the reserves are being depleted. Therefore, unconventional energy sources need to be developed. In addition, energy security is seen as important, especially in an uncertain politic climate.

Secondly, greenhouse gas (GHG) emissions are increasing. The levels of carbon dioxide around the globe have been increasing steadily since pre-industrial times. The new Intergovernmental Panel on Climate Change Fifth Assessment Synthesis Report (IPCC 2014) states that the human effect on climate change is clear and carbon dioxide emissions caused by man are bigger than ever. Also, the globally-averaged land and surface water temperature has increased by 0.85 °C during 1880 to 2012.

Biomass is one source of renewable energy but it is also a feedstock for producing chemicals, materials or fuels. First generation biofuels made from field-based renewable sources have been produced traditionally from grain, maize, corn or oil crops. However, as only the grain from the crop is used, a large land area is required. Additionally, the process inputs, especially fertilisers, are problematic. Especially in cold climates, it is questionable whether these first generation biofuels will help to reduce greenhouse gas emissions. Kajaste (2014) has reviewed greenhouse gases in the biorefinery production chain. It can be seen that first generation ethanol from grain or sugarcane can have a much higher greenhouse gas emission than from 2nd generation feedstock (i.e. lignocellulosic biomass).

In the analysis, also all the fossil inputs such as hydrogen produced from natural gas should be considered since these can have a great effect on greenhouse gas emissions and the biofuel product yields.

The challenge in the production of new raw materials is the more complicated and costly production technology, which means higher risk for investors. A combination of unfavourable economics and the risk of legislation changes has slowed down the development in the biofuel area. Yet the mandate to blend a certain percentage of biofuel in diesel and gasoline in EU has created a demand for biofuels. Furthermore, in the Renewable Energy Directive (EU 2015) it is specified that biofuel from new production plants has to have from 2018 at least 60 % lower carbon footprint compared with fossil fuel that it is replacing.

The economics of 2nd generation biofuels is a key challenge and there is a need for new technology that could reduce production costs. Lignocellulosic biomass in the global perspective is also a limited resource that needs to be utilized effectively together with other forms of renewable energy. The total sustainable worldwide biomass energy potential including woody biomass, energy crops and straw biomass is 270 EJ/a, which is about 50 % of the total global energy consumption today (Ladanai and Vinterbäck, 2009). Feasible biofuel production needs to fulfil several criteria. From a techno-economic point of view, it should help to reduce greenhouse gas emissions, be economically viable, and use the raw materials efficiently.

Recently, it has been discussed if using Nordic slow growing forest for energy purposes is sustainable from greenhouse gas reduction point of view. The problem is that growing forest acts as a carbon sink, and harvesting roundwood from growing forest for energy products usually only gives GHG emission reductions in the long time perspective, such as 80 years. On short term, the growing forest uptakes more CO_2 than would be the total CO_2 reduction in case it was used for energy production that replace use of fossil fuels. Using fast-decaying residual biomass either from harvests or from industrial processes is often a preferable option, as the residues would in any case release their carbon content quite rapidly if left to decay. In this case GHG emission reduction can be reached already on shorter timescales (e.g. 20 years).
(Koponen et al., 2015)

One way to make the economics of biofuel production more profitable is the biorefinery concept, i.e. many products are produced instead of one. For example, the old sulphite mill in Borregaard (2017) utilizes each fraction so that maximum value is obtained for valuable products; specialty cellulose, ethanol, lignosulphonate etc. Of course, the challenge is to sell many different products to sometimes relatively small markets compared with those for fuel products. There has also been interest in the chemical industry in producing chemical products from renewable feedstock, for example bio-ethylene from ethanol, biopolymers from lactic acid etc. In a biorefinery, the material that cannot be utilized in other ways is usually combusted in order to produce heat and power for the process. Integration is therefore an important aspect since biofuel, chemical production is often integrated with a pulp mill, or power plant or the raw material might even originate from the integrated plant.

When lignocellulosic biomass is converted into fuel and petrochemicals, the challenge is to find out which products and processes are feasible for each raw material. There are numerous alternatives. For example, synthesis gas produced by gasification of lignocellulosic biomass can be converted into products in a similar way as from synthesis gas derived from natural gas. In addition, the sugars obtained from biomass can be converted into any product by fermentation or through chemical reactions.

At the beginning of a feasibility study or design project, it is easy to make conceptual changes at low cost. However, there is not much information available on the production process producing for example fuel, which is required to assess process performance. For example, process equipment dimensioning is missing and many physical parameters used for process design may be unavailable or uncertain. Therefore, especially for biorefineries with many possible products and production routes, an enhanced approach is needed which enables fast screening of large number of alternatives to be later analysed in more detail by rigorous methods. This will also focus process development and design on the most critical aspects affecting performance.

1.1 Objectives of the study

The aim of this thesis is to evaluate lignocellulosic biorefinery concepts where biofuel, chemicals, heat and power are produced from lignocellulosic materials such as wood and agricultural residues. The evaluation is performed in different level of modelling, scope and indicators so that the most interesting processes in the preliminary studies are selected for a more rigorous further analysis. This enables screening of a large number of process routes and raw materials. Conclusions are drawn on how the various stage evaluations compare and what the reasons for the differences are. A hypothesis is presented that the separate processing of the biomass components i.e. lignin and carbohydrates, would be more efficient than their combined processing, or the recovery of just one material fraction. For this approach, novel pathways based on separate lignin and carbohydrate processing have been developed and evaluated.

Paper I. The paper presents a novel approach for multilevel modelling and optimization of biorefining routes and raw materials to be used in preliminary evaluations. The modelling levels of biorefining processes are discussed. The databank requirements for extending a conventional process flowsheeting simulator to incorporate biomass components are described.

Paper II. The paper discloses evaluation of the different biofuel and chemical production routes for multiple raw materials at the 1st level (material balance) and what key performance criteria at this stage that can be used?

Paper III. The paper describes how the feasibility of processes at the 2nd level can be evaluated with a conceptual flowsheet during R&D and the site integration of the process checked with pulp &paper mills or CHP plants. The minimum energy consumption, potential to produce power, and power consumption can be estimated.

Paper IV. The paper describes how evaluation of product routes at the 2nd level can be done with a conceptual flowsheet and maximum heat integration. New process concepts based on separate lignin and carbohydrate fraction processing are presented. These are compared to conventional routes with 2nd level models and literature data.

Paper V. The paper describes how more rigorous evaluation of novel and established biorefinery processes at the 3rd level with flowsheet simulation and realistic process integration can be done. The models include heat and power production and auxiliary units.

As a whole, the papers present new process concepts based on separate lignin and carbohydrate part processing and discuss how process concept screening can be done by various levels of modelling and evaluated in the early development and pre-design stages. Furthermore, the papers show how the evaluation improves in accuracy and presents the sources of uncertainties and inaccuracies.

In this study the level of the models used in the articles are shown in Figure 1. Here the modelling levels are the following:

1) Simple material balance models (no energy balance; typically spreadsheeting)
2) Flowsheeting with shortcut models (material & energy balance)
3) Flowsheeting with rigorous models (material & energy balance)
4) Specialized models suitable for special purposes such as scale-up of processes (detailed phenomena-based model)

The integration scope levels are the following:

1) No energy integration
2) Heat integration in process unit

3) Inclusion of heat and power production (e.g. CHP)
4) Inclusion of other plants on the site (e.g. pulp plant) besides the CHP unit
5) Inclusion of community (e.g. district heating and other energy systems)

This work is focussing on selecting feasible concepts for further development; therefore, the emphasis is on the levels 1-3. The modelling methods are discussed in more detail in the Chapter 6.11.

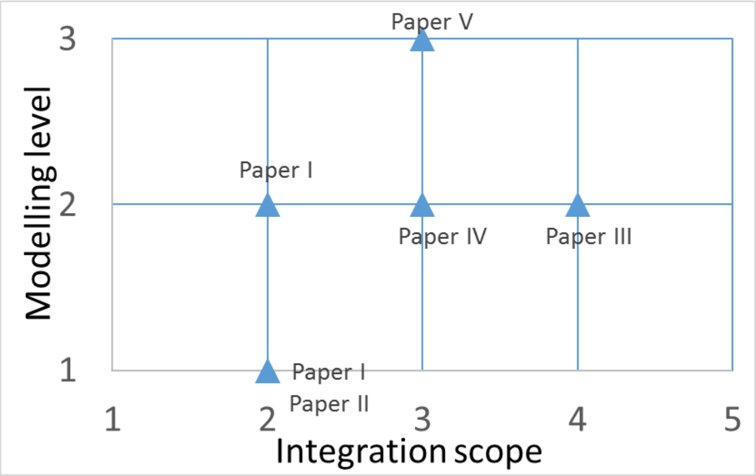

Figure 1. The modelling levels and scope of the articles in the thesis.

2. Characterisation of biomass

Lignocellulosic material consists of cellulose, hemicellulose, lignin, extractives and ash. Cellulose consists of monosaccharides, mainly glucose. Hemicellulose consists of several monosaccharides: typically mannose, glucose, galactose, xylose and arabinose, which vary depending on the biomass (Hamelinck et al., 2005). The monosaccharides can be classified into hexoses (C6) that contain six carbon atoms including glucose, galactose and mannose and pentoses (C5) including xylose and arabinose that contain five carbon atoms. The sugar content determine the theoretical maximum product yields when biomass is converted into product by biochemical processes.

One way to characterize the feedstock is by ultimate analysis, i.e. a fraction of each atomic species. The most common atomic species in biomass are carbon, hydrogen and oxygen. Biomass also contain some sulphur, nitrogen, and ash. The ash mainly contains metals salts including calcium and potassium. Typically, biomass has a low energy density for two reasons, it has a high oxygen content and it contains absorbed water as moisture. The energy content of biomass is typically determined by measuring the heat of combustion or estimated by correlation based on the ultimate composition (Sheng and Azevedo, 2005). The ultimate composition and heating value will determine the performance of biomass in gasification. Practically, forest biomass used for fuel or energy production is in the form of small wood, logging residues and stumps. In addition, agricultural residues such as wheat straw and bagasse were studied in Paper II. Lal (2005) compared the potential of agricultural residues and concluded that one has to be careful not to remove too much agricultural residue since it will decrease the soil organic content and reduce the yield in the long term. McKendry (2002) reviewed energy and other biomass crops available for energy production. For example, Miscanthus, commonly known as Elephant grass, has been identified as a highly interesting fuel crop, providing an annual crop, being easy to grow and harvest, and when harvested giving a high dry matter yield.

Some raw materials such as wheat straw are more challenging in gasification as the ash becomes soft and melts at low temperature that material such as wood with higher ash melting temperature. In gasification the feedstock and typically steam or oxygen are heated to high temperatures (750-1300 °C) and converted into product gas. The product gas consists mainly of carbon monoxide and hydrogen, and this process is discussed in more detail in Chapter 3.11. Other important variables are the heating value, the ultimate composition, i.e. composition of different elements, and sugar composition affecting yeast or bacterial fermentation.

A third way to characterize raw material is the molar hydrogen/carbon ratio and oxygen/carbon ratio, also called van Krevelen diagrams (Gabrieli and Ruther, 2007, p.122). The lower the O/C ratio and the higher the H/C ratio, the higher the energy content of the fuel. The biomass species are studied in Paper II based on the sugar/lignin vs. C5/C6 sugar ratio in Figure 2 and based on elemental ratios in Figure 3. It can be seen that the softwoods pine and spruce are in one end of the diagrams and hardwood birch in the other end.

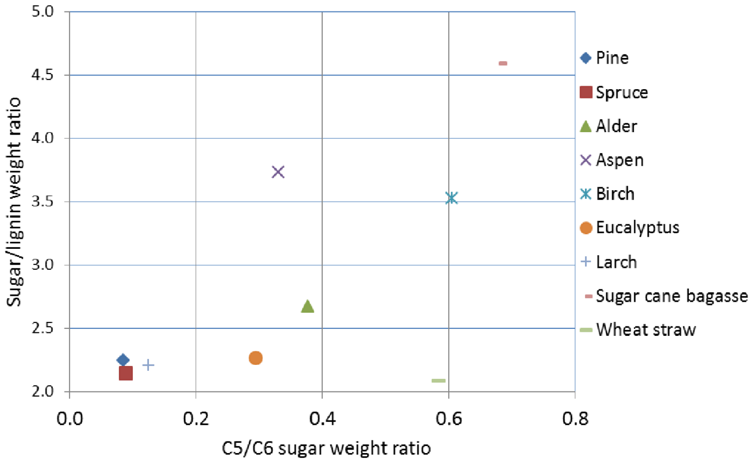

Figure 2. Biomass sugar/lignin vs. C5/C6 sugar weight ratios (data from Paper II, with updated data shown in Table C in Appendix).

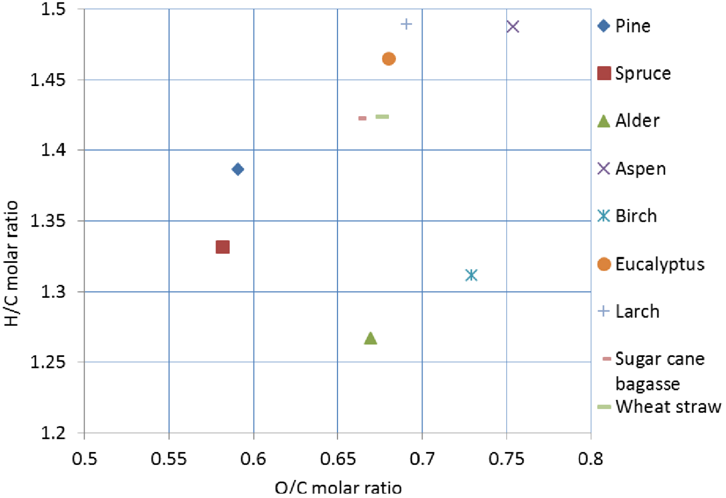

Figure 3. Biomass H/C vs. O/C molar ratios (data from Paper II with updated data shown in Table C in Appendix).

3. Biomass conversion into fuel and petrochemicals

All the biomass can be processed directly by gasification or pyrolysis into intermediates or first fractionated for example, into a carbohydrate and a lignin rich fraction. Each fraction can separately be processed further into final products.

3.1 Thermochemical processing of biomass

The typical thermal processes used for biomass are pyrolysis and gasification, which are characterised by different processing temperatures, residence times and product yields (Table 1).

Table 1. Typical yields of products obtained by thermal treatment of biomass at various reaction conditions (Ronsse et al., 2012).

Process	Solid	Liquid	Gas
Partial pyrolysis (torrefaction) low temperature (250 -280°C) medium residence time (minutes)	**75 wt%**	20 wt%	5 wt.
Slow pyrolysis (carbonization) low temperature (350-450°C) long residence time (hours)	**35 wt%**	30 wt%	35 wt%
Fast pyrolysis (liquefaction) medium temperature (400 to 600°C) short residence time (seconds)	12 wt.%	**75 wt%**	13 wt%
Gasification high temperature (750 to 1350 °C) variable residence time	10 wt%	5 wt%	**85 wt%**

3.1.1 Gasification and utilisation of synthesis gas

Gasification

A common way to utilize biomass is to produce synthesis gas by gasification of dried biomass at high temperatures (around 800 °C), using oxygen or steam. Alternatively, gasification can be performed directly without drying for aqueous products such as black liquor, cellulose sludge or algae under supercritical water conditions. Water reacts as a reagent at supercritical conditions and no drying of biomass is necessary, for example, Zöhrer et al. (2014) have demonstrated gasification of wet residues from biogas production.

The raw material for conventional gasification can be any kind of lignocellulosic biomass. However, with a lower heating value and high oxygen content biomass, less of the chemical energy is converted into synthesis gas energy when compared to feedstock with a higher heating value (e.g. coal). When oxygen containing or low heating value feedstock such as wood is gasified in order to reach the gasification temperature, biomass needs to be over-oxidized, i.e. in addition to carbon monoxide and hydrogen also carbon dioxide is produced. This is due to the higher amount of oxygen, originating both from the feedstock and fed oxygen, being present in the gasifier (Prins et al., 2007). Gasification can be done directly: oxygen or air and steam is fed to the gasifier in order to keep the temperature at the desired level (autothermal gasification) of around 800 °C. The disadvantage with air is that the nitrogen present will dilute the synthesis gas. Another way is indirect or allothermal gasification, where the carbon residue left from the gasification is burned to satisfy the energy demand of the process. Rauch et *al.* (2014) reviewed different gasifier technologies, usages of syngas and the status of gasification projects. Black liquor from pulp production can also be gasified. A review about black liquor gasification was done by Naqvi et al. (2010).

A typical scheme for synthesis gas production from biomass is shown in Figure 4. The biomass is first chipped and dried typically to 10-20 wt% moisture content. The gasifier shown here is a direct gasifier where oxygen and steam are fed to the gasifier. The oxygen needed in the gasifier is produced from air, typically by liquefying air and separating oxygen from nitrogen. This requires a significant amount of electricity. The gas from gasification contains ash and char particles that are separated with a cyclone and ash filter. The formed tar components and possibly methane are reformed into carbon monoxide and hydrogen. Typically, the syngas has too small a H_2/CO ratio for subsequent use. Therefore, the ratio needs to be adjusted by water gas shift reaction at 250-400 °C. Synthesis gas and steam can be also converted by shift reactions into hydrogen and carbon dioxide. The so-called ‘dirty shift’, which tolerates a volume of H_2S of several hundred ppm, can be employed before gas cleaning (Kurkela and Simell, 2008). Often the gas is washed in order to remove H_2S, CO_2, NH_3, HCN and often also COS. The absorption medium can be for example amines, Selexol or cold methanol (Rectisol). The absorption medium has typically to be regenerated using steam and pressure reduction.

In biomass gasification, not only light gases (CO, CH_4, CO_2 and H_2) are formed but also heavier decomposition products, ranging from ethylene to heavy aromatics. The tars and also possible methane can be removed by employing catalytic reforming at high temperature (McKeough and Kurkela, 2008) or scrubbing at low temperature.

Impurities such as H_2S, COS, NH_3, alkali metals and HCN described in more detail by (Spath and Dayton, 2003, p.9) need to be removed to convert the synthesis gas by catalysts into different fuels and chemicals. The majority of carbon dioxide can also be removed. Finally, the highly purified synthesis gas is compressed to the pressure required for further chemical synthesis.

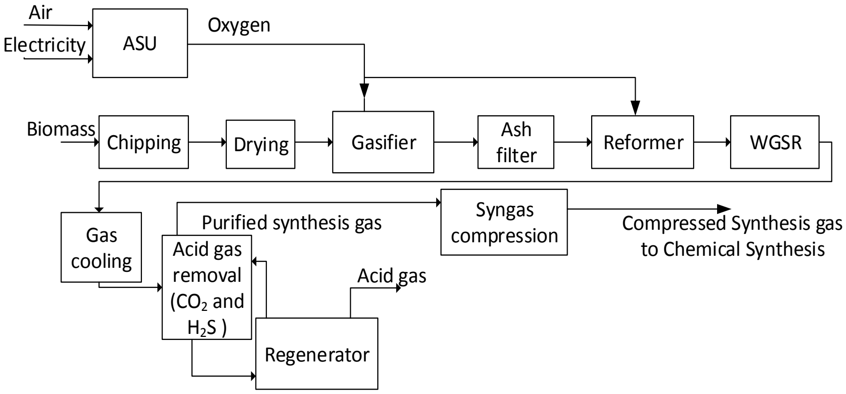

Figure 4. Modified block diagram of biomass for a gasification plant producing synthesis gas based on Simell et al. (2014).

Utilization of Synthesis Gas

Synthesis gas, also known as syngas, can be used in numerous applications for both fuel and chemicals production. The conversion of synthesis gas typically involves chemical synthesis at elevated temperatures and pressures. Subsequently, the reaction products, such as methanol, are separated from the syngas by cooling and condensation so that unconverted reaction products are recycled back to the reactor feed. Some of the gas needs to be withdrawn as purge gas to prevent build-up of inert components. Finally, the products are purified to final purity by removing undesired components such as water. This can be done by distillation or by drying a gaseous product with a medium that absorbs water.

Methanol for example can be produced by catalytic reaction from synthesis gas. Many of the chemical syntheses require highly pure gas and therefore the synthesis gas has to be cleaned of the following impurities: H_2S, COS, NH_3, HCN, chlorides, tars etc. (Spath and Dayton, 2003).

Since the H_2/CO ratio in syngas is usually too small for methanol synthesis, water gas shift is employed to increase the ratio. A possible pretreatment to reduce the tar amount before synthesis is presented by McKeogh and Kurkela (2008).

Methanol synthesis can be carried out in various ways. Examples of low-pressure processes include the ICI process, using a copper oxide catalyst at 50-100 bar (Rogerson, 1970). Recently, various optimized concepts with increased pass-to-pass conversions have been developed such as isothermal operation and even liquid phase operation (Spath and Dayton, 2003)

Dimethyl ether (DME) is another fuel that can be obtained from syngas, with properties similar to liquefied petroleum gas. It can be used as diesel, but it requires an infrastructure suitable for liquefied gas. Synthesis gas can be converted directly into DME, with a dual function catalyst, through methanol synthesis, shift and the DME synthesis reactions. When the DME reaction is performed simultaneously with methanol synthesis, the equilibrium in the methanol reaction is shifted towards the product. Therefore, by this route, a much higher conversion is achieved and lower pressure can be used than by methanol synthesis. (Kaneko, 2009).

Gasoline can be manufactured from DME or directly from methanol by the methanol to gasoline (MTG) process with a ZSM-5 catalyst (Philips et al., 2011). Methanol can also be converted into olefins in the methanol to olefins (MTO) process, as described by Sha et. al. (2015).

Alternatively, synthesis gas can be converted into hydrocarbons by the well-known Fischer-Tropsch (FT) process, used in Germany during the Second World War to produce synthetic gasoline. FT synthesis is a non-selective process producing a wide range of hydrocarbons with 1 to 100 carbons. Iron and cobalt catalysts are mostly used. The FT process is operated both at high temperatures (330-350 °C), for the production of gasoline and light olefins, and at low temperatures (220-250 °C), for the production of waxes and diesel (Kaneko, 2009). FT synthesis was traditionally done in circulated fluidized bed reactors but more recently, slurry reactors or tubular fixed bed reactors have been mostly used (Spath and Dayton, 2003) The high molecular wax can be hydrocracked and isomerized in an oil refinery into high quality diesel fuel, lube oil and naphtha, which can be cracked into olefins.

Synthesis gas can also be converted into methane (synthetic natural gas; SNG). Carbon monoxide and dioxide are converted with hydrogen, by e.g. nickel catalyst into methane and water (Hiller, 2009). The process is also used for hydrogen or ammonia production to remove the remains of carbon monoxide from hydrogen. The reaction is strongly exothermic. SNG can also be produced by fluidized bed technology in one stage (Kopyscinski et al., 2010).

3.1.2 Pyrolysis utilisation of pyrolysis oil and torrefaction

When biomass is treated thermally without oxygen the yield of products varies depending on the temperature, residence time and reaction medium (Table 1). The main technology is the fast pyrolysis of biomass into bio-oil. Fast pyrolysis is a high-temperature process, in which biomass is rapidly heated (in seconds), then converted into gases, bio-oil and charcoal.

The bio-oil obtained by fast pyrolysis can be upgraded, as presented by Gabrieli and Ruther (2007). Possible routes for upgrading are the following: decarboxylation and hydrodeoxygenation or cracking. They are all based on the reduction of the oxygen content in the bio-oil. Bio-oil produced by flash pyrolysis contains a lot of oxygen and thus hydrodeoxygenation will consume a lot of hydrogen. The product consists of hydrocarbons if all oxygen is removed in the hydrogenation

3.2 Biomass fractionation to carbohydrate and lignin

Usually biomass needs to be pretreated to improve the formation of sugars or the ability to form sugars in subsequent enzymatic hydrolysis. Various pretreatment methods exist; including sulphite or organosolv pulping that makes the fibre part more susceptible to further enzymatic hydrolysis or other pretreatment such as mechanical treatment, steam and other explosion methods, hot water or alkaline extraction as reviewed by Harmsen et. al (2010). The explosion processes, such as steam, CO_2 and ammonia explosion (AFEX), employ pressure reduction of the fibres to make them more suitable for enzymatic hydrolysis.

Cellulose and hemicellulose, which are polymers of different sugar monomers, are separated from lignin and extractives and hydrolysed into their monomer units by enzymatic or acid hydrolysis. The fractionation should be done in a cost-effective way that preserves the sugars without degradation and avoids formation of inhibitory components for further biochemical reaction (Sun et al., 2002). The pretreatment is often a balance between the severity (time and temperature) and the yield in hydrolysis. Too high a temperature produces a high amount of inhibitors (furfural, HMF and formic acid), which are harmful for micro-organisms. Too low a severity results in lower yields in hydrolysis. Hot water extraction or dilute acid hydrolysis or oxidative processes mainly hydrolyse hemicelluloses into monosugars by added acid or acids formed by the autohydrolysis of biomass. It also makes the cellulose part easier to hydrolyse by enzymes. The alkaline methods such alkaline extraction or pulping with solvents such as ethanol are based on dissolving the lignin from the fibre part, which aids hydrolysis of the fibre part. Some methods, such as catalysed steam explosion, combine the mechanical reduction of fibres and the effect of added acidic substances, such as SO_2 or sulphuric acid.

A general flowsheet on the conversion of biomass into products via pre-treatment, fractionation and further conversion of sugars is presented as Figure 5. Firstly, the biomass is fed to the pre-treatment step together with steam and chemicals. In this case, steam is injected directly into the process. Subsequently, the mixture is cooled and hemicelluloses are solubilized into monosugars mainly. The cellulose is next hydrolysed into monosugars, typically by using enzymes. Conversion of cellulose without enzymes into monosugars requires strong acid, which needs to be recovered, or high temperatures, which results in the formation of a large amount of inhibitors Galbe and Zacchi (2002).

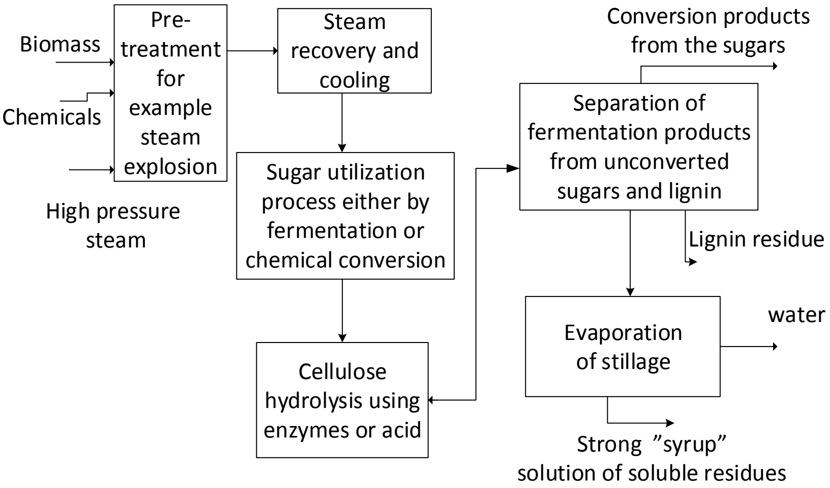

Figure 5. A common flowsheet where biomass is converted into monosugars, which are further converted into product (Zacchi and Sassner, 2008).

Monomer units (monosaccharides) can be processed into chemicals or fuels either by biochemical routes using microorganisms or through chemical reactions, for example hydrogenation.

Fermentation

Hamelinc et al. (2005) summarized the production technology and the techno-economic performance of bioethanol production from lignocellulosic biomass. In order to convert the cellulose into fermentable sugars, either an enzymatic or an acid hydrolysis is required as discussed earlier. In some cases, the sugar hydrolysis step by enzymes and fermentation are combined into simultaneous saccharification and fermentation. The hydrolysis may create also different inhibitory compounds for fermentation. The technologies to overcome the inhibition are discussed by Chandel et al. (2011).

The higher the sugar (especially C6) content in the feedstock the greater the amount of raw material that can be converted into a product by fermentation. With traditional yeast, such as *Saccharomyces*, hexoses (glucose, mannose and galactose) can generally be fermented into ethanol with high yield, whereas pentoses (xylose and arabinose) are converted less efficiently by conventional yeast (Sonderegger and Sauer, 2003). Although engineered yeast can use pentose sugars more efficiently, simultaneous co-fermentation of C5 and C6 sugars is still challenging (Young et al., 2010). Therefore, the C5/C6 sugar ratio also indicates the fermentation behaviour. In addition, the recovery of fermentation products is crucial for the techno-economic performance of fermentation based routes. Two enhanced process alternatives for recovery of product from ABE fermentation and their techno-economics performance are described by Kurkijärvi et al. (2016).

Typically, after fermentation, some sugar remains in the stillage, as shown by (Zacchi and Sassner, 2008). It can be concentrated by evaporation and burned together with the lignin-containing solid residue. However, biogas production has the advantage that no energy-intensive stillage evaporation is needed.

Chemical upgrading of sugars

Sugars can be converted chemically by aqueous phase reforming (APR) into hydrogen and carbon dioxide or hydrocarbons, or hydrogenated into hydrocarbons. Sugars or sugars alcohols might also be cleaved in hydrogenation i.e. hydrogenolysis to smaller products, for example ethylene glycol. Aqueous phase reforming (APR) is similar to steam reforming reaction. However the oxygen-containing feedstocks such as sugars, alcohols, sugar alcohols, acids, can be reformed in the liquid phase, typically at 250 °C and 50 bar into CO_2, CO, H_2 and C1-C6 alkanes (Wei et al., 2014).

Lately, aqueous phase reforming with co-fed hydrogen has been studied for the conversion of sugar alcohols (Kirilin et al., 2010) and biomass hydrolysate (Li et al, 2011) into hydrogen or light hydrocarbons. When external hydrogen is the co-feed, liquid range hydrocarbons were produced (Zhang et al., 2014).

For conversion of feedstock into sugar alcohols suitable to APR, simultaneous acid pre-treatment and hydrogenation into sugar alcohols have been reported for cellulose (Yin et al., 2012) and even spruce with a high yield (Palkovits et al. 2010). Thus, biomass could be converted into sugar alcohols without an enzymatic hydrolysis step.

Utilization of lignin part

After fermentation and removal of ethanol, lignin typically remains as solid residue unless it is removed earlier. Various options such as pellet production, heat and power production are described by Zacci and Sassner (2008). More recently, different uses for lignin have also been studied. An extensive review about a lignin utilization options is presented by Halladay et al. (2007). The uses include formaldehyde resins, aromatic chemicals, activated carbon or even carbon fibre production.

Halladay et al. (2007) presents also the concept of lignin gasification from a bioethanol plant, but no material and energy balances are presented.

Only very few studies are available for concepts combining lignin residue gasification and separate sugar utilization, for example by ethanol fermentation. Laser et al. (2009) compared ethanol production from switchgrass using Ammonia fibre explosion (AFEX) pre-treatment. A high energy yield of biofuel was obtained, close to 80 %, based on the raw material LHV energy content.

3.2.1 Other conversion methods

The utilization of by-products such as black liquors and hydrolysates to produce chemicals and heat has been studied by novel methods employing liquid phase oxidation (wet oxidation process) by Mudassar et al. (2014, 2015a, 2015b, 2015c). Under suitable process conditions, useful product acids such as acetic acid, formic acid, glycolic acid and lactic acid were produced in addition to heat, CO_2 and water. The products can be recovered and used as industrial chemicals, esterified with alcohol to produce green solvents, or decomposed into fuel gas by pyrolysis.

3.3 Heat and power production in biofuel conversion

In lignocellulosic biorefinery processes, heat and power are not only required as utilities but they are often produced as by-products. The heat and power consumption of the process and the potential to produce steam, electricity and district heat from the heat liberated is important for the feasibility of the process. The amount of heat liberated from a process depends on the process and site integration. The value of the heat produced is determined by the production cost of the heat it is replacing.

There is an extra benefit if a process can be run alternatively in two modes: either capable of using excess heat and power for a larger amount of biofuel production (in summertime), and in winter being heat sufficient and power excessive when waste heat is not available and more electricity is needed in the market. This resembles to some extent the ‘power to liquids’ process concepts presented for utilizing the cheap excess power available from time to time from wind and solar power sources. Another approach would be to convert power into hydrogen and subsequently fuels through the hydrogenation of carbon dioxide (Gahleitner, 2013).

4. Properties of fuel products

An important part of biofuel production is the different quality properties of fuels such as volatility, solubility, cold flow properties, cetane or octane number, chemical composition and energy content, as shown in Table 2. The production of biofuels is often a trade-off between the production cost and the fuel properties of the particular compound. Gaseous biofuel (SNG, DME etc.) needs changes to existing infrastructure and car engines. DME has a reasonably high cetane number and methane has a high octane number. The disadvantage is the storage of these components. DME can be stored similarly to liquefied natural gas, requiring new infrastructure, fuel stations, etc. In contrast, methane can be stored either pressurized at room temperature or liquefied as LNG. Yet DME is significantly easier to store as it can be liquefied at ambient temperatures as opposite to methane.

Both methanol and ethanol have high octane numbers (Table 2) and higher water solubility and need different construction materials in engines and storage vessels compared to hydrocarbons. The vapour pressure of these components is also higher than for heavier alcohols but lower than gasoline. Suitable vapour pressure for gasoline can be controlled by mixing lighter hydrocarbons to the fuels. Because of incompatibility with many existing car engines, a relatively low amounts of ethanol (up to 10 vol %) can be mixed according to the EU fuel standard (EU, 2009). However, a high proportion of ethanol is used in dedicated E85 fuels.

Other alcohols, such as butanol and propanol, may be mixed (15-12 vol %) in gasoline (EU, 2009). Ethers, such as ethyl tert butyl ether (ETBE), have been conventionally added to gasoline to enhance octane number and clean burning. Dibutyl ether, diethyl ether and diethoxybutane have similar characteristics. MTHF could be blended in larger volumes, up to 30 %, in gasoline (Hayes, 2009)

For diesel fuel, the cloud point is important, because in cold climates some components in diesel solidify and plug the fuel filters. The diesel range alkanes obtained through FT synthesis are chemically compatible and have very high cetane numbers, which makes them burn clean. However, the product obtained from FT synthesis (mainly n-alkanes) does not have sufficiently good cold properties. The heavy part needs to be hydrocracked into hydrocarbons with the right chain length. In addition, n-alkanes solidify even at room temperature. Therefore, they may be partially isomerized into iso-alkanes to lower the cloud point. Isomerization can be performed in an oil refinery, although this involves losses, because a side reaction of isomerization is the cracking of diesel range hydrocarbons into smaller hydrocarbons. Schablitzky et al. (2011) presented higher naphtha and kerosene yields compared to diesel in the hydroprocessing process of Fischer-Tropsch wax. The hydroprocessed and isomerised product can be blended into conventional diesel in very high fractions, or even used alone.

The diethoxybutane and dibutyl ether also have favourable cetane numbers. In addition, dibutyl ether has very favourable cold properties (melting point -97.9 °C). (Lide, 2005). A mixture with dibutyl ether reduced the cloud point of diesel fuel Lown et al. (2014)

It is also very important to consider the toxicity of fuel components and safety such as the tendency of ethers to form peroxides. The harmful concentration of methanol (200 ppm, 8 h) is somewhat higher that gasoline (300 ppm, 8 h) and significantly higher compared to ethanol (1000 ppm, 8 h) according to (HTP, 2014) and (ACGIH, 2012).

Another important aspect of biofuel is the air emissions of various biofuels compared with standard fuel (gasoline or diesel). Typically, ethanol and methanol reduced emissions of hydrocarbons and carbon monoxide by means of increased emissions of acetaldehyde and formaldehyde, which both are potential carcinogens (HTP, 2014). Diesel fuel produced by Fischer-Tropsch synthesis resulted in much lower soot formation compared to standard diesel containing aromatic components. The cleanest burning fuels were hydrogen, methane and light alkanes up to butane (Gaffney and Marley, 2009).

Table 2. Selected properties of fuel components collected from literature summarised from Paper II and the additional sources marked with notes.

Component	Formula	Boiling point	Octane number	Cetane number	Vapour pressure	Flash point	Lower heating value
		°C			KPa	°C	MJ/kg
Gasoline	C_4-C_{12}	30-190	95-98		45-90	<0	43
Diesel	C_{12}-C_{20}	170-340		>45	<1	>56	43
FAME	$C_{19}H_{34}O_2$	300-340		>50		>100	36
Methanol	CH_4O	64	122-133		32	7	20
Ethanol	C_2H_6O	78	121-130	8	16	13	27*
Dimethyl ether	C_2H_6O	24	-	55-60		-42	27.6-28.8
Paraffinic diesel e.g. FT diesel	C_{12}-C_{20}	180-360		80-110	<1	>56	43-44
E85***	$\sim C_{2.7}H_7O_{0.85}$	30-190	100		40-80		29.2
Dibutyl ether	$C_8H_{18}O$	141		91-100		25	42.8
Diethyl ether	$C_4H_{10}O$	35		140		-45	34.0 **
Diethoxybutane	$C_8H_{18}O$			96.6		45	~34
N-butanol	C_4H_9OH	118	94	12	0.7 kPa	37	33.11
Isopropanol	C_3H_7OH	82.3	~100	17	4.4 kPa		30.15
MTHF	$C_5H_{10}O$	80	80		39	-11	32
Methane	CH_4	-161	130		Not applicable	-188	50

* NREL, (2011)

** Gray et al. (1972)

*** Special high ethanol content fuel that contains 15 vol % gasoline and 85 vol % ethanol.

5. Evaluation criteria by performance indicators

5.1 Background on process performance evaluation in process development & design

In order to evaluate process alternatives, performance criteria that are measured through various indicators are required.

One challenge is that in a production plant design project the main technical principle is selected at a very early phase. At this stage there is only very limited information available of the economics and technical details. So, the evaluation is based on incomplete and often partly inexact data. Later in the project when the project is better understood, there are fewer possibilities to make large conceptual changes (Cziner and Hurme, 2005). The design paradox is that in early R&D, stage there is a large freedom to make changes, but there is limited information available. This also means that if an unfeasible process alternative is chosen at an early stage, it might be very difficult to change the decision later. Therefore, there is a need for design tools and methods, which can help to make a good decision with limited data. For biorefinery processes, this is even more important, since there are so many alternatives, both in terms of the main production method, pre-treatment method and raw material.

Process development, and especially conceptual design, is regarded as the most important design stage since the major decisions affecting the entire lifecycle of the process are made then (Tuomaala et al., 2000).

Tuomaala et al. (2000) stated that the criteria affecting the plant performance could be classified into three categories:
1) economy and profitability
2) safety-health-environment (SHE)
3) technological criteria

The technological criteria can be divided into the following sub-criteria: technological novelty, operability, technical performance and availability. Operability can further be divided into controllability and flexibility, and availability into reliability and maintainability.

The criteria are measured by special indicators, which are either relative or absolute. Relative indicators are relative values compared to another value presented e.g. as percentages (such as yield). Absolute indicators are absolute values in mass, energy or money etc. Common criteria and their indicators are shown in Table 3.

Table 3. Some performance criteria and their indicators (Tuomaala et al. 2000)

Criteria	Relative Indicator	Absolute indicator
Profitability	ROI, IRR	cash flow, NPV
Safety	safety indices (Dow, ISI)	accident rate
Health	health indices	chemicals exposure, hours of sick leave
Environment	environmental indices	emission rates, carbon footprint
Technology: technical performance availability operability technological novelty	material yield selectivity energy yield carbon efficiency second law efficiency	raw material consumption energy consumption, exergy losses i.e. true thermodynamic losses

5.1.1 Other process performance evaluation methods

Several authors have considered the exergonomics of biofuel processes and operation, for example, gasification (Karamarkovic, 2010). Kohl et al. (2014) compared different methods of energy efficiency and exergy efficiency assessment for methane production from biomass. The conclusion was that although exergy has potential for the further improvement of the process, it is relatively complex to calculate. Primary energy efficiency (see Eq. 7) describes well the influence of the process on the usage of primary energy resources.

In related work, Kohl et al. (2015) performed an exergoeconomic analysis of the integration of torrefied pellet production and pyrolysis oil production with an existing CHP plant.

The sustainability of biofuel production depends on the economic, environmental and social impact throughout the product's entire life cycle. Therefore a total evaluation of the complete fuel chain (cradle-to-grave or well to wheel for transport fuels) is important. LCA (life-cycle analysis), which calculates this aspect, is a valuable tool for assessing the environmental impact. Other aspects besides GHG included in life-cycle analysis are typically acidification caused by sulphur and nitrous oxides, hydrochloric acid and ammonia, particulate matter and troposphere ozone emissions, which cause harm to humans especially though respiratory diseases (Bayer et al., 2010).

Other environmental impacts of biorefineries include eutrophication due to nitrogen and phosphor fertiliser runoff polluting nearby rivers and lakes. Cutting trees and collecting logging residues or stumps affect the biodiversity of the ecosystem in the forest. Growing biomass for energy or fuel production occupies a certain amount of land and water that would otherwise be available for another purpose. The environmental impact of biorefinery chains has been studied (Williams et al., 2009). In their study, the most significant effects of biorefineries were from combustion of residual biomass such as lignin residue that might cause particulate, NO_X and sulphur oxide emissions if the lignin residue contains sulphur. Volatile components such as ethanol evaporate and create VOC emissions and waste formed from the neutralization of acid with lime. A method to assess the VOC emissions during process development was developed by Hassim (2010). Also, biorefineries where sulphuric acid is neutralized with lime, etc. produce calcium sulphate, which has limited use. Biorefineries where an acid such as lactic acid is produced by fermentation should use a method for product recovery, such as reactive extraction, which prevents the formation of a large amount of waste product because of the neutralization of the acids formed.

Emergy analysis is an ecologically oriented energy-focused environmental accounting method expressing all process inputs (such as energy, natural resources, services) and outputs (products) in solar energy equivalents. The emergy for a product represents resources as the solar energy needed to create a product or service. Emergy is a measure ('memory') of how much work the biosphere has done to provide a product including air, water and other free resources. Emergy analysis for a biofuel is presented by Sha et al. (2013) and for the production of ethylene, Sha et al. (2015) compared the different processes producing ethylene using both renewable and non-renewable feedstock, and the renewable feedstock resulted in approximately 60 % lower use of biosphere resources per kg of ethylene.

5.2 Performance criteria used in this study

5.2.1 Greenhouse gas emissions

For fuel, the production rate or reduction in greenhouse gas emissions is an essential criterion since renewable material is often used instead of fossil one to reduce greenhouse gas emissions.

Greenhouse gas (GHG) emissions are expressed as equivalents of CO_2. For example, CH_4 and N_2O emissions are multiplied by the Global warming potential (GWP) factor to get the equivalent carbon dioxide emissions.

The fossil emissions related to biomass are usually caused by harvesting and transport, since the harvesters and vehicles use fossil fuels. Excess electricity, heat or other products generated in the process can be "credited" as they replace the product produced from other sources. The emissions related to the construction of the plant are normally not considered.

It is important to note that only the fossil emissions are counted. Renewable feedstock (unless farmed) itself does not involve fossil inputs, since the carbon dioxide emissions in the combustion of fully biomass-derived products have been compensated with the uptake of an equal amount of carbon dioxide as the plant grew. However, the uptake depends significantly on the studied time horizon. The reduction of greenhouse gas emissions can be defined according to Equation 1.

$$GHG_{reduction} = 1 - \left(\frac{GHG_{biofuel}}{GHG_{substituting,fuel}}\right) \tag{1}$$

$GHG_{reduction}$ = Greenhouse gas reduction expressed in eq. CO_2 emissions.
$GHG_{biofuel}$ = Greenhouse gas reduction expressed in eq. CO_2 emissions.
$GHG_{substituting\ fuel}$ = Greenhouse gas reduction expressed in eq. CO_2 emissions.

It should be noted that the choice of substituting fuel (gasoline, natural gas etc.) significantly affects the obtained greenhouse gas reductions. In this study, the GHG emissions for GHG biofuel are calculated by Equation 2.

$$GHG_{biofuel} = GHG_{trans} + GHG_{input} + GHG_{elec} + GHG_{heat} \tag{2}$$

GHG_{trans} = the greenhouse gas emissions caused by fossil input in the biomass transport.
GHG_{input} = the GHG emissions caused by inputs of chemicals and additives used in the process.
GHG_{elec} = the GHG emissions of electricity input needed for the biofuel production. Produced excess electricity is subtracted.

GHG_{heat} = the emissions caused by heat production. Produced excess heat is subtracted.

5.2.2 Economic indicators

Net present value (NPV) calculates the present value of investments by discounting future cash flows and investment cost at a specified rate. The higher the risk, the higher the required rate on the invested capital. Net present value is described in Equation 3,

$$NPV = f_s\left(\sum_{i=1}^{i=n} C_i - \sum_{j=1}^{J=n} C_J\right) - C_{FCI} \tag{3}$$

Where,

C_i =the product sales revenue

C_j =is raw materials and utility cost. The inputs and product have been calculated for the economic lifetime of the investment.

C_{FCI} =the fixed capital investment

f_s = the unacost present value factor (Humphreys, 1991)

The fixed capital investment is calculated by the capacity exponent method from the reported costs for a similar plant or process unit. Production cost considers the cost of producing a product. The costs including variable and fixed operating cost and investment costs are added together.
The production cost is calculated according to Equation 4.

$$c_{Cost} = \frac{\left(\left(\sum_{j=1}^{j=n} E_j C_j - \sum_{b=1}^{b=n} E_b C_b + E_{cost,enzymes}\right) t_{op} + c_m - FCI\, a_f\right)}{E_i\, t_{op}} \tag{4}$$

C_{cost} = the production cost in eur/MWh for the main product.

C_j = the cost for input item (raw material, heat and power) (eur/MWh)

E_j = the amount used in MWh during one hour of operation.

C_b = the price for each energy-based by-product (electricity or biogas) (eur/MWh)

E_b = the amount of by-product produced in MWh during one hour of operation

$E_{cost,\,enzymes}$ cost of enzymes (eur/h)

t_{op} = the annual operation time (here for example 8000 h/a)

c_m = the maintenance cost in eur/a

FCI = the fixed capital investment of the plant in euros

a_f = the annuity factor, for 13 % internal rate and 15 years payback time

E_i = the product amount (MWh/h)

The replacement cost per tonne of CO2 equivalent for substituting a fossil fuel with a biofuel is calculated in Eq 5. Here regular gasoline is substituted with liquid biofuel and natural gas with gaseous biofuel.

$$c_{CO2,red} = \frac{t_{op}\left(C_{cost}-C_{fossil}\right)}{GHG_{sav}} \qquad (5)$$

In Equation 5,

C_{fossil} = the prices of the fossil fuels in eur/h

C_{cost} = the prices of the biofuels in eur/h,

t_{op} = annual operation hrs of plant 8000 h/a,

GHG_{sav} = the reduction of equivalent greenhouse gas emissions t/a when biofuel replaces the corresponding fossil fuel.

5.2.3 Technical performance indicators

One of the most common indicators for a production plant is the material yield of the main product. Since the biofuels for example ethanol and FT diesel products have a different energy density, it makes sense to compare different fuel products on an energy basis (e.g. heating value).

Efficiency to fuels can be calculated in terms of higher or lower heating value. The higher heating value i.e. gross heating value means that a fuel is combusted. The combustion products are cooled down to 25 °C at atmospheric pressure, and the water is condensed.

The lower heating value i.e. net heating value assumes that the water remains in the vapour state so the latent heat of vapour is not utilized. This is more realistic in many practical applications since the flue gases often leave temperatures above the dew point. For wet biomass, the lower heating value takes into account the energy needed to evaporate the moisture in the fuel.
The efficiency (energy yield) based on the lower and higher heating values used in this study is described according to Equation 6.

$$\eta = \frac{\left(E_{gas,fuel}+E_{liq,fuel}+E_{chem,prod}+E_{elec,output}\right)}{\left(E_{biomass}+E_{ext,heat}+E_{elec,input}\right)} \qquad (6)$$

where

η = the efficiency to fuels and chemicals with LHV or HHV.

$E_{gas,fuel}$ = the energy of gaseous fuel produced by the corresponding heating value.

$E_{liq,fuel}$ = the energy content of liquid-produced fuel.

$E_{chem,prod}$ = the energy content for the chemical product.

$E_{elect,output}$ = the excess electricity amount obtained as byproduct if all the electricity generated is not used.
$E_{biomass}$ = the corresponding energy of the feedstock for the corresponding heating value. Produced excess electricity or heat is subtracted.
$E_{ext,heat}$ = the energy of external low temperature heat fed to the process
$E_{elec,input}$ = the input of external electricity to the process.

The problem is that the efficiency shown in Eq. 6, does not take into account the different value of energy in heat, power and district heat Kohl et al. (2014). It takes more fuel to generate the same amount of electricity as an equal amount of heat, due to the different efficiencies in the conversion process. This comparison is done by converting each input (biomass, electricity, secondary heat) back to primary energy, which is typically a fuel. This can be done by using primary energy factors, which are the inverse of conversion efficiencies from primary fuel to each input.

The primary energy efficiency was calculated according to Equation 7.

$$\eta_p = \frac{E_{fuel,tot}}{P_{biomass}E_{biomass}+P_{elec}E_{elec}+P_{sec,heat}E_{sec,heat}} \qquad (7)$$

η_p = the primary energy efficiency
Efuel,tot = the total amount of fuel produced in each process including both liquid and gaseous fuel on a higher heating value basis.
Eelec = the amount of electricity needed (negative if excess electricity is produced as byproduct).
Esec heat = the secondary heat feed.
p = the primary energy factor, which is the inverse of energy efficiency on a higher heating value basis when a particular input is produced from primary fuel.

subscripts
biomass = biomass,
elect = electricity
sec = secondary heat
fuel,tot =total amount of fuel produced

6. Multilevel modelling for biorefinery processes (Paper I)

Process modelling and simulation are needed when processes are commercialised to design production plants and evaluate different alternatives. Process modelling is generally used as much as possible, since it is much faster and cheaper than experimental work. However, a significant amount of experimental work is still necessary when developing new production processes in order to prove that they work reliably. The simulation software programs used in this study were Aspen Plus and Pro/II, both steady state process flowsheet simulators. In the simulator, graphical user interface input and output streams were connected to blocks, which represent unit operations such as distillation. The substances present in the studied process and the models used for calculation of thermodynamic properties such as vapour-liquid equilibrium were selected.

When the model is solved, the material and energy balance equations for the process model are solved under steady state (time- independent) conditions. The main inaccuracies of the model are use of inaccurate models for representing unit operations or calculating thermodynamic properties such as vapour pressure.

6.1 Background on modelling system including biomass

In process modelling including biomass, the biomass has to be represented in a different way than substances with a defined molecular weight, for example based on its measured properties such as composition and heating value.

A general representation of biomasses by the composition and properties suitable for a general biomass database is presented with the following parameters:

1) Weight percentage division into sub-classes: cellulose, hemicellulose, lignin, extractives
2) Division of cellulose and hemicellulose into their monosaccharide species
3) Ultimate composition of the biomass (C, H, O, N, S, etc.)
4) Heating value of biomass (LHV; allowing calculation of heat of formation, which is needed in some flowsheet simulation programs also for components representing biomass)

Because of the large number of available biorefining processes, and typically also requiring experimental data, not all refining process options can be modelled at unit operation level directly but rougher modelling is needed. The early phase of a project limits the availability of data, which also hinders early utilization of rigorous models. Commercialisation of a research idea into a well-functioning production facility is a multiphase project described in detail by Cziner and Hurme (2005). In the commercialisation process, knowledge and the ability to evaluate it more accurately increases and different types of models are needed in different stages of the design for process analysis. Yet, the end use of the models defines the accuracy needed. Models include two dimensions: the modelling level, i.e. the level of accuracy of the models, and the scope that the model covers (Figure 1) in Chapter 1.

6.1.1 Multilevel modelling

The modelling levels can described in the following way: At low modelling levels the product yields are calculated from the biomass database values based on the exact raw material composition, reaction stoichiometry and reported data of reaction yields when available. For example, the yields of ethanol fermentation for a lignocellulosic biomass are calculated based on raw material monosugar content, hydrolysis and fermentation reaction yields estimated from reaction stoichiometry and experimental data (experimental yield % of theoretical yield). A low-level model involving spreadsheets allows calculation of many production routes and raw materials with a moderate effort.

On the mid-level, integrated models are created for a subprocess such as acid gas removal, including also auxiliary operations such as heat recovery, preheating, acid gas removal and solvent regeneration. The models are simplified, aggregated from several operations and combined with experimental knowledge to allow more straightforward but accurate calculation. These models are less rigorous than unit operation models.

The most accurate high-level models are rigorous unit operation models, which can be used directly in process simulators (e.g. Aspen Plus). This level allows a detailed but more laborious simulation, which often has to be complemented manually by experimental results for yields, conversions and efficiencies.

For performance evaluation and screening of the most feasible production routes and raw materials, different performance criteria are used at different modelling levels. For the low-level models, material, heat and hydrogen conversion efficiencies and simple economic criteria, such as the difference of the values of products compared to the value of raw material, can be considered. Subsequently, for mid and high-level models, capital cost estimation based on either literature or equipment-size can be used. The operating costs are calculated from the simulated raw material, auxiliary chemical and utility consumptions.

Multilevel modelling enables efficient evaluation of a large number of process routes with limited data, first using low-level models and selecting the feasible alternatives for mid-level model evaluation. Finally, the most feasible alternatives selected using mid-level models are evaluated with high-level models.

Biorefinery evaluations can be done with a flexible modelling tool, which links different models for conversion operations as desired. The models on different levels are arranged modularly in both parallel and serial way, allowing model substitution by more accurate ones when they are available in process development. The models on different levels can be used in parallel by supplementing a low-level model with a more rigorous one when available, since the modular structure allows an easy addition of new models.

Feedstock and route optimization are done by varying multipliers for the interconnecting rates $0 \leq x \leq 1$, which adjust the relative ratios between different subprocesses. The objective function in the optimization can be for example material, energy or hydrogen conversion efficiency or an economic objective function.

Case studies

Case study 1. Biomass refining routes are evaluated for producing liquid fuels using material, energy or hydrogen conversion efficiencies (low-level models). Three raw material alternatives are studied: birch, eucalyptus and straw.

The processes are modelled the following way: First syngas yields from different biomasses are calculated with a high-level model employing using Gibbs energy minimization with a flowsheet simulator. Next, the following process routes are calculated with a low-level model: methanol production; FT diesel production; ethanol production from methanol by carbonisation; ethanol production from biomass by hexoses fermentation; ethanol production from hexoses; ethanol from both hexoses and pentoses, and ABE fermentation.

Here, the process routes were evaluated by energy efficiency calculated starting from biomass on dry and lower heating value (LHV) basis. Among the studied raw material and production routes to liquid fuels, methanol production from birch gave the highest energy conversion efficiency 75 (LHV %).

Case study 2. The by-product and capital costs of forest residue to methanol process (230 000 t/a methanol) were estimated with a mid-level model. Process streams energy contents are the following: Based on heat and material balance simulation, the energy flows of the process streams are 200 MW for the fed biomass and 144 MW for the methanol produced. For amine separation and distillation duties, 39 MW heat is needed together and the plant is self-sufficient with respect to heat. The main electricity consumers in the process are the synthesis gas compressor (7 MW) and the oxygen production (3 MW). Grey (non-process) energy costs are mainly related to feedstock harvesting, chipping and transportation, estimated with an add-on logistic model, are about 3 % of biomass energy content. Plant capital costs estimated using mid-level models based on capacity exponent correlations and the investment cost is 170 MEUR.

7. First level models (Paper II)

The objective of Chapters 7-10 is to evaluate several production routes with different levels of accuracy based on Papers II, IV and V and different performance criteria. The promising process routes from Paper II were chosen for further study in Paper IV and for final evaluation in Paper V. In addition, the effect of process integration was studied in Paper III. Special attention was paid to finding possible more efficient conversion routes could be found, which could perform better than conventional ones based on the chosen performance criteria.

7.1 Introduction

In Paper II, multiple conversion routes were studied and evaluated based on the fuel properties and product yields for the different raw materials. Due to the different energy densities of the products, the energy yield of the main product from dry raw material (Eq.6) was used as a performance criterion. Also mass yield was calculated, since for chemicals where the energy content is less important, the mass yield is a better criteria. Yield calculations are calculated from the reaction stoichiometry, with an exception for gasification and reforming where the energy balance is also incorporated.

In this chapter, the studied reactions are calculated based on maximum conversions and selectivities, except for gasification, reforming, water gas shift reaction and FT. Also, the analysis is repeated with realistic product yields later in chapters 8-10. The chemical formulas and details for the studied conversion paths are presented in Paper II. The studied raw materials were: pine, spruce, black alder, aspen, birch, eucalyptus, larch, bagasse, wheat straw, and pyrolysis oil derived from pine.

7.2 Process concepts studied

7.2.1 Gasification

The following gasification based routes were studied: hydrogen production, methanol synthesis, ethanol production from methanol by carbonylation, acetic acid production from methanol by carbonylation, DME synthesis, ethylene and propylene production from methanol by MTO synthesis, hydration of MTO olefins into ethanol and propanol, methanation of synthesis gas and production of FT diesel as described by Spath and Dayton (2003). For gasification, all biomass raw materials were studied first separately and secondly only the lignin and extractives part was studied for pine and birch.

For gasification-based routes, the gasification and reforming part of the conversion route was modelled with a separate flowsheeting model, according to the typical gasification process concept shown in Figure 4 in section 3.11. A flowsheet model was used since it could estimate the yields, which are connected to the energy balance. Here, gasification was performed at 800 °C and 5 bar with extra steam injection. The temperature for the reformer was raised to 950 °C by oxygen injection.

The gasification was modelled based on the ultimate composition of biomass and its higher heating value. For these calculations, PRO/II simulation software was used. Biomass was represented by the species carbon, hydrogen, oxygen, nitrogen, sulphur and calcium oxide according to its ultimate composition. Here calcium oxide represents ash. Both gasification and reforming were calculated with the Gibbs energy minimisation model to obtain the maximum yields. Later in Chapters 9-10 Gibbs energy minimisation was used and methane amount was corrected to obtain more realistic yields. The Gibbs energy minimization model calculates the chemical equilibrium for selected components and process condition such as temperature and pressure, without knowledge of the actual chemical reactions taking place. The main source of error is deviation of the system from chemical equilibrium and if all components that are formed are selected in the calculation. The composition of the lignin and extractives part was estimated based on the elemental composition of the biomass and the sugar part and a literature value was used for the lignin heating value.

The lignocellulosic biomass feedstock was dried from 50 wt-% moisture on a total basis down to 13 wt-% with indirect drying and the evaporated moisture was fed as steam to the gasifier. However, pyrolysis oil and the lignin and extractives part was fed to the gasifier at different moisture content. Pyrolysis oil contained 25 wt-% moisture. The lignin and extractives part was calculated both for 13 wt% and 40wt% moisture content, to give more realistic gasification yields. The energy consumption of drying was not considered in Paper II but later in Papers IV and V.

7.2.2 Further conversion of synthesis gas

The conversion in the water gas shift reaction was calculated based on the H_2/CO ratio needed for each further conversion reaction. For the FT reaction, a distribution of hydrocarbons according to the Anderson–Schulz–Flory distribution with a conservative α value of 0.87 was calculated. According to Sauciuc et al. (2011) typical values range from 0.95 to 0.85 for Cobolt catalyst. With a high alpha value, heavier product is formed, and with lower alpha values, more gasoline and light hydrocarbon gases that are undesirable products are formed. This also slightly effects the needed H/C ratio. The used alpha value 0.87 gives a slightly conservative estimate on the potential yield and for higher alpha value slightly higher hydrocarbon product yield is obtained. For all other conversion reactions, full conversion and 100 % selectivity were assumed.

7.2.3 Sugar utilization processes

For routes based on the sugar platform, the biomasses were represented by their sugar composition, i.e. the amount of both C6 and C5 sugars for all raw materials except pyrolysis oil. Both fermentation and chemical conversion routes were studied. In this, full conversion of sugars was assumed, except for ABE fermentation, which was calculated according to the maximum reported yield, i.e. 0.42 g ABE/g C6 sugars (Thaddeus et al., 2004) and 0.28 g/g C5 sugars (Ounine et al., 1983). Incomplete hydrolysis and realistic yields of less than 100 % in fermentation reactions were considered in Chapters 8-10.

The following fermentation-based routes were studied:

- Ethanol production from C6 sugars,
- Ethanol production from both C5 and C6 sugars,
- Acetic acid anaerobic fermentation utilizing both C6 and C5 sugars,
- ABE fermentation, utilizing both C6 and C5 sugars,
- Aerobic digestion that also utilizes both C6 and C5 sugars.

Subsequent upgrading reactions of sugars

The following conversion paths from fermentation-derived products were considered:

- Ethylene from ethanol,
- Diethoxy butane production from ethanol,
- Ethanol and ethyl acetate production from acetic acid,
- Dibutyl ether production from butanol,
- Conversion of biogas to synthesis gas by steam reforming.

The chemical conversion routes studied for sugars were:

- C6 sugar conversion to C12 alkane combined with C5 sugar conversion to MTHF,
- C6 and C5 sugar conversion to hydrogen and alkenes.

For the sugar-derived products obtained through hydrogenation, the required amount of hydrogen and the energy content of the products were computed in Paper II. The exact hydrogen balance was calculated only for pine and birch, which are discussed below in more detail.

7.2.4 Separate sugar and lignin processing

Besides original pathways, additional biofuel production pathways for separate sugar and lignin utilization were calculated considering the exact hydrogen balance. The sugars were converted into products by fermentation or chemical conversion and the lignin part was gasified. The pathways studied included:
Ethanol production with methanol production from the lignin part,

- Hydrogen production by aqueous phase reforming of the sugar part and gasification of the lignin part,
- Hydrocarbon production of the sugar part by aqueous phase reforming with added hydrogen obtained by gasification of the lignin part.
- Biogas production of the sugar part combined with gasification of the lignin part.

For these process routes, the total energy content of products was compared with the feedstock energy content. In cases where hydrogen was the limiting reactant, the product yield was adjusted accordingly.

7.2.5 Results

Raw material analysis

To study the behaviour of the different biomass feedstocks, the energy content of the various biomass fractions was calculated. The energy contents of various feedstocks compared to syngas is shown in Figure 6. For feedstocks with a high lignin fraction, such as pine, the lignin part corresponds approximately 40 % of the total energy content of biomass. However for, biomass with a low lignin fraction, such as sugarcane bagasse, lignin covers only 20 % of the total energy content of biomass. In contrary, in case of 'high lignin' feedstock such as pine the energy content of the sugar part is lower (50 %) than that of 'low lignin' feedstock such as sugarcane bagasse (65 %). Also, the ratio of C_5/C_6 sugars often affects the potential yields of fermentation products, since some process routes that cannot effectively use C5 sugars, such as traditional ethanol fermentation.

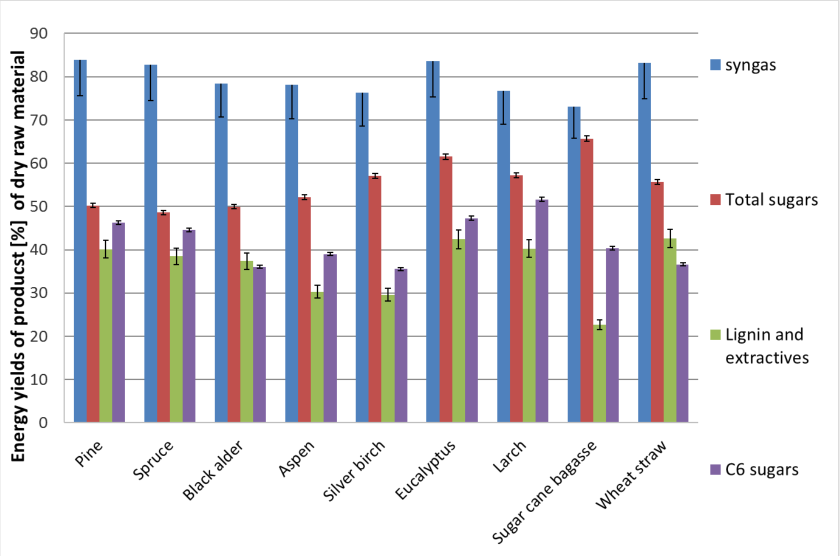

Figure 6. Energy content of sugar, lignin and synthesis gas obtained by gasification for the different raw materials as % of dry raw material energy content by lower heating value (LHV). The uncertainties estimated for energy yields shown using error bars are for syngas ≤10 % of maximum value, for sugars ± 1 % and for lignin and extractives +- 5 %.

The uncertainty in the predicted syngas yields consists of deviation of carbon conversion in gasification from 100 % and the energy content of tar components removed from cleaned syngas.

Gasification based routes

As seen in Figure 7, a clear trend can be seen between the sugar/lignin ratio and the fraction of energy of dry raw material that can be converted into synthesis gas. This is because higher fraction of lignin both results in a higher heating value and lower oxygen content of the raw material. Therefore, the synthesis gas yield is higher for high lignin raw material.

The trends are more obvious for the lignin/sugar ratio than lower heating value of biomass, O/C ratio, higher H/C ratio or ash content.

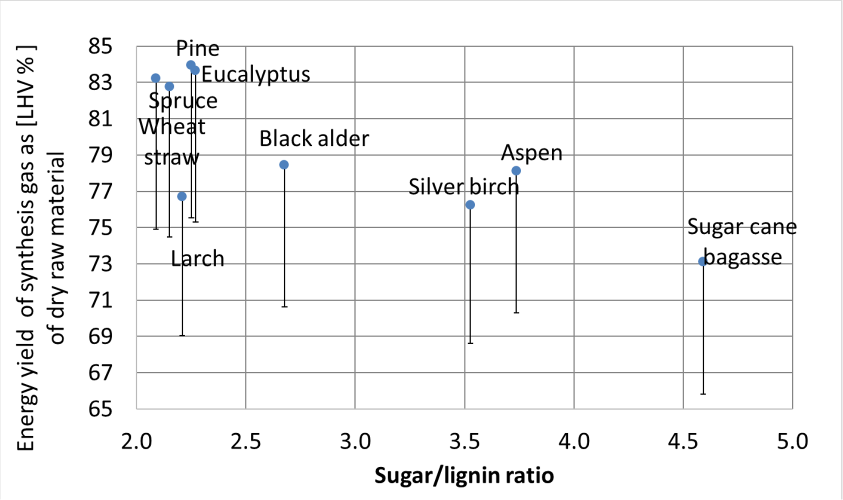

Figure 7. Synthesis gas energy yield by lower heating value (LHV %) from dry feedstock vs. feedstock sugar/lignin content. The uncertainties in the synthesis gas energy yields are shown using error bars and they are estimated to be ≤ 10 % of syngas energy yield

A high O/C ratio and low heating value leads to a situation in direct gasification where the feedstock has to be over-oxidized (add more than oxygen than what is needed to convert the feedstock into CO and H_2) to keep the gasification temperature in gasification already at 800 °C (Prins et al., 2007), (Ptasinski et al. 2007). The exact optimal gasification temperature depends on the feedstock and the details of the gasifier. The optimal gasification temperature is a trade-off between having fast enough reaction kinetics and achieving almost complete carbon conversion, but keeping the minimum possible temperature. At a higher temperature more of the product gas energy content is converted into heat, especially when there is enough oxygen in the gasification to over-oxidize the feedstock. Kurkela and Simell (2008) stated that the suitable temperature in direct gasification with oxygen was 750-850 °C and therefore 800 °C was used in here in the calculations. When the synthesis gas has a higher share of carbon dioxide, its heat content increases. Therefore, a higher amount of the energy in the feedstock is consumed to keep the required temperature in direct gasification. Indirect gasification might result in a higher efficiency, especially for feedstocks with a high O/C ratio.

It was observed that the syngas conversion efficiency was practically independent of the biomass used in the gasification. This is because the raw material only slightly affects the H_2/CO ratio of the synthesis gas, which actually determines the yields in subsequent reactions. It means that the problem of finding an optimal raw material and conversion path can be divided into two separate problems: first, to estimate a suitable gasification concept and raw material that gives a maximum yield of syngas, and second, to find a maximum conversion efficiency pathway from syngas into the desired product.

Figure 8 presents the theoretical energy yields (LHV %) of the different products from synthesis gas. The conversion of the energy content into liberated heat is presented by raw material energy content, minus the energy yield (100 – LHV %). As can be seen, hydrogen production involves the smallest loss of chemical energy, followed by methanol synthesis. Of the direct fuel production routes, the largest energy loss is in methanation and FT synthesis.

However, here the methane yields are underestimated, since methane is reformed in the reforming step, but produced again in the methanation step resulting in a lower yield. For methane production with higher yields, reforming that only reforms tars but not methane, as described in later chapter 9 can be used. The conversion of syngas into acetic acid (a non-fuel product) involves the highest conversion of energy into reaction heat.

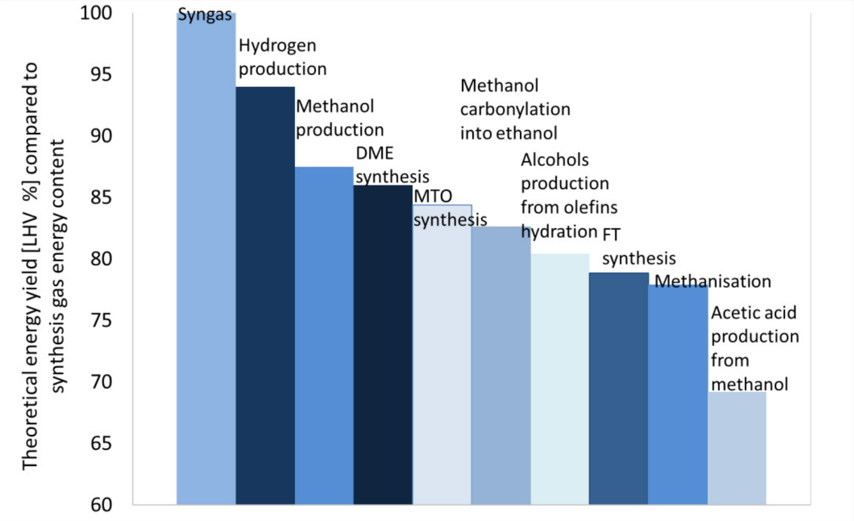

Figure 8. The theoretical energy yields (LHV %) from synthesis gas into products.

Sugar part utilization

A higher sugar/lignin ratio in the raw material results to a higher share of the biomass energy content being present in the sugar part. It can be seen that, the energy yields from sugars to products (Figure 9) (also independent of raw materials) are larger than from synthesis gas to products (Figure 8). For example, ethanol fermentation retains nearly 100 % of the sugar energy content. The energy yield from sugars even increases beyond 100 %, due to endothermic reactions such as ethylene production or ethanol and hydrogen production by aqueous phase reforming. This is because other energy inputs (hydrogen and heat) have not been considered. Here the energy yields are compared only to the sugar energy content, which does not include the energy content of the needed hydrogen. Therefore energy yields of ethanol produced via acetic acid and C5 and C6 alkanes produced via sugars are very high.

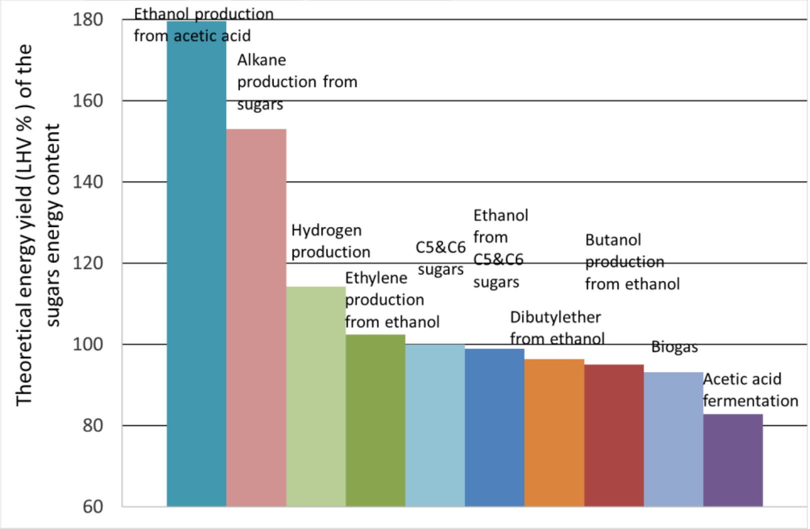

Figure 9. The theoretical energy yields of sugars to products (LHV %).

Separate lignin and sugar processing

The energy yields (LHV %) of the conversion paths utilising separate lignin and sugar processing are compared with conventional routes for pine and birch feedstocks in Figure 10. The yields for routes based on separate lignin and sugar processing are higher compared to gasification-based routes except the syngas itself. For example, combined ethanol and methanol processing results in a higher energy yield of product (75 -85 %) compared to < 75 % for methanol synthesis from synthesis gas. Separate lignin and sugar processing employs aqueous phase reforming (APR) technology based hydrogen production. For hydrogen production by APR from sugars, calculation shows a very high energy yield (more than 90 %), indicating that the APR process step in the process is endothermic, and converting heat into chemical energy increasing the energy content of the products. Here, the external energy inputs have not been taken into consideration.

In alkane production from sugars that uses hydrogen formed by gasification of the lignin part of pine, not all the hydrogen is consumed. However, for birch, not enough hydrogen is produced which is needed to convert all the sugars into pentane and hexane. Therefore, C5 sugars can only partly be converted into MTHF, which affect the energy yield. Thus, the energy yield depends also on the relative amount of sugar vs. lignin in the raw material.

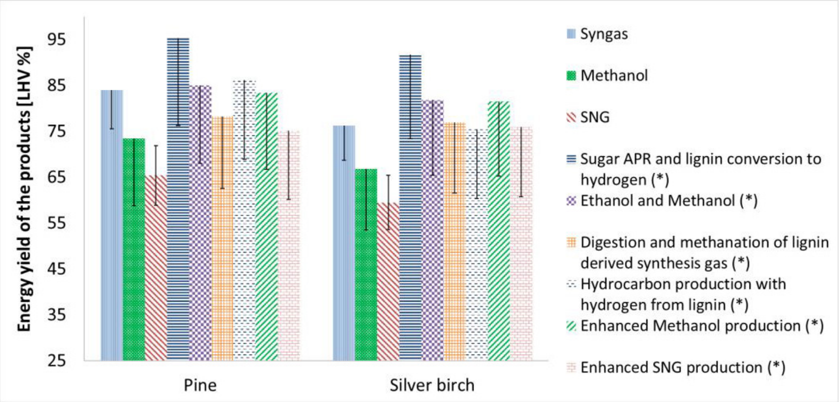

Figure 10. Energy yields (LHV %) in separate sugar and lignin utilisation routes (marked with *) in comparison with other process routes for pine and birch. The estimated uncertainties shown using error bars are ≤ 10 % for synthesis gas and ≤ 20 % for all other process routes, except ± 10 % for SNG).

7.2.6 Conclusions

It was found that the highest yields energy yield from biomass to products can be achieved by separate processing of lignin and sugar part, both for high and low lignin contents, such as pine and birch, respectively. This is because, in sugar processing, the loss of chemical energy into heat is usually lower than in synthesis gas processing. Moreover, gasification of biomass with high heating value and low oxygen content part of biomass (lignin) is slightly more effective than direct gasification of biomass with higher oxygen content and lower heating value.

The 1st level method used has two limitations: no balances were included in the analysis (except for gasification and reforming) and maximum yields were assumed. This also means that neither the amount of by-products such as heat nor the need of external heat input have been calculated, except for gasification and reforming. Therefore, care should be taken when using 1st level method for processes where the heat balances plays a significant role. At this stage, stoichiometric yields are calculated. Chemical equilibrium or product selectivities are not included, and therefore the obtainable yield might be significantly lower. Separate lignin and sugar processing can also need a high amount of energy for product separation. This is considered in latter Chapters 9-10.

8. Models with site integration (Paper III)

In order to evaluate biofuel processes it is not enough to consider the potential yield from raw materials to products alone, but also the net heat and power demand of the process. In addition, side products and heat or power generated significantly affect the feasibility of the production route. This information is related to the process and site integration. In fact, the feasibility of the process much depends on how the process is integrated to the power production and other processes such as pulp and paper mills at the site.

To study process integration, a more detailed model of the process is needed, including the process temperatures at different process steps. In this chapter, process integration is studied assuming maximum heat recovery, which can be calculated based on the heating and cooling demands in the process without knowledge of the actual heat exchanger network design (Linnhoff, 1998). Although the hot and cold utility demands for the process are somewhat underestimated compared to a real plant, the approach is general and therefore more suitable for comparison of process alternatives in R&D when the details of the process concept have not yet been specified.

The biofuel production process is evaluated according to the energy yield (Equation 6). Not only the energy input of the feedstock is considered, but also the heat and power input. The results are based on Paper III and elaborated further in this thesis with new findings, based on improved knowledge from Papers IV and V.

Two common processes are studied in Paper III: Case 1-Fischer-Tropsch diesel and Case 2- cellulosic ethanol production from spruce. In case 1, atmospheric pressure gasification using oxygen, low-temperature FT synthesis and hydrocracking of FT wax into diesel and gasoline is employed. In case 2 bioethanol is produced together with biogas from the distillation stillage and pellets from the insoluble solids (lignin etc.). The cases were chosen to represent two opposite cases from a site integration point of view. A significant amount of heat is liberated from the biofuel process in case 1, whereas in case 2, a large amount of heat is needed in the process but low-temperature secondary heat is available in the process.

Case 1 is studied with simplified flowsheet models in PRO/II to estimate the net heat and power demand in the processes. In case 2 the heating and cooling demands and product yields are calculated based on Wingren et al. (2008). The PRO/II flowsheet model used in Paper II is extended to include gas cooling, gas compression and FT synthesis. Furthermore, the power and steam production at a power plant is included in the scope, estimated with a separate calculation. Finally, the integration of the processes to a typical Nordic pulp mill is studied.

8.1 Case 1: FT diesel

Spruce with a given composition and heating value and 50 wt-% moisture is dried to 15 wt% moisture. The process concept is presented in Figure 11. The biomass is gasified at 800 °C and 1 bar, reformed, and acid gas is removed with Selexol absorption process. FT synthesis is made at 20 bar and water is separated. The FT wax is hydrocracked in an oil refinery yielding FT diesel, light (C5-C9) and gaseous hydrocarbons (C1-C4), according to Calamma and Gambaro, (2010). The hydrocarbon gases produced could provide enough hydrogen for hydrocracking in the refinery's hydrogen plant.

8.2 Case 2: Lignocellulosic ethanol, biogas and pellet production

Bioethanol production by simultaneous saccharification and fermentation (SSF) is employed according to the scheme is presented in Figure 12. Softwood with 50 wt% moisture is fed with SO_2 and steam to the pre-treatment stage. The outlet product is flashed to recover steams at 1 bar and 4 bar. Product yields are based on data by Wingren et al. (2008) assuming separate on-site biopower plant, which is however not using produced pellet from the bioethanol plant. The distillation feed contains 3.8 wt% of ethanol and the ethanol concentration in final product is 99.5 wt-%.

Multiple columns are used to improve energy efficiency along with molecular sieves for the final drying of the ethanol. The lignin residue is dried and converted into pellets. The drying is using secondary heat available in the process. The stillage from distillation is sent to anaerobic digestion for biogas production.

8.3 Heat and power use and production

In the FT diesel case both high pressure steam from a biomass boiler and FT plant are fed to a condensing turbine to generate the power needed.

In the Case 2 ethanol, case biomass is combusted to generate high pressure steam, part of which is fed to the process and partly used to produce sufficient medium-pressure steam in a back-pressure turbine. The rest is fed to a condensing turbine (see Figure 12). The calculations have been updated to include boiler efficiency of 87 %.

8.4 Energy balance and product yields

In Figures 11 and 12 the flows of energy by LHV are presented for the cases.

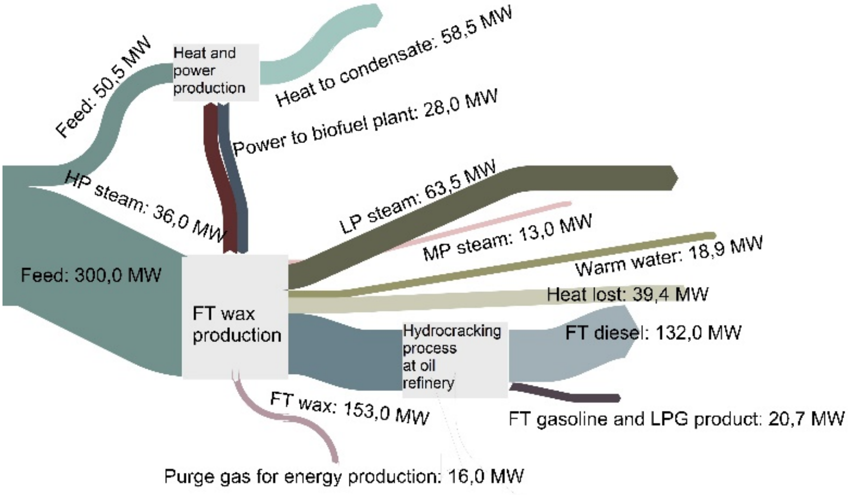

Figure 11. Sankey diagram representing the flows of energy for the FT diesel case (based on LHV).

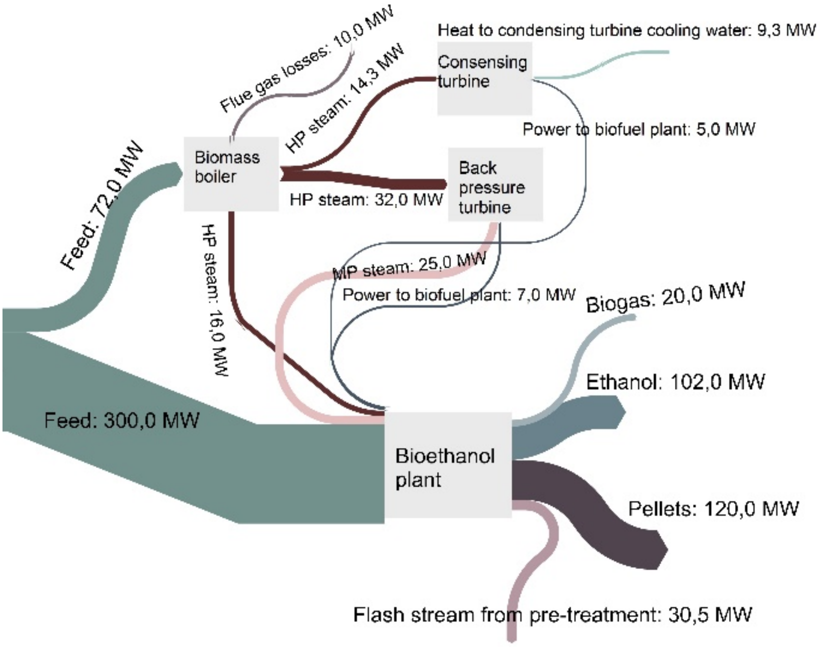

Figure 12 Sankey diagram of the bioethanol process (based on LHV).

The results show that the FT diesel process produces a significant amount of heat as by-product. The high pressure (HP) steam (36 MW) is used for power production. However, not all the power needed by the FT diesel plant can be produced from the recovered heat because of the large power requirement. For example, compression of synthesis gas from atmospheric pressure to 20 bar consumes the majority of 28 MW of power needed. Therefore, additional 50.5 MW of biomass is combusted to generate power (Figure 11). Similar FT-wax product yields as in case 3 calculated by Hannula and Kurkela (2013) are obtained. Their calculations on 0 % moisture basis for 300 MW of biomass feed show that 150 MW of FT-wax and 61 MW of district heat are produced and 1 MW of electricity is imported. The differences of district heat and power production are due to different assumptions in the models and different gasification pressure.

It should be noted that the superheating of steam and pre-heating of feed water for steam production is not considered. Therefore, the power production potential in this Chapter is underestimated. In the more rigorous analysis in chapters 9-10, this is included.

The bioethanol process, on the other hand, requires external heat and power when the stillage residue is not combusted. The energy content of ethanol and biogas (122 MW, in Figure 12) is lower than the energy content for the fuel products from the FT diesel plant (169 MW in Figure 11). Yet a significant amount of chemical energy is available in the stillage residue as seen in Figure 12 used here for pellet production (120 MW). Also, a significant amount of raw material energy is converted to HMF and furfural in the flash stream, which is considered in Chapters 9 and 10. Therefore, a case with combined production of ethanol and utilization of the lignin residue could result in a higher liquid fuel yield compared to cases 1 and 2 if lignin can be used as feedstock for that purpose.

8.5 Site integration to a pulp and paper mill

Integration to a typical Nordic pulp and paper (P&P) mill is described by and Fogelholm and Suutela (2000). The pulp and paper mill has an annual capacity of 600 000 metric tons of air-dried pulp and operation of 8000 h. Table 4 presents the heat & power production and usage of the plant.

Table 4 Heat and power production for a typical Northern European Kraft pulp and paper mill producing 600000 tonnes of pulp annually (Fogelholm and Suutela, 2000).

	Heat Generation		Heat and Power usage		Power Plant		Sold
	Black liquor boiler	Bark boiler	Pulp mill.	Paper mill	Back pressure power	Con-densing. power	
Heat MW	375.0	87.5	187.5	135.4	91.7	47.9	0.0
Power MW			41.3	48.8	90.0	16.9	16.9

Both bark and black liquor are burned to produce heat and power (Table 4). Both the pulp and paper mill consume a significant amount of heat in the form of steam, which is produced in a back-pressure turbine. The remaining steam is utilized for electricity production in a condensing turbine. It can be seen that there is no excess heat and 17 MW of power is sold. Subsequently the FT and ethanol processes are compared standalone and integrated to the pulp and paper mill. The integrated biofuel process inputs and outputs are calculated by subtracting the standalone P&P inputs and outputs from those of the biofuel P&P integrate (Table 5).

The FT case is integrated to the P&P mill in the following way. The heat generated from the FT plant is used in the P&P mill replacing steam produced in the bark boiler, which is closed. Therefore the bark is now fed to the FT plant instead of the bark boiler and the power production of the mill is reduced by 32 MW (Table 5), i.e. input of power to FT plant and the power reduction from condensing power (4 MW) . Since only 76 MW of the heat can be supplied from the FT plant, the deficit 11.5 MW is obtained by reducing the condensing power production heat input from 47.9 MW to 36.1 MW reducing the condensing power power output by 4 MW. The integrate requires now 15 MW power from grid.

In the integrate EtOH case, the ethanol plant uses the steam normally used for condensing power production and 5MW power from grid. Therefore, the power production of the mill is reduced by 22 MW. The gaseous fuel by-product purge gas in the FT case and biogas in the ethanol case could be used to substitute fossil fuel in the lime kiln.

Table 5 .The energetic data of the cases integrated to a P&P mill.

	Input/MW		Output /MW				LHV %		Note
Process	Wood	Power	Biofuel	Pellet	Power	Heat	Liquid and gaseous fuel	Fuel, pellets and heat	
FT alone	351	0	169	0	0	76	48	70	
EtOH alone	372	0	122	120	0	0	33	65	
Integrated FT	200	32	169	0	0	0	73	73	1;2
Integrated EtOH	300	22	122	120	0	0	38	75	1
Integrated EtOH+FT	300	23	190	0	0	0	59	59	1;3

Note 1: Net values; standalone P&P inputs of outputs
Note 2: Bark fed to FT.
Note 3: Pellets fed to FT.

In the last case of (ETOH +FT) both an ethanol plant (300 MW feed capacity) and a smaller Fischer-Tropsch plant with 120 MW feed capacity are included. The FT plant utilises only the solid residue from the ethanol plant and it is directly scaled down based on the FT-case. In Table 5, inputs, outputs, and LHV % are shown for the standalone and integrated biofuel processes as net values. The energy yield (LHV %) here is calculated according to Equation 6, first liquid and gas fuels and then for all the products, including pellet and heat.

8.6 Discussion

The energy yield (LHV %) increased in all the cases when the process was integrated. In the FT case, LHV % for liquid and gas products (L&G) increased from 48 % for standalone to 73 % and for the EtOH case from 33 % to 38 %. For the EtOH case, the efficiency of the integrated plant including pellets is very high, 75 %, although the economic value of pellets is lower when compared to liquid and gaseous fuel. In the case of ETOH+FT, the L&G LHV % is 59 %, which is between the values of integrated FT and ETOH processes. The high L&G efficiency in the integrated FT case is caused by the excess heat from the FT plant is used to replace heat from bark combustion. In this case, 100 MW of bark can be fed to gasification instead of fresh wood. The sacrifice is that power needs to be imported, which also affects LHV %.

The results presented here were for an integrated P&P mill. The site integration of case EtOH +FT plant would be more advantageous to a standalone pulp mill.

Since part of the steam is not consumed in the paper mill, there is 135 MW more steam available compared to the integrated P&P mill. The steam utilisation in the standalone pulp mill could be reduced by first turning off the bark boiler (87 MW steam). In addition, the ethanol plant consumes 41 MW of steam. In that case, both the solid residue from the bioethanol process and the bark could be fed to the FT plant, totalling about 220 MW feedstock, which would increase the efficiency considerably. Even additional lignin from the Kraft pulp mill recovery cycle could be precipitated and fed to the gasification plant further increasing the capacity and efficiency of the biofuel plant.

By comparing the efficiencies to fuel in Table 5 and Figures 11 and 12, it can be seen that the energy yield to biofuels depends on the level of integration. Advantageous site integration should be identified already in the early design phase since the integration affects efficiency. Also, power and heat availability affect feasibility and therefore both self-sufficient operation and operation with external heat input are studied in Papers IV and V.

Biofuel processes that require a lot of heat could be advantageously when integrated to a heat source. For example, a bioethanol process can be integrated to an existing CHP plant so that the bioethanol plant utilises the sugar part of the biomass for ethanol production. The solid lignin would be combusted in the CHP instead of biomass. A clear benefit is increased efficiency of the integrated system compared to the efficiency of a stand-alone system, which has been shown using real plant data from the Örnsköldsvik bioethanol plant and an existing biomass CHP plant (Starfelt et al. 2010).

Limitation in the analysis here include the following: The drying of neither biomass for FT case nor for lignin residue in the ETOH case was not studied in detail. In addition, the FT yield from lignin-rich residue to FT fuel is considered same as that from spruce, which is a conservative estimate. Detailed calculation for separate lignin and sugar processing for lignin-rich residue is presented in Chapters 9-10. The only efficiency criterion used was LHV %, which does not consider the value difference of energy sources. This wide scope is studied in Chapter 9 in terms of primary energy efficiency, which takes into account the different conversion efficiencies for the different energy-based inputs to the process.

8.7 Conclusions

In this chapter site–integration of FT diesel and ethanol production was studied to biomass CHP plant and a pulp and paper mill. The efficiency of integrated production plants consisting of both biofuel plants, CHP plants and P&P mills can be significantly higher than for standalone plants. Therefore, advantageous site-integration options should be investigated already in the R&D phase. Generally, biofuels production processes that produces heat as by-product, such as the FT diesel case can be site-integrated advantageously, so that liberated heat from this process replaces heat produced by combustion. However, the temperature of the heat liberated in the biofuel process is very important for its usefulness. High temperature heat can be efficiently converted into power whereas low temperature heat typically have limited used for drying etc. Heat deficit biofuel processes, such ethanol fermentation can be integrated advantageously to existing biomass CHP plants so that they use a fraction of the original biomass and the rest is combusted in the biomass CHP plant instead of the whole feedstock. By-products from pulp and paper mills such as bark, lignin separated from black liquor or pre-hydrolysates from dissolving pulp production can be used as feedstocks in lignocellulosic biofuel production. They can be used as feedstock instead of forest residues. Also, the integrated biofuel processes and P&P mills typically have a higher efficiency than the standalone plants.

Besides lower efficiency, stand-alone mills usually have higher investment costs since more infrastructure (utility systems etc.) must typically be built. Also, production plants producing by-products that are difficult to transport, such as heat, have to be integrated in order to enable efficient use of all by-products. Since the economic feasibility is usually a key challenge for a biorefinery, standalone plants are usually unrealistic unless the plant is of a very large scale or the produced products are very valuable ones, which is not typical for biofuels or bulk petrochemicals. For economic profitability, efficient use of all by-products is often needed.

9. Development of novel routes to biofuel (Paper IV)

9.1 Introduction

The objective of this chapter is to develop novel biofuel routes based on separate lignin processing and compare these routes with the conventional ones (ethanol, SNG and methanol production), since the results in Paper II indicated high yields. Separate lignin and sugar part processing result in higher biofuel yields and higher profitability (Laser et al., 2009). Based on the material and energy balances, the efficiencies of the processes were calculated. In addition, a study was made of the carbon footprint and economic feasibility of the processes.

Compared to the results attained in Paper IV the electricity production is updated for case MEOH and the biofuel amount produced was updated with a more realistic process heat consumption for cases SNG, EtOH&MeOHa&b, and ENHHCa&b as described in Appendix Table D (for abbreviations see Table 6). In all cases, the raw material is softwood (pine) logging residue. The studied biomass-based process concepts are presented in Table 6.

Table 6 The studied process concepts.

Case	Description	Subcases	Novelty
MeOH	Conventional methanol production by gasification and conversion of synthesis gas to methanol	No subcases	Conventional process
SNG	Conventional synthetic natural gas production by gasification and conversion of synthesis gas to methane.	No subcases	Conventional process
EtOH	Conventional bioethanol production by steam explosion pre-treatment and heat and power production by combustion of residual lignin.	No subcases	Conventional process
EtOH& MeOH	Ethanol and methanol production from biomass by steam explosion pre-treatment and conversion of residual lignin to syngas and methanol.	a) Heat self-sufficient b) Employing external heat	Enhanced process
ENHMeOH	Novel enhanced methanol production by one-step biomass conversion to sugars, hydrogen production from sugars by aqueous phase reforming, residual lignin gasification and methanol production from hydrogen-enriched syngas.	a) Heat self-sufficient b) Employ external heat	Enhanced process
ENHSNG	Novel enhanced methane production by one-step conversion to sugars for hydrogen production from sugars by aqueous phase reforming and residual lignin gasification and methane production from hydrogen-enriched syngas.	a) Heat self-sufficient b) Employ external heat	Enhanced process
ENHHC	Novel hydrocarbon production by aqueous phase hydrogenation of biomass-based sugars by hydrogen obtained from gasification of lignin residues.	a) Heat self-sufficient b) Employ external heat	Enhanced process

The MeOH, SNG and EtOH cases are conventional lignocellulosic biorefinery processes, which are compared with the enhanced processes, EtOH&MeOH, ENHMeOH, ENHSNG and ENNHC. The latter three processes are new processes; concepts are presented for the first time in Paper IV. The material and energy balances are calculated for the same raw material in all of the processes. Two sub-cases, a and b, are considered in EtOH&MeOH, ENHMeOH, ENHSNG and ENHHC. In sub-case a, the process is adjusted to be self-sufficient on process heat. In case b, the deficiency of low temperature heat used for drying, distillation and acid gas medium regeneration is replaced by transferring heat from a nearby plant. This increases the biofuel yield since the product gas is not combusted in order to satisfy the process heat demand.

The simplified block diagrams of the processes are shown in Appendix in Figure A and more detail for each case is described below. In the processes all the heat is used in the process, no district heat is exported and power production is maximized.

MeOH case: Methanol production from pine

Chipped pine is dried from 50 wt% moisture content to 13 wt%. The gasifier is operated at 800 °C and 1 MPa and the reformer at 950 °C. The gas is cooled and fed to a shift reactor where the H_2/CO ratio is adjusted to approximately 2.1, which is suitable for methanol synthesis. Then the gas is cooled and acid gases are removed by scrubbing. The purified synthesis gas is compressed for methanol synthesis. After the methanol reactor, the gas is cooled to separate the methanol. The unreacted gas is recycled back to the reactor. The condensed mixture of methanol and water is sent to methanol distillation the methanol concentration of 99 wt-% is reached. The non-condensables are sent to combustion.

SNG case: Synthetic natural gas production from pine

The process is similar to the MeOH case except for the synthesis section and product separation. The reformer uses a catalyst such as zirconia, which catalyses only the decomposition of tar but not methane. A higher ratio of H_2/CO of approx. 3.1 is required for methane synthesis at 31 bar. Due to the exothermic nature of the methanation reaction, the reaction is performed in four steps with cooling in between each catalyst bed in order to prevent overheating. So that the temperature is kept between 300 and 600 °C after each catalyst bed. Finally, the gas is cooled and water is separated by condensation. The gas is compressed to 6 MPa and dried by contacting the wet gas with tetra ethylene glycol that adsorbs the water from the gas.

EtOH case: Bioethanol production from pine with combined heat and power production

In the EtOH case, pine chips are treated with SO_2 and steam. After steam explosion, the product is flashed and the vapour is condensed to recover furfural. The pre-treated wood slurry is cooled and diluted before the SSF operated at ≥40 °C. Both hexoses and pentoses are fermented.

The fermented mixture is distilled to remove the ethanol and part of the water. The residue of distillation is directed to product separation of lignin-containing fibres and evaporation of residual sugars. The solids and the strong evaporated liquid from the evaporator are used as a fuel in the biofuel boiler. For details, see Paper IV.

EtOH&MeOH case: Combined ethanol and syngas-based methanol production from pine

Ethanol is produced in the same way as in the EtOH case but the lignin residues and liquid remaining after evaporation are gasified after drying and the syngas is converted to methanol, as in the MeOH case via reforming, water gas shift and methanol synthesis. The concentrated liquid remaining from the evaporation and lignin residue is sent to lignin drying. The methanol plant is similar to the one described in the MeOH case but with a smaller capacity. Finally, the product is distilled to a mixture of 57 wt% methanol and 41 wt% ethanol.

ENHMeOH case: Methanol production from pine with aqueous phase reforming of sugars and lignin gasification

Pine biomass is fed to a combined hydrolysis and hydrogenation step together with an acid catalyst at 160° and 5 MPa, and sugar alcohols are formed.

After aqueous phase reforming at 240°C, the gas phase is separated from the solid and liquid in a phase separator. Solid lignin residue is converted into synthesis gas as in the EtOH&MeOH case. The gas containing hydrogen and carbon dioxide from aqueous phase reforming is heated to 490 °C and sent to a reverse water gas shift reactor, where part of the carbon dioxide is converted into carbon monoxide. The gas is combined with the gas obtained from lignin gasification and reforming. The advantage is that a higher yield of methanol is obtained. The gas purification and MeOH synthesis are identical to the MeOH case.

The ENHSNG case: SNG production from pine with aqueous phase reforming of sugars

The ENHSNG case is identical to the ENHMeOH case except that methane rather than methanol is produced from the synthesis gas. The methane production is described in the SNG case. In the ENHSNG case, the yield of carbon monoxide and hydrogen is higher than in the SNG case.

ENHHC case: Hydrocarbon production from pine with aqueous phase hydrogenation with hydrogen produced by gasification of lignin residue

The carbohydrate part of the biomass is hydrogenated into sugar alcohols as in the ENHMEOH and ENHSNG cases. The sugars are further hydrogenated into alkanes by aqueous phase hydrogenation, using the hydrogen produced by gasification of the lignin residue. Next, water, solids and hydrocarbons are separated and hydrocarbons are distilled. Lignin is recovered and sent to gasification.

9.2 Methods for process analysis and evaluation

The details of the model used in are described in Tables A and B in Appendix.

9.2.1 Material and energy balances

The material and energy balances were calculated for each case using the Aspen Plus simulation program with an add-on calculation in Excel, as described earlier. In Paper IV, the processes were studied with models similar as in Chapter 8 but Aspen Plus v 8.2 was employed as the simulation tool instead of PRO/ II and biomass was represented as a non-conventional component.

The changes to the process conditions were as follows:

- Heat integration was studied with maximum heat recovery for all streams in the process, including power and heat production.
- Gasification pressure of 10 bar was chosen instead of 1 bar as in Chapter 8. This results in a more optimal process with lower electricity demand in synthesis gas compression.
- Reforming is done at a lower temperature (950°C) using a catalyst.

The energy balance error was found to be less than 2 % in all the cases depending on small differences in enthalpies between different models, which were combined to calculate the overall energy balances.

The energy content of the raw material was obtained from the excess heat calculated by the Aspen flowsheet simulation model.

9.2.2 Heat and power demands

The heat integration was made based on maximum heat recovery: i.e. minimum external heating and cooling demands. For this purpose, the heating and cooling demands were summed to construct a grand composite curve to check whether there was an excess or deficit of heat at each temperature interval. If there was a deficit of heat, the heat required was assumed to be generated from biomass incineration at 89 % efficiency.

If there was excess heat in the process, it was used for generating high-pressure steam, which in turn was used for cogenerating heat and power. Also, medium and low-pressure steam and hot water were generated from high-pressure steam in the steam turbine at temperature levels of 200 °C, 150 °C, 90 °C and 65 °C.

The improvements in modelling accuracy were as follows:

- Power and heat production was considered in heat integration, which was based on maximum heat recovery as in Chapter 8.
- Power production was studied more rigorously taking feed water preheating into account.
- Acid gas removal was considered to require a fixed amount of heat per mass of acid gas removed.
- The heat demand of feedstock drying was estimated for convective drying by hot air.

Lignin drying requires a lot of energy. In this work, the lignin is assumed to contain approximately 34 wt% solids after mechanical dewatering. The lignin residue is dried in a belt dryer, utilizing heat above 65 °C. A drying heat of 4 MJ/kg of water evaporated is employed (Fagernäs et al. 2010).

The electricity consumption in the process was estimated by summing the power consumptions of the compressors and pumps. The power consumption in oxygen production was estimated to be 280 kWh/t for pure oxygen, which is somewhat higher than the 245 kWh/t stated by Hong et al. (2009), because the oxygen required must have higher purity.

9.2.3 Efficiency indicators

The green house gas (GHG) reduction, NPV, LHV energy yield and primary energy efficiency was calculated by Equations 1, 3, 6 and 7 and the inputs for GHG, cost and economic calculations are given in the Paper IV.

Here a unacost present value factor of 6.67 is used to convert the sum of the cash flows into a present value, corresponding to a 13 % internal rate and 15 year lifetime of the investment as shown in Equation 8.

$$f_s = \frac{(1+i)^n - 1}{i(1+i)^n} \qquad (8)$$

where

fs = the unacost present value factor
i = internal rate
n = life time of the investment

No operating labour costs are included at this stage because they are expected to be on the same level for all the routes and the effect on the economic feasibility is rather small for large-scale plants.

9.3 Results and discussion

The calculated performance criteria (as presented in detail in Chapter 5.2) for the process are presented in Figure 13, which describes the economical, technical or sustainability performance of the processes. The updated indicators for Paper IV are presented in Figure 13 and Appendix D in detail.

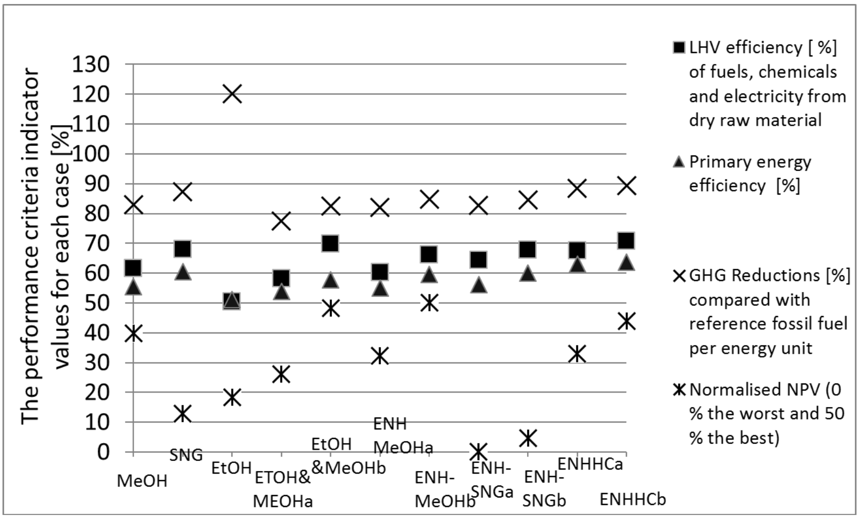

Figure 13. Summary of the performance criteria indicator values for each process. Regarding processes, a sub-case refers to the case without external heat input and sub-case b to the case with extra low temperature heat being added from outside. GHG reductions refers here to Greenhouse gas reductions.

It can be seen from Figure 13 that the total product LHV efficiencies for two of the novel processes developed in this thesis (both cases of EtOH&MeOHb and ENHHCb) are somewhat higher than in any conventional process (MeOH and EtOH). Most of the liquid fuel enhanced processes represent superior energy yields (66-71 %), especially in 'b' form, compared to the conventional ones. Case ENHSNG compared to SNG presented similar or lower LHV energy yield. The new process concepts are also capable of using external low-temperature heat as a heat source (from 31 to 47 MW) for biomass drying; see Appendix Table D. This low-temperature heat can be secondary heat, for instance from a nearby pulp mill or power plant. The benefit is that this heat, which is usually wasted, can be utilized to 100 % LHV efficiency to produce liquid or gaseous fuels. On the other hand, these processes can also be run in a heat self-sufficient mode, producing less fuel.

The most energy-efficient processes in producing mainly liquid are the new EtOH&MeOH and ENHHCb processes (70-71 LHV %).

The processes with the highest potential for GHG reduction (as tonnes of CO2 equivalents saved per year) by producing biofuels and electricity are the

ENHHCb, ENHMeOHb, ENHSNGb EtOH&MeOHb processes, substituting 525-571 CO2 eq. kt. per year (Figure 14).

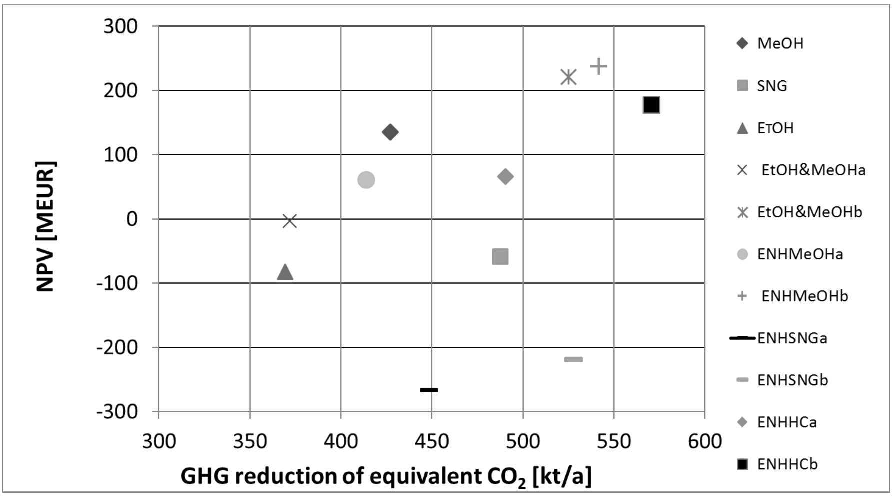

Figure 14 GHG emissions reduced as CO2 equivalent (kilotons per year) vs. net present value of the process concepts.

The highest GHG reduction % of CO2 equivalents when 1 MJ of fuel produced substituting 1 MJ of gasoline (Equation 1 in chapter 5) was obtained for the EtOH process. Yet, the process has the lowest CO_2 reduction potential as kt/a since the LHV efficiency is the lowest.

In this study, the NPV (shown in Equation 3) was used as the economic indicator; the most important terms affecting the NPV are the feedstock price, product prices and capital cost. By comparing the NPV (Figure 14), it can be seen that three of the new processes (ENHMeOHb, EtOH&MeOHb and ENHHCb) are very profitable: the NPV is between 177 and 238 MEUR, although the estimated investment cost is higher than for the conventional cases. High amount of liquid production favours high NPV, since the price for liquid fuels is high compared to SNG. All SNG processes are unprofitable with the prices presented.

In Figure 14, where both the GHG reduction potential (kt/a) and the NPV (MEUR) are presented for the processes studied, The ENHMeOHb case has the highest NPV (238 MEUR) with 2nd highest GHG reduction (542 kt/a). ENHHCb is the most efficient GHG reducer (571 kt/a) with a lower NPV (177 MEUR). The EtOH&MeOHb process has the 2nd highest NPV (221 MEUR) with 3rd highest 525 kt/a GHG reduction.

The main shortcomings of the calculations are the following: Since some parts of the processes are new, the assumptions for product yields were obtained on laboratory scale, and these should be verified on pilot scale. The exact costing of the processes is not possible in the development stage since the equipment design has not yet been made. Therefore, the costing is based on the scaling of costs of existing facilities and process sections when available, and for the processes in the laboratory stage, analogical systems were used for the costing of those sections. At this stage, the heat integration study can be based only on maximum heat recovery potential (i.e. minimum heating and cooling demand). Yet, in a real industrial-scale plant, the full heat integration potential is not feasible due to economic uncertainties. In addition, some of the complex operations were calculated with the less rigorous methods available in flowsheeting programs. Both the integration and the modelling aspect are further elaborated for selected processes in Chapter 10.

10. Rigorous modelling with heat integration (Paper V)

The interesting process concepts (EtOH&MeOH and ENHHC) utilizing separate lignin and sugar part processing were selected from previous chapter for more rigorous study and comparison with the conventional processes (MeOH and SNG).

Also distillation was modelled in more detail, as shown in Table B in Appendix. The aim of this part is to answer two questions; firstly, can lignocellulosic liquid biofuel production be intensified by utilizing separate carbohydrate and lignin processing? Secondly, can excess heat and power potentially available be used effectively in these processes? The main criteria in this evaluation are the GHG reduction potential and the profitability of production.

10.1 Modelling

The following operations were calculated separately with detailed Aspen models (version 8.4): Gas purification and regeneration of Selexol solvent, low temperature cooling with ammonia, gas drying in the SNG process with TEG, TEG regeneration and biomass & residual gas combustion. Simpler spreadsheet calculations were used in the EtOH&MeOH process for calculating the final product and lignin residue drying.

The fuel consumption in the transport of biomass and the power consumption in oxygen production were also calculated. The error in the energy balance calculations was less than 3 %, which is sufficient for comparison of the different processes.

10.2 Energy integration

The heat consumption was not calculated using minimum utility demand as in Paper IV but with more realistic heat integration where the heating and cooling demand are calculated for a flowsheet including all the heat exchangers. Here, also realistic heat exchange between real process streams was considered. The heat exchanger specification were adjusted if needed so that there was no temperature crossovers in the heat exchangers. Power production was done in the following way: high temperature heat above 250°C was utilized for steam production. The feed water and feed water make-up were pre-heated for steam production. The pressure of the high-pressure (HP) steam produced was adjusted to utilize the heat from the chemical synthesis. The superheated steam was fed to an extraction backpressure steam turbine to obtain low-pressure steams and power.

MeOH process

A steam level of 48 bar was chosen to allow the utilization of the heat from methanol synthesis ≥270°C for steam generation. The steam for steam reforming and gasification was obtained at 10 bar. The low-pressure steam was obtained at 1.6 bar for methanol distillation and regeneration of the Selexol solvent. The lowest temperature level heat (≥ 65 °C) from the turbine outlet and 1.6 bar steam were used for the methanol column and for drying the feedstock.

SNG process

In the SNG process, also excess heat was available for steam production. Higher pressure steam (80 bar) was generated due to the higher temperature required for the methanation ≥ 300°C. Again, the heat not used for steam production was used for the feedstock dryer. In the extraction turbine, part of the 80 bar steam was expanded to 10 bar steam, which was used for gasification and drying. Subsequently the rest of the steam was expanded to 1.75 bar, and used for the regeneration of Selexol.

EtOH&MeOH process

The EtOH&MeOH process requires extra heat. To satisfy the heat demand in subcase 'a', extra biomass was combusted in the power plant. In subcase 'b' the heat needed was obtained from an external source.

ENHHC process

Similarly, the ENHHC process also requires extra heat and therefore, in the subcase 'a' ENHHC product gas containing ethane and methane was combusted in order to produce the needed heat. In the subcase 'b' external heat was used.

10.3 Energy balances and yields

MeOH process

In the methanol production process, it can be seen that a significant amount of heat is liberated in synthesis. This can be utilized for steam and power production in the power plant so that the process produces 2.5 MW of excess power (Table 7). In this process, the largest consumer of energy is the drying of feed biomass and the distillation of methanol. A similar energy yield of methanol and power excess was obtained as in Hannula and Kurkela (2013). When the efficiencies were compared on an equal basis for dry biomass they obtained 56 % LHV into methanol for dry biomass (for condensing power production and hot gas filtration before reforming at 550 °C) and 61 % (for CHP production and hot gas filtration before reforming at 850 °C) compared to 58 % obtained in this study (Table 7).

SNG process

The main difference between the SNG process and the methanol process is that heat from methanation is liberated at a higher temperature and the product yield is higher. Due to the higher product yield, not enough power can be generated for the process and extra electricity has to be imported from the grid. The higher yield also depends on the fact that in the reforming step the catalyst only reforms the tar components but not the methane. The energy yield of SNG here (70 %; Table 7) is slightly higher than the 62 % biomass to chemical energy yield reported for the Güssing plant (Rehling et al. 2011), yet their simulation based energy yield was 66 %.

EtOH&MeOHa process

In the EtOH&MeOHa process, a similar product energy yield (57 %) was obtained as that found earlier in the methanol process (58 %); see Table 7. Here a consistence of 20 wt% was assumed in the simultaneous saccharification and fermentation. With a lower consistency, the energy needed for product recovery would be significantly higher. In this process, which does not utilize external energy, about 71 MW of wood and the residual gas was combusted in order to produce heat and power for the process demands. Drying mechanically dewatered lignin with 66 wt% moisture content is the largest consumer of energy. Here the lignin was dried using a belt dryer to approx. 13 wt% moisture content.

The moisture content of lignin and heat demand of the sugar processing part of the process had a significant influence in the energy yield of the whole process. If the gasification was carried out on lignin with higher water content, for example 40 wt %, a significantly smaller part of the raw material energy was be converted into chemical energy in synthesis gas. However, Laser et al. (2009) have reported an LHV efficiency of close to 80 % for separate sugar and lignin residue gasification for switchgrass dried lignin residue gasification and low steam consumption for the ammonia-based pre-treatment method.

The results indicate that in the EtOH&MeOHa process the limiting factor for the biofuel yield in biofuel production was not the conversion efficiency from raw material to fuel but the heat demand of the process. Here, extra biomass, purge gas and non-condensables were combusted to generate heat. An energy yield of 57 % by LHV into ethanol and methanol was obtained (Table 7).

EtOH&MeOHb process

In the EtOH&MeOHb process, it was found that the biofuel yield could be increased significantly by utilizing external low temperature heat, as shown in Figure 8 in Paper V and Table 7. In fact, the process can act as a 'waste heat and power to gas and liquids' process for producing liquids at 89% HHV and 77% LHV efficiency for the added low temperature heat and some power. Low temperature heat would be available from power plants or pulp mills especially in summer. The process could run in summer in 'b'-mode to utilize the excess heat and power available to produce motor fuels, and during winter in 'a' mode to produce some bio power.

ENHHC processes

In the ENHHC process, significantly less energy is needed for product recovery, compared to EtOH&MeOH process. If the hydrolysis yield can be increased further, the yield of liquid hydrocarbons will be significantly increased. Also in the ENHHC process the limiting factor for fuel yield is the availability of low temperature level heat for lignin drying and regeneration of Selexol solvent. Therefore, this process is also capable of running in two modes: the 'b' mode utilizing external low temperature heat and power and 'a'-mode being energy sufficient but producing less fuels and some power (Table 7). In the 'a' mode, the energy yield of the product was 68 % based on LHV and part of the produced gas is combusted to satisfy the process heat demand. The assumptions made include that the majority of the water can be recycled back to the simultaneous pretreatment and hydrogenation and the solids can be separated from water with no further evaporation of the water phase after product separation.

The product yield by energy in the ENHHC process in 'b' mode is higher than in other processes 72.5 % by LHV (Table 7). Added heat and some power from outside the process can be converted into hydrocarbons with a very high LHV efficiency of 116 %. This is because the heat from outside replaces the heat produced by combustion of biomass or by-products involving heat losses.

10.4 Performance indicators calculations

Several energy, economic and GHG indicators such as LHV efficiency, NPV, production cost, GHG reduction, GHG reduction cost i.e. cost of reducing one tonne of GHG, and GHG reduction cost compared to gasoline (or natural gas for the gas products) were calculated and the main indicators are presented in Table 7.

Figure 15 presents the main indicators graphically, and Figure 16 gives the net present value vs. the equivalent carbon dioxide savings (kt/a) for the processes. Since fuel and other costs vary, a sensitivity analysis on the NPV is presented in Figure 17. The variables are the product, biomass price and product yield, and it can be seen that the NPV of all the processes is most sensitive to the product price and yield. Figure 17 presents the sensitivity analysis showing the effect of product and raw material prices and yield to NPV.

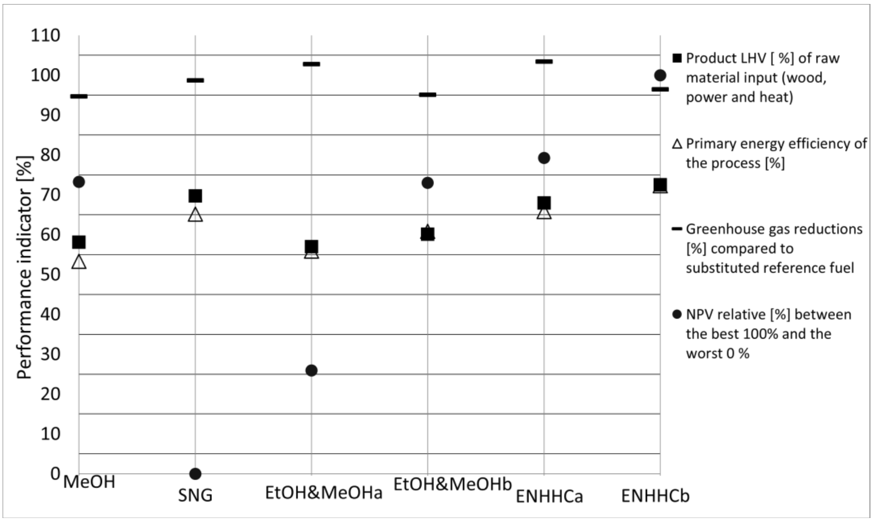

Figure 15. The main performance criteria of the processes.

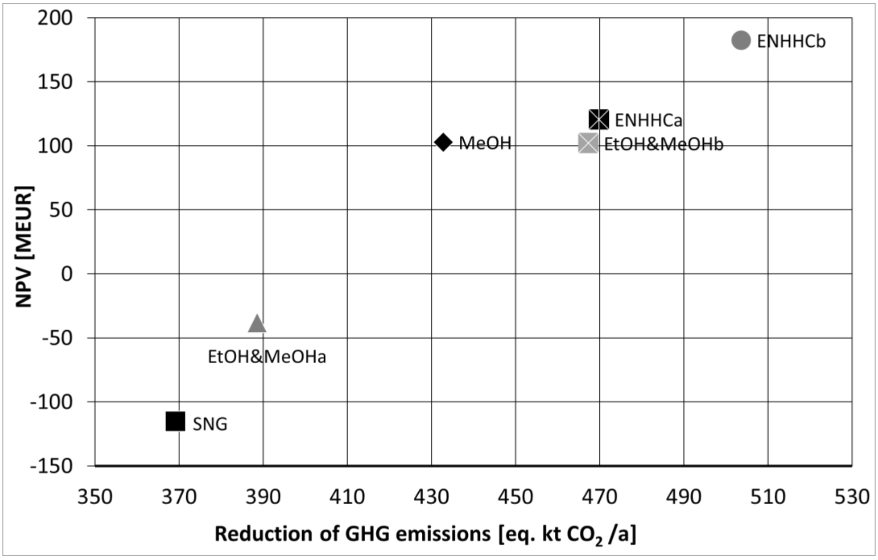

Figure 16 Savings in GHG emissions vs. NPV for the calculated processes

Table 7. Key performance data of the studied processes.

Cases	Unit	MeOH	SNG	EtOH &MeOH a	EtOH &MeOH b	ENHHCa	ENHHCb
Biomass feed input rate	(LHV) MW	300	300	300	300	300	300
Liquid output rate	(LHV) MW	171.9	-	167.7	214.8	137.0	137
Gaseous fuel output rate (LHV)	MW	0	210.5	0	0	61.9	101.8
Total energy flow content of fuels	(LHV) MW	171.9	210.5	167.7	214.8	198.9	238.8
Electricity surplus	MW	2.5	-1.90	3.3	-7.5	5.0	-6.0
Additional heat flow inputs as low temperature heat	MW	0.0	0.00	0.0	50.0	0.0	23.2
Energy yield of products with heat and power	LHV %	58.1	69.7	57.0	60.1	68.0	72.5
NPV	MEUR	103	-115	-38	102	121	182
Production cost	EUR/ MWh	89	70	104	93	76	69
eq. GHG reduced	kt. CO_2/a	433	369	389	467	470	504
GHG reduction cost	EUR/t CO_2	282	320	360	336	258	260
The difference of GHG reduction cost and reference fuel cost[a]	EUR/t CO2	123	206	187	158	115	111

a) The difference between GHG reduction cost and reference fuel cost describes the cost of replacing reference fossil fuel with biofuel to reduce GHG emissions.

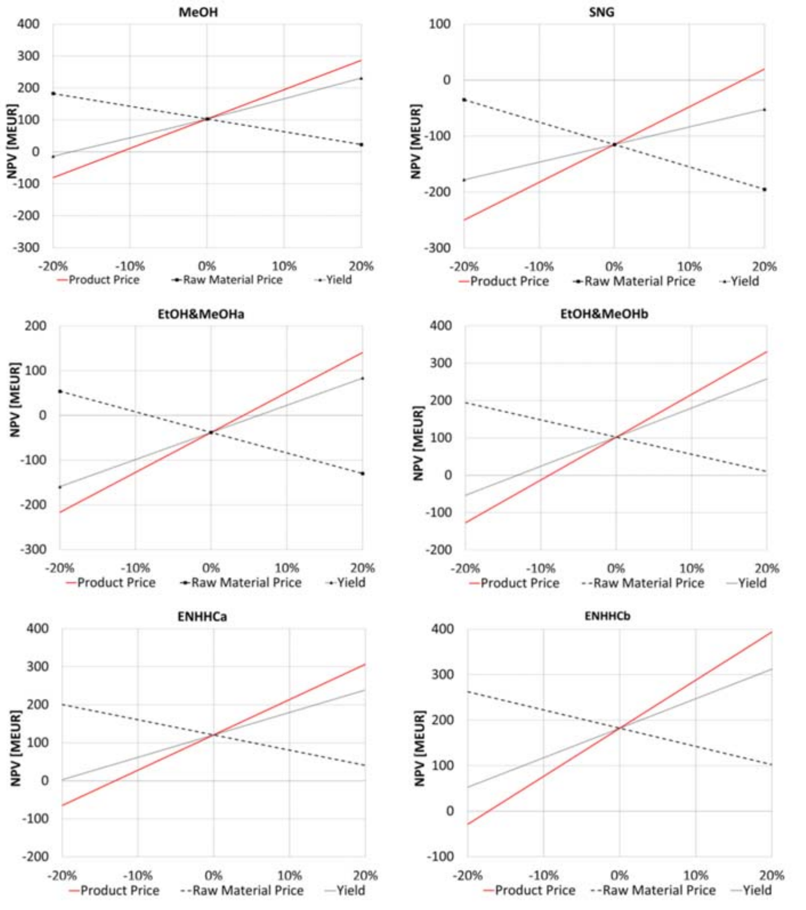

Figure 17. The sensitivity analysis of NPV vs. change in each variable in ± 20 % on x-axis.

10.5 Discussion

Three of the processes are energy self-sufficient (or excessive) producing power, another three are power deficient, and two are also heat deficient in low temperature range (see Table 7). These latter two (‘b’ cases) (EtOH&MeOHb and ENHHCb) are in fact operating modes that utilise external heat and power if available; the processes can be run also in energy sufficient mode (‘a’ cases).

The ability to use external low-temperature heat also has a significant beneficial effect on the economics as seen in Table 7, when comparing subcases ’a’ and ‘b’ of the EtOH&MeOH processes.

The process energy yields (LHV% including heat and power) in Table 7 vary between 57-72.5 %. The clearly highest energy yields are in the ENHHCb, SNG and ENHCCa processes (approx. 73, 70 and 68 %). The others are in the range of 57-60 %. In the economic analysis, the ENHHCb and ENHHCa processes give the highest NPV (182 and 121 MEUR). This is because of the high product yields and low investment costs. Two other profitable processes are EtOH&MeOHb and MeOH (NPV ≈ 100 MEUR). The SNG process is the most unprofitable (NPV = -115 MEUR), since the product gas has a much lower price than liquid biofuels. The ENHHCb and SNG (69 and 70 Eur/MWh) cases had the lowest production costs.

The ENHHCb process gives a higher profit and energy yield than ENHHCa, since low-cost waste heat and power can be utilised in case b with high efficiency. If the cost of low-temperature heat were lower (e.g. when the waste heat does not have any alternative use and it would be dumped), the NPV would be even higher.

The ENHHCb process has the highest GHG reduction potential (504 kt/a). This is because of the high energy yield efficiency (LHV %) and large usage of excess heat, which has a low GHG value. Also the lowest GHG reduction costs, approximately 260 EUR/t CO_2 eq., are obtained in the ENHHCa and ENHHCb processes. Greenhouse gas emissions depend on several variables: the yield of the product that substitutes the fossil fuel, the type of product substituted (gasoline or natural gas), and the amount of power used and produced and the amount of excess heat used. Electricity with low GHG emissions would favour case 'b' processes.

The GHG reduction costs when a tonne of CO_2 eq. is reduced (the last row in Table 7) can also be expressed as an additional cost of biofuel compared to a fossil reference fuel (gasoline or natural gas). The lowest replacement cost is gained by the ENHHCb and ENHHCa processes (111 and 115 Eur/t CO2 eq).

When comparing the process modes, it can be seen from Table 7 that in ENHHC both modes produce the same amount of liquid fuel but that mode 'b' produces 1.6 times the amount of gaseous products compared to ENHHCa. In fact, the low temperature heat (with some power) is transformed to gaseous fuels by 116 % LHV efficiency by the ENHHCb process, since this heat replaced the combustion-produced that involved energy losses. In the MeOH&EtOH process, the product increase from utilizing waste heat and power is not gas but liquid fuel (alcohol mix), which may be more convenient when considering the fuel storage. The transformation efficiency for the waste heat and power added is less (77 % LHV), which is nevertheless good in comparison to the total LHV efficiency (in the range of 60 %). However, it should be noted that the product in the ENHHC case is hydrocarbons whereas in the EtOH&MeOH case a mixture of methanol and ethanol is produced.

The uncertainties of the ENHHC processes are related to scale-up, since the study is based on laboratory-scale yields for the individual steps, which should be verified on a larger scale and for a process working with several steps combined. Besides, the processing assumptions made should be checked in pilot scale.

It was found that the routes employing separate processing for lignin and carbohydrate part (ENHHCa and EtOH&MeOHa) are heat-deficient in the low-temperature area but produce some excess power. Therefore, it is beneficial to integrate these processes with another process having an excess of low-temperature heat (e.g. power plants or pulp mills).

As a conclusion, the answers to the two research questions presented earlier are: Lignocellulosic liquid biofuel production can be intensified compared to lignocellulosic methanol production by utilising separate carbohydrate and lignin processing (by ENHHC) but not by the EtOH&MeOH process. However, compared to conventional lignocellulosic ethanol production, enhancements are made possible by this approach in both cases. Secondly, excess heat and power from outside can be utilized effectively in these processes in ENHHC at 136% HHV / 116% LHV efficiency and in EtOH&MeOH at 89% HHV / 77% LHV efficiency. Thus the enhanced processes utilising separate processing for the lignin and carbohydrate parts, especially the ENHHC, seem quite promising.

It was also found that the EtOH&MeOH and ENHHC cases could be run self-sufficiently in winter and utilize excess heat and power in summer. This would be beneficial when the process is integrated to a CHP plant with varying annual district heat demand. In addition, the fluctuation in annual availability of heat could be reduced by drying lignin when excess low temperature heat is available and storing energy in the form of dried lignin residue. Furthermore, cheap peak electricity could be converted into extra hydrogen by electrolysis of water, and the hydrogen could be co-fed into the plant increasing the yield in the fuel production by hydrogenation of carbon dioxide in the process.

11. Holistic results analysis and discussion

11.1 Modelling levels in multilevel modelling

In this thesis, biorefinery processes were modelled on different accuracy levels. The aim was to first use simple models, which could be applied for screening multiple process routes and raw materials. The promising routes could then be selected for further study using shortcut flowsheet models (2nd level). The final evaluation of process routes was done with rigorous flowsheet models (3rd level). Here the 1st level models are simplified models for estimating maximum yield, the 2nd level models estimate also the heat demand of the process with more realistic product yields, and finally the 3rd level models also include realistic heat integration and more detailed modelling of auxiliary processes.

11.1.1 Multilevel modelling tool

A multilevel tool developed was presented in Chapter 6.1.1, and it was used for e.g. calculation of separate lignin and sugar processing routes. It was found that this kind of tool could be extended in such a way that different modules - power plants, acid gas removal, drying etc., could be connected to a superstructure. The superstructure with separate, more rigorous blocks could also be used to calculate different operation points in terms of heat and power production and streams from one process to another.

11.1.2 The 1st level (paper II)

Compared to conventional flowsheeting models, which were applied on the 2nd and 3rd modelling levels, the 1st level model is used to quickly estimate the yields for a large number of raw materials and process options. This initial evaluation can be done for process ideas to check feasibility of performing R&D work on the alternatives. To our knowledge, a model similar to the 1st level models has not been applied to calculate both gasification, separate lignin and sugar processing routes of biomass. However, the 1st level models do not give any information of the heat and power demand and the ability to generate electricity from the produced process heat.

11.1.3 2nd level (papers III-IV)

In Papers III and IV, shortcut flowsheeting models (2nd level models) capable of estimating the heat and power consumption in the process were created. In addition, the maximum potential to produce power from process heat could be assessed. However, the model did not include heat integration and auxiliary process steps (acid gas removal and evaporation), which were estimated separately with simple models. For example, the heat demand in the regeneration of solution used for acid gas absorption was estimated using a fixed value for the energy consumption per kg of acid gas removed. In addition, shortcut distillation was used to model distillation in Paper IV.

The maximum available heat in the process was calculated by estimating all the heating and cooling demands in a process at chosen temperature intervals.
The heating and cooling demands were summed starting from the higher temperature to check if there was an excess or deficit of heat in the process. If there was a deficit of heat, it was assumed that part of the product was combusted to generate heat with a typical efficiency (89 % by the higher heating value) in order to satisfy the process heat demand. If all the liberated heat was not needed in the process, power was produced from the excess heat. A typical minimum temperature difference of 10 °C between hot and cold streams in heat exchanges was assumed in the calculations.

In Paper III, modelling was done with PRO/II, and for Paper IV, the processes simulation models were created using Aspen 8.4. The raw material was defined as a non-conventional component. Only the heat of formation, heat capacity and density were specified. The heat of formation was derived from the ultimate composition of biomass and its higher heating value. In the model, the non-conventional component was split into atomic species (carbon, hydrogen, oxygen, nitrogen, sulphur, chlorine) and ash, represented by a solid component such as calcium oxide before the gasification step. Due to a lack of data for all components, C6 sugars were represented by the model component glucose, C5 sugars by xylose and HMF by benzenetriol.

11.1.4 The 3rd level (Paper V)

The 3rd level models were constructed in Aspen 8.4. In the 3rd level models, unlike the 2nd level models, rigorous models were used for distillation (stage-by-stage models) and a multi-effect evaporation. Furthermore, also auxiliary units such as acid gas purification, gas drying, and cooling using ammonia were calculated using Aspen models.

11.1.5 Sources of inaccuracies and limitations of the modelling

One of the largest sources of errors in biorefinery process estimation is the accuracy of gasification models used for predicting synthesis gas yields, as described by Kangas et al. (2014). When equilibrium models are used, generally the hydrogen and CO content are overestimated whereas CH_4 and C_2H_4 are underestimated.

The methane content was fixed in Chapters 9-10. The observed methane content for a fluidized bed gasifier is approximately 9 vol % on dry basis in the gas for wood residues at 840 °C and 2.5 bar (Kurkela and Simell, 2008).

Another source of inaccuracy is the actual carbon conversion on the gasification step. In Chapters 7-10, the models predict full carbon conversion but with low lambda (air to fuel ratio to stoichiometric air to fuel ratio), the carbon conversion deviates from 100 % and therefore the cold gas efficiency of synthesis gas is lower than predicted.

Tar components formed in gasification are very difficult to predict accurately. Although this aspect is important in tar removal, the tar component does not significantly affect the efficiency in a fluidized bed or downdraft gasifier, particularly if the process concept includes a reforming step where the heavier components will be reformed into synthesis gas. This is because the equilibrium models can predict actual gas composition at the reformer outlet significantly more accurately than gasification because of the catalyst and higher temperature. On the other hand, updraft gasifiers produce high tar content gas and tar energy content cannot be ignored. This means that the modelling approach used here applies best for fluidized bed gasifiers with a downstream reforming step. The same approach could however be used for down draft gasifiers, if measured gas composition of methane and other light hydrocarbon gases was available. For updraft gasifiers, it is expected that the measured gas composition deviates more from the predicted gas composition and the model probably would not result in a satisfactory prediction of the product gas composition.

One limitation of modelling, even in the most accurate 3rd level models, is that the reaction kinetics affecting the size of reactors is not considered. For the ethanol, fermentation, aqueous phase reforming and pre-treatment yields in the 2nd and 3rd models and selectivities are based on literature data since the models cannot predict yields for other conditions and raw materials. However, the desired conversion (lower than equilibrium conversion) specified at this stage can be used at a later design stage to back-calculate the actual reactor size based on GHSV data etc. from laboratory measurements. Naturally, care must be taken in equilibrium-limited reactions, such as water gas shift and methanol synthesis, when specifying yields that can be achieved considering reaction equilibrium limitations.

One important limitation in the evaluation is that the production yields and selectivities based on laboratory work are presumed to be achieved for an industrial-scale unit. When available, data from an integrated system or pilot scale would be more reliable. Care has to be taken also when comparing cost estimates for different technologies. For less developed technologies with lower technical readiness level, the investment cost estimate for a production plant tend to be more under predicted than for technology with higher technical readiness level. Additionally, the first production plants based on a new process are typically significantly more expensive than the nth production plant constructed as when the technology is mature, the investment cost becomes lower.

11.2 Energy yield

The differences in predicted energy yields for the products in the 1st, 2nd and 3rd levels are presented in Table 8 based on Chapters 7-10. The differences in the LHV % predictions are because of differences in operation, models used, selected power to heat ratio, heat integration and power consumption estimation.

It should be noted that 1st level models are ideal yield based and the calculated yields include only biomass as raw material. Heat and power are included for the 2nd and 3rd level. This is one reason why the energy yield decreases. The low energy yield on the 3rd level for SNG is because on 2nd level mainly heat was produced and therefore nearly all of the consumed electricity was imported, which is less efficient than power production from available heat. For the 1st level, the EtOH&MeOH, ENHMeOH, ENHSNG and ENHHC cases are calculated with 13 wt-% moisture (as in Papers IV and V) in Section 7.2.5.

The 1st level vs. 3rd level LHV efficiency deviated least for SNG process (Table 8) that was self-sufficient on heat and where most of the power could be generated from the liberated high-temperature heat. On the other hand particularly for processes where part of the product needs to be combusted (EtOH&MeOHa and ENHHCa), to satisfy the process heat demand the LHV % calculated by 1st level models deviated significantly from the 3rd & 2nd level LHV %, since heat demand of the process is not considered in 1st level models. However, in the cases SNG and ENHHCa, the 3rd level model predicted a somewhat higher LHV % due to the process' own power production from liberated high temperature heat in the process, which reduced the needed power input to the process.

Table 8. The calculated energy yields (LHV %) with various level models for pine and the average value of the absolute values of the differences of the between modelling levels. Case 'a' refers to heat self-sufficient operation and in case 'b' heat is imported.

Model level	MeOH	SNG	EtOH	EtOH&MeOH	EtOH&MeOH	ENHMeOHa	ENHMeOHb	ENHSNGa	ENHSNGb	ENHHCa	ENHHCb	Av[1]	STDAV[2]
Unit	%	%	%	%	%	%	%	%	%	%	%	%	%
1	73.4	65.3	45.7	84.9	84.9	83.3	83.3	75	75	86	86	14	7
2	61.5	68.0	50.3	58.1	69.9	60.2	66.2	64.4	67.7	67.6	70.8	3	3
3	58.1	69.7	-	57.0	60.1	-	-	-	-	68.0	72.5		

1) Av refers to the average value of absolute values of the differences between the LHV value at modelling level and the LHV value at modelling level +1.

2) STDAV refers to the standard deviation of absolute values of the differences between the LHV value at modelling level and the LHV value at modelling level+1.

11.2.1 Differences caused by heat utilisation and power demand

The power and heat demand for the processes varied between different models. As seen in Table 9, the product amount was about 11 MW higher for the 2nd level models. The reason was mainly that the power generation, which consumed part of the process heat, was larger on the 3rd level compared to the 2nd level. Therefore, in processes calculated with 3rd level models either more feedstock or side product combustion was needed to satisfy the process heat demand. Also, more process heat was converted into power on the 3rd level, which also increased losses to flue gas. The estimated product yield depended mostly on the process heat utilisation (only heat vs. heat and power). This had more effect than the accuracy of the model on 2nd and 3rd level models.

The estimated power consumption was about 5.5 MW larger on the 3rd level models (see Table 10). This is mostly because the power consumption of the refrigeration system needed for acid gas removal was not included in the 2nd level models (Table 10).

Table 9. The differences in the heat inputs and outputs in the processes: (2nd level – 3rd level).

Process	D_{he}[1]	D_{fche}[2]	D_{cw}[3]	D_{fgdry}[4]	D_{sel}[5]	D_{dist}[6]
Unit	MW	MW	MW	MW	MW	MW
MeOH	0.0	21.6	-3.9	-2.9	3.0	4.5
SNG	0.0	-0.2	-1.7	0.0	3.3	0
EtOH&MeOHa	0.0	12.6	-3.3	5.7	4.5	41.6
EtOH&MeOHb	-17.3	24.7	-17.4	-2.9	2.3	31.5
ENHHCa	0.0	9.1	3.4	-0.9	6.1	-2.2
ENHHCb	-0.4	-0.8	3.4	0.0	6.1	-2.2
Average value		11.2	-3.3		4.2	12.2
Standard deviation		10.7	7.6		1.6	19.3

1) D_{he} = Difference of heat input rate (2nd level – 3rd level)
2) D_{fche} =Difference of fuel and chemicals output rate (2nd level– 3rd level)
3) D_{cw} = Difference of heat output to cooling water (2nd level – 3rd) level
4) D_{fgdry} =Difference of heat to flue gas and drying (2nd level –3rd level)
5) D_{sel} = Difference of heat input to Selexol regeneration (2nd level – 3rd level)
6) D_{dist} = Difference of heat input to distillation (2nd level – 3rd level)

Table 10. The differences in the predicted unit operation in the power inputs and outputs in the processes and the standard deviation of the differences (2nd level – 3rd level).

Process	D_{PC}[1]	D_{Rp}[2]
Unit	MW	MW
MeOH	-6.9	-4.6
SNG	-6.8	-4.8
EtOH&MeOHa	-4.9	-2.7
EtOH&MeOHb	-3.5	-2.7
ENHHCa	-4.8	-3.4
ENHHCb	-6.3	-3.4
Average value	-5.5	-3.6
Standard deviation [%] of the absolute value of average value	24.4	25.3

1) D_{pc}= Power consumption difference (2nd level – 3rd level)
2) D_{rp} = Refrigeration power demand differences (2nd level – 3rd) level

11.2.2 Differences due to heat integration

It can be observed that the amount of heat transferred to cooling water was higher for 3rd level models except for the ENHHCa and b. This is because larger heat consumption due to non-maximum heat integration in 3rd level. For the 2nd level models, it was found that the number of temperature intervals in the calculation of grand composite curves affects the calculated heat demand of the process, since the limiting step is the temperature interval in which the lowest amount of heat is available.

Also the temperature crossover in heat exchangers limits the heat transfer compared to the simplified maximum heat integration potential. Therefore, when part of the biomass or side products is combusted in the 3rd level models this typically resulted in a lower yield to fuel products. Especially in the EtOH&MeOHb process heat demand calculated with 3rd level models, based on real process streams, deviates from the heat demand calculated with 2nd level models. The lower fuel and chemicals yield on 3rd level vs. 2nd level is typically explained by combustion product gas for example 21.6 MW for MeOH to provide the needed process heat.

11.2.3 Difference in predicted heat demand for unit operations for the 2nd and 3rd level models

It was observed that the differences in calculated heat duties of unit operations were usually less important, since the heat can be largely re-used at lower temperature levels. Therefore, the differences in the unit operation heat duties do not directly correlate with the total process heat demand. Heat output to cooling water is more important.

As observed in Table 9 the 2nd level models predicted a higher energy consumption for distillation and regeneration of the Selexol medium. This is partly because the 3rd level model revealed opportunities to save energy such as mechanical vapour recompression of water in evaporation, adjusting the solvent regeneration rate in acid gas removal processes. For cases apart from ENHHC, the shortcut distillation model overestimated the energy consumption in distillation. However, the limitation is the heat integration, which has a much greater effect than the differences in the predicted energy consumption for the unit operations: the heat demand for the processes was generally higher on the 3rd level. The big difference in distillation for cases EtOH&MeOH is because three columns with large heat duties in the process and the shortcut model overestimated to the heat duty compared to the stage-to-stage model.

11.3 Other performance indicators

11.3.1 Primary energy efficiency

There is a clear trend between the primary energy efficiency and the LHV efficiency as shown in Figure 18 where the primary efficiencies calculated on 2nd and 3rd level models are shown. However, primary energy efficiency gives a better picture since the different energy inputs have a different quality. Especially if a significant amount of power is used and when the power production has a low efficiency, the primary energy efficiency deviates from the energy yield. Cases EtOH&MeOHb and ENHHCb have somewhat higher primary energy efficiency than expected based on their LHV efficiencies than the other cases since they utilise secondary heat, which is converted with a high efficiency (low primary energy factor) into products.

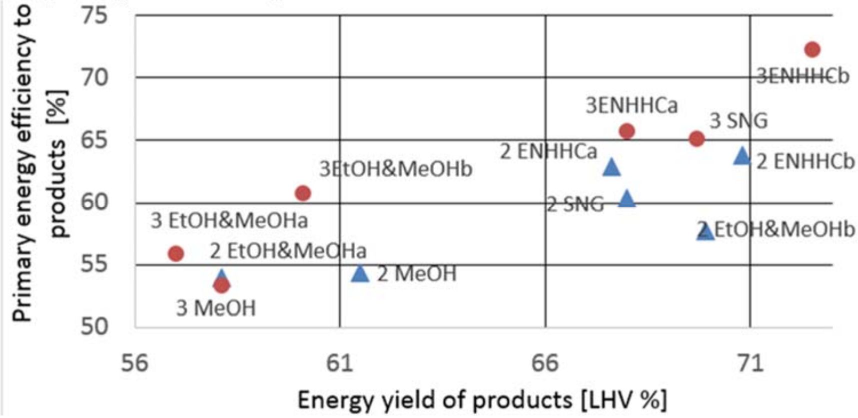

Figure 18. Primary energy efficiency calculated on 3rd and 2nd level models vs. energy yield as LHV %.

11.3.2 NPV

In Figure 19, the NPV is plotted against calculated energy yield for levels 1-3 except SNG (60 EUR/MWh) and ENHSNG due to the different product value compared to liquid biofuel (100 EUR/MWh). The NPV for the 2nd and 3rd levels only deviates by approximately ± 50 MEUR for the same energy yield. One reason for the low deviation is that the FCI estimates of the plants are very similar: 350 MEUR-400 MEUR and the same FCI estimate was used for the 2nd and 3rd level models. The trend of LHV % and NPV would be weaker for a smaller plant capacity and processes with a more different FCI.

For the 1st level models, the NPV estimate only included wood feedstock, fixed capital investment of the plant and main products. There is a strong trend here since the input of power and heat, which differ between the processes, is not included. Also the plant FCI is relatively similar.

The NPV was found to be highly sensitive to the raw material and products prices as seen earlier in Figure 17. It should be noted that in the R&D phase the uncertainty of investment cost might be large. However, rather than the absolute NPV of a process the relative NPV is useful for comparing different process alternatives, for example in a sensitivity analysis (Figure 17). Here the conditions under which another process is better than another can be checked. In addition, it should be noted that the NPV of a single production plant might be different to the NPV of integrated multiple process plants or the NPV of a region, which is important from the societal point of view.

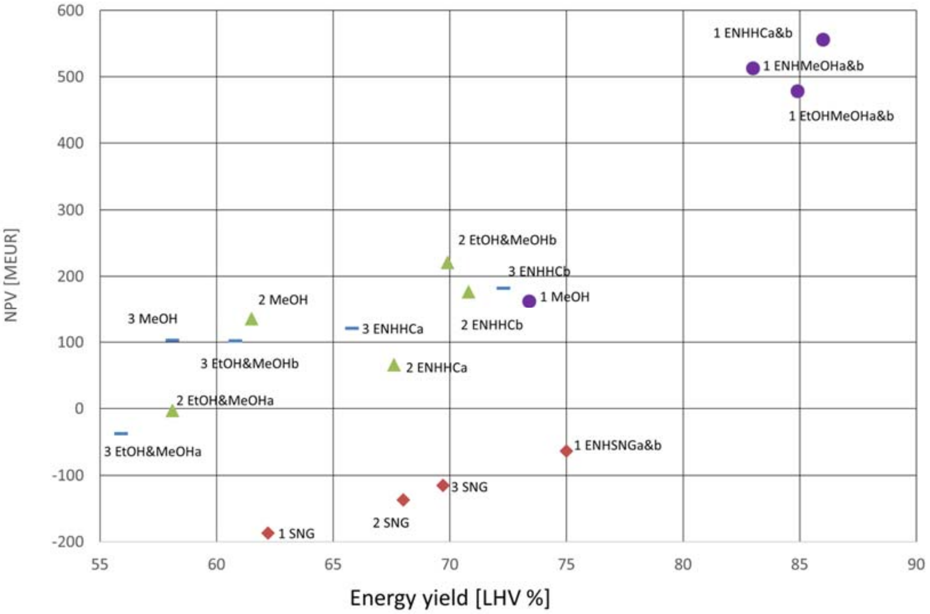

Figure 19. NPV as a function of energy yield of products by LHV %. The number before the process indicates the level of model.

11.3.3 Greenhouse gas emission criterium

The greenhouse gas emissions were used as performance criteria when evaluating the processes from the sustainability point of view. There is a clear trend between the annual GHG emission reductions with the energy yield calculated on the 2nd and 3rd levels, as seen in Figure 20.

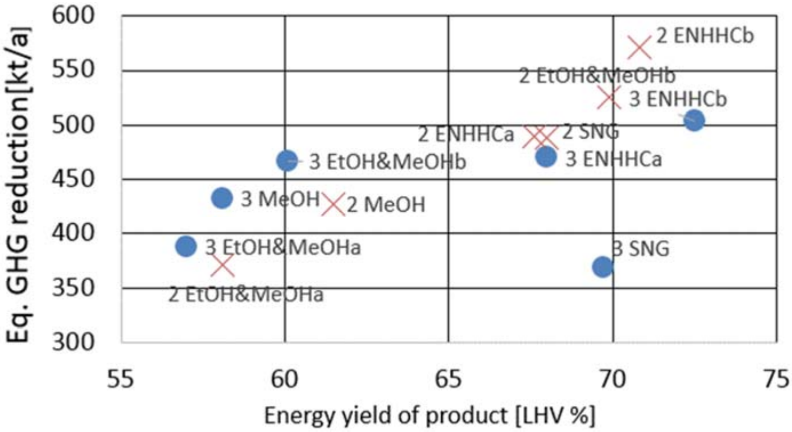

Figure 20. The energy yield of products by LHV % vs. annual greenhouse gas emission reductions kt CO2 eq/a. The number before the process indicates the model level.

The processes utilising external heat with a low GHG footprint, i.e. ETOH&MEOHb and 2nd level ENHHCb resulted in a slightly higher GHG reduction compared to trend, whereas the 3rd level ENHHCb was slightly lower since the gaseous fuel is assumed to substitute natural gas with lower GHG emissions. Since the heat was produced using renewable fuel, its effect was not significant. In addition, the effect of extra inputs such as lime etc. did not have a big influence on the GHG emissions.

The cost of reducing GHG emissions calculated in Chapter 10 was found to be a very useful indicator from the societal point of view although sensitive to the price difference between fossil and biofuel. This allows the comparison of biofuel production with other means of GHG reductions, such as carbon capture and storage (CCS) or even completely different measures such as changes in the infrastructures of cities. Since the energy yields were found to correlate well with both the NPV and GHG reduction, the effect of energy yield is even more significant on GHG emissions reduction costs as shown in Table 7.

11.3.4 Comparison of difference for energy yield, GHG and NPV on different modelling levels

The estimated energy yields (LHV %), NPV and GHG reductions on the 1st and 2nd levels are compared with those on the 3rd level (Table 11). On 2nd level, average relative differences of LHV % and GHG were about 5 and 11 % respectively. The largest deviation in the GHG for SNG was caused by the substitution of different fuel. On the 1st level both average relative differences were about 30 %, when the same FCI is used in the 2nd and 3rd level models. The difference of NPV was calculated compared to FCI because the NPVs varied much. The relative average difference of NPV to FCI was on the 2nd level 12 % and on the 1st level a very large 77 %. The conclusion of the calculation is that, the 1st level NPV values cannot be used.

Table 11. The relative differences and their standard deviations in prediction of NPV, GHG and LHV % on the 2nd or the 1st level to the 3rd level.

Process	D_{LHV23}[1]	D_{GHG23}[2]	D_{FCI23}[3]
Unit	%	%	% of process FCI
MeOH	5.9	-1.4	9.3
SNG	-2.4	32.2	-6.9
EtOH&MeOHa	1.9	-4.1	8.8
EtOH&MeOHb	16.3	12.5	29.7
ENHHCa	-0.6	4.3	-15.8
ENHHCb	-2.3	13.3	-1.5
Average of absolute values of differences	4.9	11.3	12.0
Standard deviation [%] of absolute values of average value of differences	119.5	100.2	81.8
Process	D_{LHV13}[4]	D_{GHG13}[5]	D_{FCI13}[6]
MeOH	26.3	27.5	17.0
SNG	-10.8	25.5	-22.5
EtOH&MeOHa	48.9	66.0	129.1
EtOH&MeOHb	41.3	37.9	94.1
ENHHCa	26.5	38.7	124.3
Average of absolute values of differences	30.8	39.1	77.4
Standard deviation [%] of absolute values of average value of differences	48.1	41.3	70.2

1) $D_{LHV23\ s}$ = $(LHV_2-LHV_3)/LHV_3$

2) $D_{GHG23=(}$ $=(GHG_2-GHG_3)/GHG_3$

3) D_{FCI23} = (NPV3-NPV2)/FCI

4) $D_{LHV13\,=}$ $(LHV_1-LHV_3)/LHV_3$

5) $D_{GHG13\,=}$ $(GHG_1-GHG_3)/GHG_3$

6) $D_{FCI13\,=}$ $(NPV_3-NPV_1)/FCI$

11.4 Proposed approach of modelling for process pre-evaluation

The approach employing multiple modelling and evaluations aims to tackle the problem of process screening for making make good decisions at an early stage to avoid choosing wrong process paths that cannot be changed later. However, the needed amount of input details increases and fewer process alternatives can be covered. The 1st level models are based on ideal reaction yields but the 2nd level models includes unit operation data with temperatures and pressures, which allow simple process integration studies. Yet the 3rd level models are based on realistic flowsheets, and valid only for the chosen flowsheet. The approach starts with several process alternatives and in the end focuses on a few most potential ones as in the stage gate, R&D model of NREL (DOE, 2013). The 1st level calculations estimate theoretical yield potentials, which were found useful to compare different process alternatives and raw materials.

The 1st level model calculation can be done as an initial check of the feasibility of a production path against other alternatives and raw materials together with product quality, safety and environmental acceptance. The product yield could be the first performance indicator in guiding experimental work. It should be remembered though that the energy yield here is a maximum theoretical potential. The later levels add more reality and LHV % may drop with 13 % on average (Table 8).

The 2nd level shortcut models can be used in R&D work for checking feasible product paths and discarding alternatives that have a low energy yield. The 2nd level model were found to give reasonably good prediction in many cases, because the predicted LHVs , GHG and NPV differences compared to 3rd level models were in average less than 12 % in the calculated cases as seen in Table 11. The models can be used in connection with experimental work that demonstrates feasible process alternatives and increases their technical readiness level.

The 3rd level models based on rigorous flowsheets with realistic heat integration could be used in later R&D work to check the heat consumption, power excess in more detail for evaluation and the integration of processes to different sites. The 3rd level models could be further extended by kinetic reactor model and measured physical properties of chemicals. The models could be used in a later design stage before designing a pilot plant or demonstration units. Further studies of multilevel modelling could be extended to include as performance criteria also other aspect of sustainability for example emissions to air and water and safety process indicators.

A way to extend the model to include the effect of the technical readiness level of a technology in the quantitative analysis would be allocating cost and time needed for the R&D period. The NPV of different technologies could be calculated for both the R&D phase and the economic lifetime of the investment. Alternatively, investment cost estimate for a plant based on a less developed technology could be multiplied with a factor in order to account for the higher uncertainty compared to that of a more developed technology. In addition, the expected annual operating hours could be calculated with a lowered value for a less developed technology to account for challenges with plant operation using new technologies as described by Merrow et al. (1981).

11.5 New for separate lignin and sugar processes and their integration

In this thesis new processes based on separate lignin and sugar processing were developed with the approach presented.

The performance of the new processes by energy yield, primary energy efficiency, NPV and GHG reductions are compared in Table 12. The MeOH process was selected as a base case, since it is a conventional process for liquid fuel production and methanol can be converted further in the MTG process into gasoline and gaseous hydrocarbon product similar to the product for the ENHHC case.

The energy yield, NPV and GHG reductions of biofuel production from biomass could be increased for fuel production cases as presented in Table 12 with separate lignin and sugar processing, if the process heat demand could be satisfied by external low temperature heat from e.g. a nearby power plant or pulp & paper mill. NPV is improved the most in average 37.9 % compared to the base case. Also about 10 MW more power is required compared to the self-sufficient case (Table 7). In the 'a' processes both for the 3rd and 2nd level the LHV % and primary efficiency could be somewhat improved by the new processes where NPV and GHG emission were decreased. However, in the 'b' processes LHV %, primary energy efficiency, NPV and GHG emission reductions were significantly improved. It should be noted that the product of processes varies and are in most cases both liquids and gases.

For gaseous fuel processes, ENHSNGb only increased the primary energy efficiency (Figure 18) and GHG emissions reductions (Figure 20). The reason is that since some methane produced in the gasification SNG production benefit less from separate sugar and lignin processing.

The ability to use external low temperature heat (cases 'b') is an important benefit. Integrated pulp and paper mills and CHP plants could benefit significantly from this integration. Both need sinks for heat. Therefore, also processes employing separate lignin and sugar processing could be integrated efficiently to utilize unused low temperature heat and some power.

Separate sugar and lignin processes should also be compared to other lignin utilisation options than energy production. In addition, separate carbohydrate and lignin processing could be extended to process route cases where lignin is utilised by thermochemical processes other than gasification, for example hydrothermal liquefaction.

Table 12. Comparison of the enhanced processes based on LHV %, primary energy efficiency, NPV and eq. GHG reductions compared with MEOH case.

	Energy yield (LHV %) increase %	Primary energy increase %	NPV increase %	GHG reduction increase %
3rd level liquid fuel				
3 MeOH base case	0.0	0.0	0.0	0.0
3 EtOH&MeOHa	-1.9	4.9	-136.9	-10.4
3 EtOH&MeOHb	3.4	14.1	-1.0	7.9
3 ENHHCa	17.0	23.5	17.5	8.5
3 ENHHCb	24.8	35.6	76.7	16.4
Average increase case a	7.6	14.2	-59.7	-0.9
Average increase case b	14.1	24.9	37.9	12.1
Standard deviation case a [%] of average value	177	93	-183	-1407
Standard deviation case b [%] of average value	107	61	145	49
2nd level liquid fuel				
2 MeOH base case	0.0	0.0	0.0	0.0
2 EtOH&MeOHa	-5.5	-0.9	-102.1	-12.9
2 EtOH&MeOHb	13.7	6.1	63.0	23.0
2 ENHMeOHa	-2.1	9.8	-55.5	-3.0
2 ENHMeOHb	5.8	17.4	75.8	26.9
2 ENHHCa	9.9	15.6	51.4	14.8
2 ENHHCb	15.1	17.3	30.6	33.7
Average increase case a	0.8	8.2	-35.4	-0.4
Average increase case b	11.5	13.6	56.5	27.9
Standard deviation case a [%] of average value	674	68	-148	-2339
Standard deviation case b [%] of average value	29	32	28	13

12. Conclusions

Development of biorefinery processes involves evaluation and screening of numerous raw materials and production alternatives where the production technology is at different technology readiness levels. To enhance this work, new methods and tools are needed. In this thesis, a new modelling approach based on models with different levels of accuracy and multistep evaluation was developed.

The process analysis and evaluation is done first on an ideal level, which presents the maximum potential of the process mainly based only on material balance information. On the 1st level the energy yield (LHV %) of a product is employed as a preliminary indicator, which showed satisfactory accuracy. On the 2nd level, heat balance and maximum heat integration (minimum utility requirement) are included. Because the differences of the indicators are relatively small between 2nd and 3rd level, LHV %, GHG emission reduction and NPV calculated with the 2nd level model can often be used in early phase of process development. The modelling is done using shortcut flowsheeting models. On the 3rd level, rigorous flowsheeting models are employed and the heat integration is done in a realistic (non-maximum) way.

The site integration point of view is very important and needs to be considered in selecting the scope of evaluation, because the results for the studied cases show that the efficiency was improved when two energy processes could be integrated. In this thesis, the integration of FT or ethanol processes with pulp and paper plant was studied.

In the multiple level analysis, a concept of a flexible multilevel modelling tool, which preferably also includes a biomass databank, was presented and used for evaluation at 1st modelling level. The tool allows flexible linking of models, their easy substitution by ones that are more detailed and presentation of any biomass by simple terms by their chemical compositions in the databank

In this thesis, three new biorefining process concepts were developed; producing gasoline range hydrocarbons, methanol and gaseous hydrocarbon such methane. The hypothesis was that the separate processing of lignin and carbohydrate parts of biomass might result to better efficiency than combined processing. The results revealed that separate processing is more effective in many cases but not always.

For instance, the new enhanced hydrocarbon production process developed presents the highest LHV% (72.5 %), eq. GHG reduction (502 kt. CO_2/a) and NPV (182 MEUR) among the compared processes. The calculated LHV % is significantly higher, 61 % LHV % on equal basis, than that calculated for methanol production by Hannula and Kurkela, (2013). Also the combined methanol and ethanol process with external heat input resulted in high LHV % (60.1 %), NPV (102 MEUR) and eq. GHG reduction (467 kt. CO_2/a).

The new processes developed are heat and power deficient unless part of the product or feedstock is used for heat and power production. This allows the processes to be run in two modes; a self-sufficient mode producing some power, and a heat and power deficient mode, which maximizes the fuel yield but requires external energy inputs, especially low temperature heat. This makes it possible to integrate the processes to external units producing low temperature heat, e.g. CHP plants or standalone pulp mills and switch the operating mode depending on the season, and heat and power availability. Therefore, the plants could possibly act as balancing power users in renewable energy system including a high share of wind and solar power.

The uncertainties and limitations of the study include that much of the new process development is based on laboratory scale results from literature. This is why larger scale bench and pilot studies are needed to confirm the results. Economic analyses are uncertain since the capital costing method has less than 30 % accuracy in the process development stage, and the product and feedstock prices vary and are uncertain.

Further research is needed for evaluating processes with different technology readiness levels, for example, to include other process performance criteria, such as operability, reliability, safety, and more sustainability criteria in the multilevel modelling approach. Separate processing concepts should be created and analysed, and their integration with various types of heat-excessive processes should be studied. The integration opportunities of solar economy should be elaborated considering flexibility and potential of excess power utilization via hydrogen utilisation.

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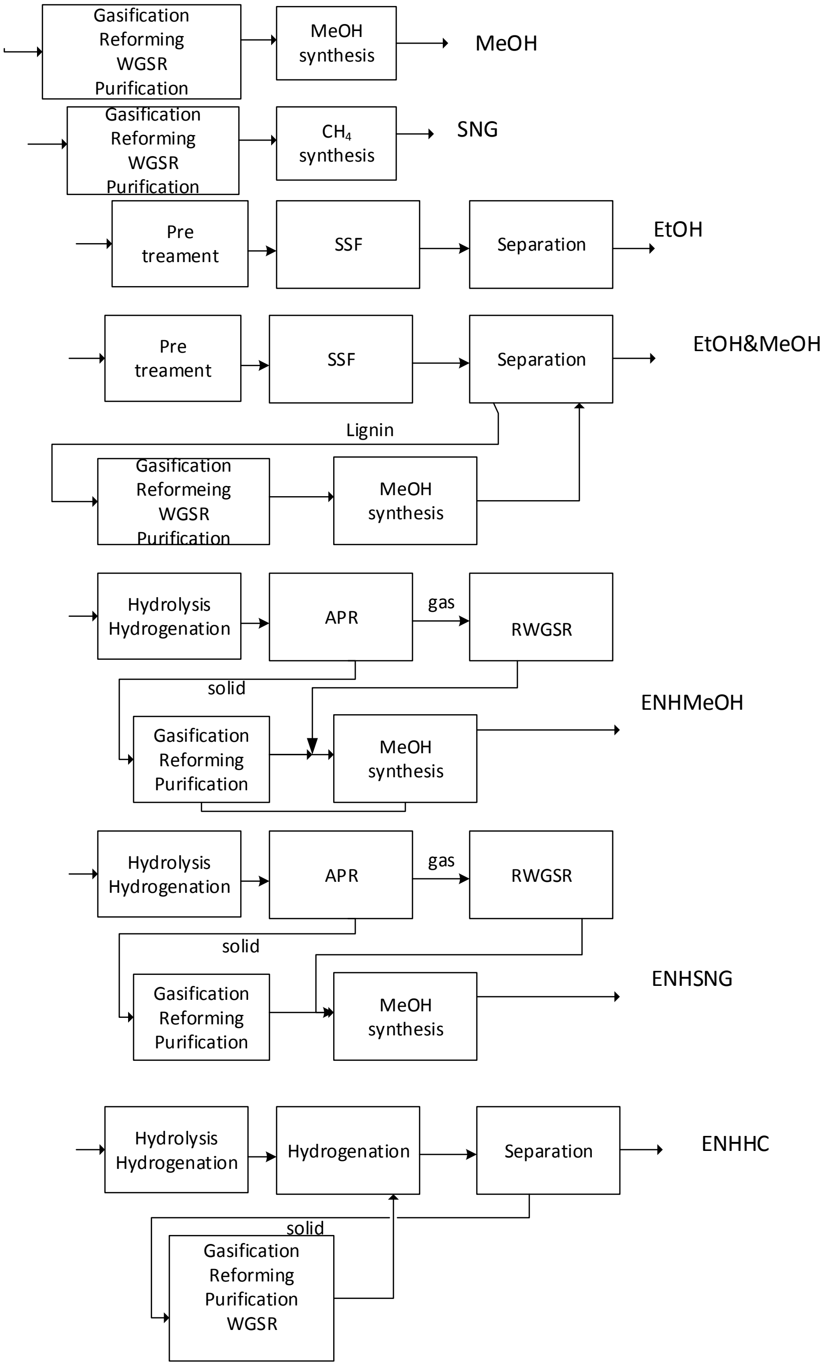
Appendices

Figure A. The block diagrams of the studied processes.



Appendix

Table A. Models used at modelling levels basic data and reactions.

	Level 1	Level 2		Level 3
Description	Simple material balance model; Paper II	Simplified flowsheet model; Paper III	Simplified flowsheet model; Paper IV	Rigorous flowsheet model; Paper V
Process routes	Approximately 40 process routes based on gasification, fermentation and sugar chemical conversion	Fischer-Tropsch production and ethanol based on literature	11 cases: methanol production, SNG, ethanol with CHP, ethanol& methanol, enhanced methanol and SNG, enhanced hydrocarbon production	6 cases: methanol production, SNG, ethanol and methanol, enhanced hydrocarbon production
Raw materials	pine, spruce, black alder, aspen, birch, sugarcane bagasse, larch, wheat straw and pyrolysis oil	spruce	pine	pine
Reactions				
Sugar conversions (fermentation and chemical conversion)	100 %	literature yield	literature yield	literature yield

	Level 1	Level 2		Level 3
Description	Simple material balance model; Paper II	Simplified flowsheet model; Paper III	Simplified flowsheet model; Paper IV	Rigorous flowsheet model; Paper V
Gasification	chemical equilibrium by Gibbs free energy minimization	chemical equilibrium by Gibbs free energy minimization	chemical equilibrium by Gibbs free energy minimization with correction for methane content	chemical equilibrium by Gibbs free energy minimization with correction for methane content
Reforming	chemical equilibrium by Gibbs free energy minimisation	chemical equilibrium by Gibbs free energy minimisation	chemical equilibrium by Gibbs free energy minimisation	chemical equilibrium by Gibbs free energy minimisation
Water gas shift reaction (WGSR)	WGSR: conversion reactor where the conversion is adjusted for suitable H_2/CO ratio	WGSR: conversion reactor where the conversion is adjusted for suitable H_2/CO ratio	WGSR: conversion adjusted for suitable H_2/CO ratio	WGSR: conversion adjusted for suitable H_2/CO ratio
Thermochemical reactions other than WGSR	100 % selectivity and conversion	FT reaction conversion specified.	MeOH by chemical equilibrium by Gibbs free energy minimisation, SNG 100 % conversion, H_2 production, chemical equilibrium with temperature approach to equilibrium	MeOH conversion lower than chemical equilibrium.

Table B. Models used at the modelling levels separations and energy integration.

Models	Level 1	Level 2		Level 3
	Simple material balance model; paper II	Simplified flowsheet model, paper III	Simplified flowsheet model, paper IV	Rigorous flowsheet model, paper V
Separations				
Acid gas removal	not considered	acid gas removal adsorption medium (Selexol) with only pressure reduction for regeneration	acid gas removal adsorption medium (Selexol) with fixed duty per kg acid gas removed	rigorous model the acid gas adsorption medium (Selexol) amount is adjusted in each case to remove the desired amount of acid gas.
Evaporation	not considered	according to literature data	fixed heat demand per tonne of water evaporated in the evaporator	multi-effect evaporator model
Drying	drying heat requirement not considered (biomass dried to 13 wt%)	heat demand not calculated	direct drying with hot water with a heat demand of 4 MJ/ kg of water evaporated	direct drying with hot water with a heat demand of 4 MJ/ kg of water evaporated

Models	Level 1	Level 2		Level 3
	Simple material balance model; paper II	Simplified flowsheet model, paper III	Simplified flowsheet model, paper IV	Rigorous flowsheet model, paper V
Distillation and condensation	ideal separation with 100 % product recovery	reported literature data for EtOH case; separation of FT product by condensation	Aspen ‘Distl´ model with Edminster approach	tray by tray model
Energy related operations				
Heat integration	not considered	maximum heat recovery based on heating and cooling demand, calculated based on literature data for ethanol case and simulation for FT case	maximum heat recovery based on heating and cooling demand	heat recovery between real process streams and check for temperature cross-over in heat-exchangers
Heat and power production	not considered	calculated for a power plant based on heat/power ratios, no pre-heating of feed water and superheating of steam	steam production and power production when excess heat available	steam and power production for all cases
Power consumption in process	not considered	compressors and oxygen production	compressors and oxygen production	compressors and oxygen production, feed water pump and low temperature cooling compressor

Table C. Updated data from Paper II Table 1 to thesis summary, yellow values are updated.

Species	C, wt%	H, wt%	O, wt%	N, wt%	S, wt%	Ash, wt%	Higher heating	Lower heating value, MJ/kg	Ref.	Xylan weight fraction	Cellulose weight fraction	Extractives weight fraction	Glucan weight fraction	Mannan weight fraction	Galactane weight fraction	Xylane weight fraction	Ref.
Eucalyptus	48.80	6.00	44.21	0.17	0.02	0.80	19.62	18.31	ECN(2017a)				0.52	0.01	0.01	0.16	
Wheat straw	46.02	5.50	41.44	1.65	0.10	5.04	18.42	17.21	ECN(2017b)	0.21	0.40	0.07	0.41	0.00	0.01	0.21	Mustajoki et al.(2010)

Table D Updated Appendix A. in Paper IV Energy values and indicators of process cases Case A; describes heat self-sufficient operation, and case B; utilisation of external low temperature heat. Yellow values are updated.

	CONVENTIONAL PROCESSES					ENHANCED PROCESS CONCEPTS					
	MEOH Case	SNG Case	ETOH Case	ETOH&MEOHa	*ETOH&MEOHb*	ENHMEOHa	ENHMEOHb	ENHSNGa	ENHSNGb	ENHHCa	ENHHCb Case
Biomass feed (HHV) and	320.5/300	320.5/300	320.5/300	320.5/300	320.5/300	320.5/300	320.5/300	320.5/300	320.5/300	320.5/300	320.5/300
Liquid fuel output (HHV) and	197.9/174.0	-	112.5/105.0	206.9/180.3	243.6/217.0	220.0/190.0	268.6/236.1	0	0	152.7/141.3	152.7/141.3
Gaseous fuel output (HHV)	22.2/19.5	233.3/210.3	5.7/5.3	0/0	19.0/17.0	0.0	4.7/4.1	226.0/203.6	260.7/234.9	74.2/67.2	109.2/98.8
Furfural output (HHV) and	0.0	0.0	5.8/5.4	0/0	5.9/5.5	0.0	0.0	0.0	0.0	0.0	0.0
Total heating value of fuels and	220.2/193.5	223.5/210.3	124.0/115.7	206.9/180.3	268.5/239.5	220.0/190.0	273.3/240.2	226/203.6	260.7/234.9	226.9/208.4	261.9/240.1
Electricity surplus MW	-14.5	-10.12	35.3	-10.2	-10.2	-15.4	-15.4	-15.9	-15.9	-8.13	-8.13
External low temperature heat	0.0	0.00	0.0	0.0	32.7	0.0	47.5	0.0	30.9	0.00	31.1
Fuel & chemical product effi-	65.7/61.5	70.7/68.0	49.7/50.3	78.13/74.3	79.0/75.0	65.5/60.2	71.3/66.2	67.2/64.4	71.0/67.7	76.7/75.1	77.7/70.8
Main product efficiency (HHV	59.1/58.0	70.7/68.0	35.1/35.0	73.7/70.0	71.7/68.0	65.5/60.2	70.1/65.1	67.2/64.4	71.0/67.7	47.5/45.9	45.3/44.6
Primary energy efficiency %	55.4	60.4	72.8	73.4	74.1	59.7	63.9	61.1	64.6	72.9	73.7
Carbon footprint (g CO_2	83.0	87.3	120.1	77.6	82.5	82.0	84.8	82.9	84.5	88.5	89.4
GHG emissions saved kt CO_2	427	488	369	372	525	414	542	449	528	490	571
Net present value (NPV) MEur	136	-137	-82	-3	221	60	238	-267	-219	66	178
Fixed capital investment MEur	350	320	270	400.0	400.0	430.0	430.0	400.0	400.0	350.0	350

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Biorefining Route Assessment by Multilevel Modeling

Kristian Melin, Markku Hurme

Helsinki University of Technology, P.O.Box 6100, 02015 TKK, Finland
kristian.melin@tkk.fi, markku.hurme@tkk.fi

Abstract

Evaluation and optimization of biofuel manufacturing routes is an attractive but complicated task due to the large number of raw material and process alternatives. Multilevel modeling tool for the evaluation of liquid biofuel processing route and raw material selection is presented. The efficiency criteria used are material, heat and hydrogen conversion efficiencies. The principle of the evaluation tool is described and demonstrated.

Keywords: biorefinery, process route optimization, multilevel modeling

1. Introduction

Sustainability demands for fuel, chemicals and energy production have resulted to aims to generate biorefineries, which produce multiple fuel, chemical or fiber products from bio-based materials. The optimization of biorefining routes and raw materials is of key importance in moving into a more sustainable society. However the modeling and simulation needed for their route optimization, is a complex task because of the nature of biomaterials compared to well defined chemical species used in conventional process simulators and their databanks. The process operations used also partly differ from well-defined chemical operations: Typical processes involved in biorefineries are fractionation processes (such as cellulose or hemicellulose or separation from biomass) and biochemical or chemical conversion processes (e.g. conversion of carbohydrates to ethanol by fermentation or thermal pyrolysis of biomass to various not well defined mostly heavy liquid compounds). These operations and materials tend to be difficult to simulate with traditional flowsheeting simulators. Therefore simulations need to include experimental data for process operations and a different format of presentation of solid biomass components in the database.

The paper describes the prototype tool for biorefinery route comparison and optimization, which implements a new approach for solid feedstock characterization, a biomass databank, and a modeling approach which is modular, expandable and uses multilevel modeling. In the end the technique is demonstrated.

2. Biorefining efficiency

The efficiency of biorefining processes can be evaluated from several points of view. In preliminary design simplified criteria often used are:
1) Material conversion efficiency (how much of the weight of the raw material is converted into the products.
2) Raw material energy conversion efficiency (how the energy content of feedstocks and products compare).

3) Economic potential (what is the cost difference of raw materials and products when the yield is taken into account).
4) Product related criteria include also the product quality as a fuel and the suitability for existing users and distribution systems.
5) From environmental point of view the efficiency of the fuel for CO_2 emission reduction is essential.

As a first criterion it is attractive to find routes that retain the maximum amount of material and energy content of feedstocks in the product. If much of the raw material energy content is liberated, even it is recovered as heat energy in the process (such as steam), it is of less value than the energy in the liquid biofuel products. For detailed feasibility studies and efficiency comparisons a capital and operating cost models are needed to evaluate the routes.

3. Biorefining process simulation

The aim of biorefinery route simulation is to optimize the process concept and the raw materials used. The fundamental problems in the biorefinery optimization are:
1) Which raw materials to use.
2) How to fractionate the raw material in an optimal way.
3) How to process these fractions further by chemical and biochemical processes.
A tool for making process efficiency and feasibility evaluations is needed to aid this work. The tool consists of biomass databank and material balance models for conversion operations, which can be linked in a desired manner (Figure 1).

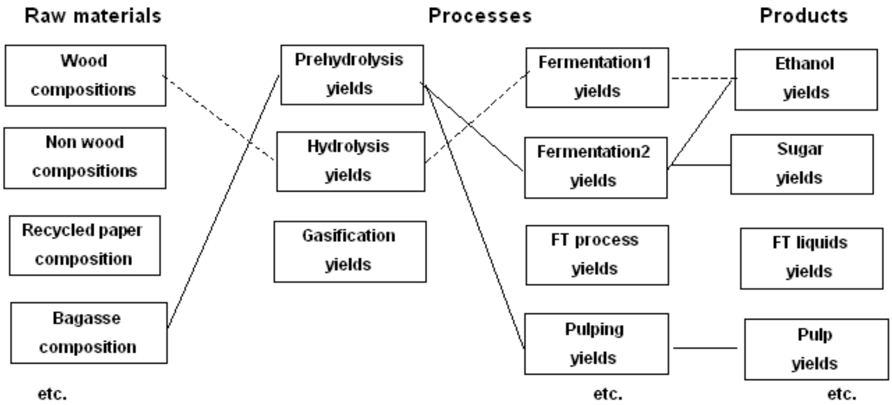

Figure 1. *The biorefinery route simulator structure*

To allow complete biorefining route evaluations different levels and accuracies of models are needed. Because of the large number of refining processes available, which typically also require experimental data, not all refining process options cannot be build from unit operation level directly but a more rough presentation is needed. Also the end use of models defines the accuracy needed. On the other hand the early phase of project may limit the availability of data, which also hinder the early utilization of rigorous models. From cost models it is known that the usage of too detailed model too early, when the input information is not yet available but has to be estimated, results to worse estimations than the usage of a less refined model.

For these reasons the different levels of models can be used in a parallel way by supplementing a shortcut model with a more rigorous one when available, since the modular structure allows an easy addition of new models to the too. In the beginning of the project the models available are less accurate.

The bioprocess route simulation is done by interlinking the process simulation modules presented in Figure 1 by interconnecting stream scaling parameters x as discussed later.

4. Biomass databank

The biorefinery route optimization problem is not a typical chemical process simulation problem, since the feed biomasses are complex hererogeneous mixtures. E.g. lignocellulosic biomass is composed of cellulose, hemicellulose, lignin and extractives as separate solid phases. Therefore biomasses differ in their constitution from ordinary organic chemicals and cannot be described in the same way as the chemicals in flowsheeting programs. Consequently a general presentation of composition and properties of biomasses was created, which allows the creation of a general biomass database.

The biomasses are presented with the following databank parameters (Table 1):
1) Wt-% division into subclasses; cellulose, hemicellulose, lignin, extractives
2) Division of cellulose and hemicellulose to their monosaccharide species
3) Element composition of the biomass
4) Heating value of biomass (LHV; allowing calculation of heat of formation)

Table 1. Example of biomass databank components (partial)

Bio-mass	C %	H %	O %	Ash %	LHV MJ/kg	Cellu lose	Xy lan	Glu can	Man nan	Galac-tane	Xy lane	Extr
Birch	47.4	5.2	46.0	0.7	18.6	0.40	0.33	0.41	0.017	0.007	0.20	0.03
Spruce	52.4	5.9	40.6	1.04	19.1	0.41	0.11	0.41	0.136	0.028	0.056	0.02
Eucal.	57.2	5.3	36.3	1.2	19.2	0.42	0.16	0.52	0.01	0.01	0.16	0.03
Straw	44.8	5.4	39.6	11.2	16.2	0.41	0.25	0.41	0.00	0.00	0.25	0.03

5. Multilevel modeling

The modeling levels can described in the following way:
Shortcut models are used for the simplest simulation for the refining route. These models represent literature-based values for different raw materials and product yields, such as gasification yields of certain biomass to synthesis gas or hydrolysis yield of monosaccharides from a biomass.

In the second level the models are *material and energy balance models*. In this level the material balance is calculated from the biomass database values considering the exact composition. For example for the fermentation of a hydrolyzed biomass the product composition is calculated based on the material balance of known monosaccharides considering also the experimental yield data.

In the third *subprocess based* level, the subprocess models are created. The subprocesses are not classical unit operation models but aggregated models for a subprocess such as the gasificator including also auxiliary equipment such as heat recovery, preheating, feed biomass drying and product gas dust removal. The subprocess models are made by detailed simulations of the process units by flowsheeting simulators. They are simplified, aggregated from several operations and combined with experimental knowledge to allow more straightforward but accurate calculation. The models are less rigorous than the unit operation models but they present a larger process system in scope.

In the fourth level the models are rigorous *phenomena based unit operation models,* which can be used directly from process simulators (e.g. Aspen Plus) through interphases such as Aspen Simulation Workbook. This level allows a detailed but more laborious simulation, which often has to be complemented manually by experimental results for yields, conversions and efficiencies.

6. Efficiency and economic modeling

For feasibility comparisons conversion efficiency and costing evaluation levels are implemented. For the first level material, heat and hydrogen conversion efficiencies can be used. Also economic potential calculation is possible. Economic potential shows the difference of values of products compared to raw materials when yields are considered.

For the second level literature based capital and operating cost and their distributions are used. Capital costs are estimated by capacity exponent functions (accuracy +-40..50%). This type of economic estimating allows making a first profitability estimate.

In the third level equipment sizing based capital cost estimation is done by equipment cost estimation based on equipment dimensions and capital cost distributions. Operating costs are calculated from the simulated raw material, auxiliary chemical and utility consumptions. This allows a cost estimate with +-30% accuracy.

7. Optimization procedure

The process models in Figure 1 can be interconnected into process concepts by chaining the process blocks. Feedstock and route optimization can be done by optimizing the connectivity of blocks. I.e. the rates of interconnecting streams in the flowsheet are varied in the optimization. This is done by modifying the connectivity scaling parameters $0 \leq x \leq 1$, which are the multipliers for the interconnecting rates.

For the optimization problem the available feedstock amounts are given in the raw material blocks. The interconnecting scaling parameters x are optimized for the superstructure. As constraints the available raw material amounts, required product rates and maximum capacities of subprocesses are given. The objective function in the optimization can be the material, energy or hydrogen conversion efficiency or an economic objective function. It should be noted that no mixed integer optimization is needed which simplifies the approach.

8. Case studies

As the *first case study* biomass refining route evaluation for producing liquid fuels is given by using material, energy or hydrogen conversion efficiencies (first level models). Three raw material alternatives are studied; birch, eucalyptus and straw.

The processes studied are the following [1]:
1) Gasification by production of synthesis gas from various biomasses. Syngas consists of H_2 and CO (plus CO_2 and H_2O as byproducts). The yields were calculated based on Gibbs energy minimization model of a flowsheet simulator (i.e. a fourth level model).
2) Methanol is synthesized from syngas after a shift reaction to control the CO/H2 ratio. This is a second level model. The efficiencies are calculated starting from biomass.
3) Fischer-Tropsch (FT) products are a hydrocarbon fuel mixture synthesized from syngas. The FT model was built into the route evaluation tool based on Anderson-Schulz-Flory distribution [2]. For the chain growth probability (α) the value 0.8 was used giving maximum on C4/C5 hydrocarbon products. This is a second level model.
4) Ethanol from methanol is a carbonation route using syngas and methanol as feeds.
5) Ethanol C6 fermentation considers fermentation of hexoses to ethanol.
6) C5+C6 carbohydrate fermentation is a less conventional route where both pentoses (C5) and hexoses (C6) are fermented to ethanol by using modified microbes.
7) ABE fermentation is production of acetone, butanol and ethanol by C5 and C6 fermentation. All the fermentation models used are second level models.

Table 2. Material and energy conversion efficiencies of the routes (15 wt% feed moisture)

	Birch			Eucalyptus			Straw		
	LHV %	mass %	Hef %	LHV %	mass %	Hef %	LHV %	mass %	Hef %
gasification	86	76	147	81	85	120	77	62	106
methanol	75	66	160	70	63	152	67	52	121
FT prod's	73	27	98	67	26	93	65	21	74
ethanol fr.methanol	71	48	100	66	46	95	63	37	76
ethanol C6 ferm	36	24		37			40		
ethanol C5/6	54	36		53			61		
ABE ferm	55	28		52			59		

The optimization results by material, energy and hydrogen conversion efficiencies of the routes are presented in Table 2. LHV% is the energy conversion efficiency calculated by dividing the fuel product lower heating value (LHV) by the raw material biomass LHV (dry). Mass% is the mass conversion efficiency calculated by dividing the fuel product mass by biomass mass (dry). Hef % is the hydrogen conversion efficiency calculated by dividing the hydrogen in fuel product by hydrogen in feed biomass (dry).

In the route optimization the route selection depends on the objective function and constraints used as can be seen from Table 2. If the objective is high energy conversion efficiency (LHV%), the methanol manufacturing from birch is selected, if liquid fuels is desired (75%). If gaseous product is allowed, the gasification of birch is most energy conversion efficient (86%).

If the goal is the high mass conversion efficiency, the selection is gasification of eucalyptus, if gas product is allowed (Meff=85%). For liquid products the methanol from birch is the optimal process (Meff=66%). Also if the goal is the high hydrogen conversion efficiency, methanol production from birch is optimal (Hef=160%)

The background for these results is the following: Eucalyptus has high gasification material efficiencies because its high carbon and low oxygen contents requiring more external oxygen, which increases the material efficiency. The syngas is however high in CO, which has lower heating value than H_2. Birch has higher oxygen content resulting to less external oxygen needed and therefore a smaller material efficiency than eucalyptus. Many straws have a high inorganic (ash) content, which decreases the conversion efficiences.

As a *second case study* energy consumption and capital costs of a forest residue to methanol process (230 000 t/a MeOH) were estimated. Process energies are the following: Based on heat and material balance simulation the feed biomass energy (LHV) is 200 MW and the energy of methanol produced 144 MW. The gross reaction heat is 51 MW. This is used for amine separation and distillation duties; 39 MW together. In addition heat is needed for feed moisture, shift water and reformer water vaporization, but these are recovered to a large extent. Therefore the plant is heat self sufficient. The main electricity users are the synthesis gas compressor 7 MW and oxygen manufacture 3 MW. Grey (non-process) energy costs are mainly related to feedstock harvesting, chipping and transportation. The last one can be evaluated by add-on logistic models. Here the feedstock collection radius is 100 km. The transportation cost can be expressed e.g. as transport MW/ biomass MW. In this case harvesting, chopping and transport is about 3% of biomass energy content. Plant capital costs can be estimated by second level models based on capacity exponent correlations (such as six tenth rule). For this capacity the investment cost is 170 M€.

9. Conclusions

The paper described a prototype tool for biorefinery route optimization, which implements a new approach in feedstock characterization, a biomass databank, and a modeling approach which is modular, expandable and uses multilevel modeling. Feed stocks biomasses differ in constitution from ordinary organic chemicals. They cannot be described with conventional models. A general presentation of composition and properties was therefore created, which allows the creation of a biomass database.

A flexible optimization tool, which was developed, is necessary for making the efficiency evaluations. The tool has a modular multilevel structure, which allows flexible linking of models, using models of different accuracy and easy replacing of shortcut models with more rigorous ones. The optimization is done by optimizing the interconnectivity scaling parameters of process streams in the flowsheet. The tool structure works itself as a superstructure in the optimization allowing the use of normal continuous optimization routines.

In the case study the route material and energy efficiencies vary much. These criteria can give only the first estimate of the route feasibility. Therefore more detailed cost calculations are needed at the higher levels of models as shown.

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II

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EVALUATION OF LIGNOCELLULOSIC BIOMASS UPGRADING ROUTES TO FUELS AND CHEMICALS

KRISTIAN MELIN and MARKKU HURME

Helsinki University of Technology, Department of Biotechnology and Chemical Technology, PL 6100, 02015 TKK, Finland

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The study evaluates wood and non-wood lignocellulosic conversion into biofuels and renewable intermediate chemical products, on the basis of material efficiency, heat content in final products (lower heating value) and properties of fuel components, as related to their use, existing cars and storage. This type of conversion efficiency analysis can be viewed as a first step in biorefinery route optimization. The upgrading routes considered here include gasification, pyrolysis with subsequent gasification, ethanol, anaerobic acetic acid and ABE-fermentation, digestion and chemical conversion of sugars into fuel. The material efficiency is calculated on the basis of potential yields. In addition, the subsequent conversion of these intermediate products to fuel components through chemical reactions has been considered. Intermediate chemicals, such as ethylene, propylene, ethyl acetate and acetic acid, have also been analyzed. Chemical upgrading of sugars, acetic acid fermentation and gasification converted most of the raw material heat content in the products. The components with good properties containing some oxygen, such as butanol, methyltetrahydrofuran (MTHF) and ethers, appeared as promising from the viewpoint of both fuel properties and biomass conversion.

Keywords: biorefinery, biofuels, biofuel properties, biomass conversion evaluation, lignocellulosic biomass upgrading

INTRODUCTION

The sustainable use of forest biomass for fuels and chemicals, instead of fossil fuels and petrochemicals, can significantly reduce carbon dioxide emissions. According to a recent estimate of Parikka,[1] the worldwide total sustainable biomass energy potential is of 104 EJ/a, representing about 30% of today's total global energy consumption. Since biomass cannot cover the whole global energy demand, to play a significant role in preventing climate change, it needs to be efficiently used. Therefore, it is important to find routes that retain the maximum amount of material and energy content of feedstocks in the products.

However, good material and heat content are not sufficient if the products do not have suitable properties. For fuels, the important properties include octane or cetane number, vapor pressure, emission produced upon combustion, cold properties, toxicity, energy density, corrosiveness, etc. Often, the properties are also related to the value of the products. Considering such factors can be also seen as a step in optimizing biomass utilization in a biorefinery. These results can be used to find potential routes that can be further analyzed more rigorously by including production costs.

Gasification based routes

Lignocellulosic biomass utilization involves converting the biomass into intermediates and subsequently converting such intermediates into chemical or fuel components. The most common intermediates are synthesis gas (mixture mainly of CO and H_2), pyrolysis oil, sugars, lignin, cooking liquor and biogas. If the intermediate, for example synthesis gas, can be purified to a level suitable for subsequent processes, the same procedures can be applied for intermediates, as in oil refining or petrochemical industry. The synthesis gas can be produced by the gasification of dried biomass at high temperatures (around 800 °C), using oxygen or steam. Alternatively, gasification can be performed directly on wet biomass under supercritical water conditions (under which water will react with the biomass). Supercritical gasification of paper sludge and black liquor was described by Rönnlund *et al.*[2] The synthesis gas can be used in numerous applications for both fuel and chemical production. For example, methanol can be produced by methanol synthesis from synthesis gas containing a very low level of sulfur below 1 vol ppm, but a high fraction of residual CO_2, by a catalytic reaction. Examples of low-pressure processes are, for example, the ICI process, using[3,4] a copper oxide catalyst at 50-100 bar, and the Lurgi process, demonstrated in Germany in the 1970s.

Alternatively, the synthesis gas can be converted into hydrocarbons by the well-known Fischer-Tropsch process, used in Germany in the Second World War to produce synthetic gasoline. FT synthesis is a nonselective process producing a wide range of hydrocarbons with 1 to 100 carbons. Iron and cobalt catalysts are mostly used. High selectivity can only be achieved for methane and high molecular mass wax. The FT process is operated[5] both at high temperatures (330-350 °C), for the production of gasoline and light olefins, and at low temperatures (220-250 °C), for the production of waxes and diesel. FT synthesis was traditionally done in circulated fluidized bed reactors but, nowadays, slurry reactors or tubular fixed bed reactors are mostly used. The high molecular wax can be hydrocracked and isomerized in an oil refinery into high quality diesel fuel, lube oils and naphta, which can be cracked into olefins.

Dimethylether (DME) is another fuel component that can be obtained from syngas, with properties similar to liquefied petroleum gas. It can be used as diesel, but it requires an infrastructure suitable for liquefied gas. Synthesis gas can be converted directly through methanol into DME, with a dual function catalyst, which involves the methanol synthesis reaction, shift reaction and the DME synthesis reaction. When the DME reaction is performed simultaneously with the methanol synthesis one, the equilibrium in the methanol reaction is shifted towards the product. Therefore, by this route, a much higher conversion is achieved and lower pressure can be used than by methanol synthesis.[6]

Methanol can be also converted into olefins in the MTO process with ZSM-5 catalyst,[7] or into gasoline with methanol, in the gasoline (MTG) process. However, gasoline has a high olefin content, exceeding the specification for gasoline. The olefins produced can be either hydrated into alcohols with water, or recovered as such.[8]

Clean synthesis gas (CO and H_2) and steam can be catalytically converted by shift reactions to hydrogen and carbon dioxide. The process is usually performed stepwise, over a high temperature range, between 310 and 500 °C, using iron–chromium oxide catalysts, and over low temperatures (approximately 180-270 °C), using copper–zinc catalysts.[9]

Alternatively, the synthesis gas can be converted into methane containing a gas called SNG (Synthetic Natural Gas). Carbon monoxide and dioxide are converted with, for example, nickel catalyst into methane and water.[10] The process is used in hydrogen production plants and for ammonia production, to remove the carbon monoxide from hydrogen gas. The reaction is strongly exothermic.

There are no commercial plants yet to perform mixed alcohol synthesis. The low selectivity and conversion prevented the commercialization of mixed alcohol synthesis. The obtained yields are recorded by the US Renewable Energy Department.[11] Also, isosynthesis, which produces branched hydrocarbons, such as isobutane and isobutene, has not been commercialized yet.[12] Temperatures of approximately 400 °C and pressures from 150 to 1000 bar are needed.

On the other hand, oxosynthesis, also called hydroformulation, has been commercialized in chemical industry for producing, for example, butyraldehyde or propenaldehyde. It involves the reaction of CO and H_2 with olefinic hydrocarbons, to form an isomeric mixture of normal and isoaldehydes. Oxosynthesis is a rapid reaction catalyzed by soluble cobalt or rhodium complexes.[13] In this paper, mixed alcohol synthesis, isosynthesis, MTG process and hydroformulation were not considered. Hydroformulation was not considered, as the process producing biofuel alcohols would need many processing steps, if all components are produced from lignocellulosic biomass.

In addition, acetic acid is produced commercially from methanol and carbon monoxide through carbonylation. Catalyzed processes are used, for example Monsanto or Cativa, with rhodium or iridium metal complexes.[14]

Pyrolysis

Another main technology is the pyrolysis of biomass into bio-oil, which means heating of biomass in the absence of oxygen, leading to its decomposition into different products. Fast pyrolysis is a high-temperature process in which biomass is rapidly heated (in seconds), then converted into gases, bio-oil and charcoal. The bio-oil from pyrolysis is corrosive, contains water and has to be upgraded prior to its usage as a traffic fuel. The pyrolysis upgrading routes presented by Gabrieli *et al.*,[15] including decarboxylation and hydrodeoxygenation or cracking, are all based on the reduction of the oxygen content in the bio-oil.

Fermentation route

Cellulose and hemicellulose, which are polymers of different sugar monomers, can be separated from lignin and extractives, and hydrolyzed into their monomer units by acid, alkaline or enzymatic hydrolysis. The monomer units or the monosaccharides can be processed into chemicals or fuels either by biochemical routes, using microorganisms, or by thermo-chemical routes. In conventional ethanol fermentation, traditional yeast or bacteria can only ferment hexoses (C6 sugars). A variety of bacteria are able to metabolize and ferment both hexose and pentose sugars, but all produce a mixture of fermentation products.[16]

Anaerobic acetic acid fermentation has the advantage that no carbon is lost as carbon dioxide. The disadvantage is that the already low concentration of acetic acid is toxic for the *Clostridium* bacteria. The acetic acid can be esterified with ethanol, using acid catalyst to ethyl acetate. The low boiling azeotrope of the ethyl acetate with water and ethanol can be used to drive the reaction equilibrium towards the product. Ethyl acetate is less corrosive than acetic acid. Esters can be hydrogenated into alcohols using suitable catalysts, usually at a fairly high temperature (250 °C) and high pressure (200-300 bars).[17] By this route, the yield of ethanol is significantly higher than that obtained by ethanol fermentation. The needed hydrogen can be produced by gasification into synthesis gas and converting CO into hydrogen and CO_2, by the water gas shift reaction.

Butanol can be produced by dehydrogenation from ethanol into acetaldehyde, followed by aldol condensation into crotonaldehyde, with subsequent hydrogennation into n-butanol. Partial hydrogenation of crotonaldehyde yields butyraldehyde. Ethylene can be obtained[18] by the dehydration reaction with solid acid catalyst above 200 °C with alumina, silica, manganese and ferric oxides, special zeolites with a high yield of 99%. Correspondingly, propylene can be obtained from isobutanol. For the commonly used petrochemicals, these routes are interesting, due to the less severe reaction conditions, compared to the traditional steam crackers used in the petrochemical industry. Under acidic conditions, combined with the removal of the formed water butyraldehyde and ethanol, diethoxybutane with attractive diesel fuel properties can be obtained.

The ABE (acetone, butanol, ethanol) fermentation of sugars with *Clostridium acetobutylicum* bacteria produces n-butanol, acetone, ethanol, hydrogen and carbon dioxide. The hydrogen produced can be used, for example, to hydrogenate acetone into isopropanol and to produce methanol from hydrogen and carbon dioxide through methanol synthesis. Butanol, isopropanol and ethanol can be converted into ethers (dibutylether, di-isopropylether and diethylether) with attractive fuel properties as a diesel fuel.

Obviously, sugars can be also used as raw materials for microbes in the production of raw material for biopolymers, such as lactic acid, succinic acid, etc.

Other routes

The production of alkanes, similar to that of FT-diesel from sugar, has been described by Huber *et al.*,[19] who reported selective formation of alkanes (C7 to C15) with dehydration/hydrogenation over bifunctional catalysts at around 250 °C and 52-60 bars, in a four-phase system. The hydrogenated phase is separated from the water phase when the reaction proceeds. Alternatively, sugars or sorbitole obtained through hydrogenation of sugars can be treated by hydrogenolysis, to obtain ethylene glycol, used as an anti-freezing fluid, and glycerol, as described by Dasari.[20]

Sugars can be also converted to valuable gasoline fuel components, by dehydration through 5-hydroxymethylfurfural (HMF) and hydrogenolysis by various paths, as presented by Román-Leshkov *et al.*[21] The gasoline components have high octane numbers, low solubility in water and a higher energy content than ethanol, which enables them to be mixed in a higher fraction than ethanol. By the Biofine process, levulic acid and a valuable chemical intermediate can be produced,[22] to be further used for the production of methyl tetrahydrofuran gasoline fuel, succinic acid – raw material for biopolymers, etc.

Biomass can be also converted into biogas by anaerobic digestion using mesophilic (30-35 °C) or thermophilic (50-55 °C) bacteria. The process is relatively slow, 50% of the dry matter being decomposed[18] within 10 days. However, not all biomass can be converted, for example, lignin does not decompose. The produced biogas contains carbon dioxide, methane and small amounts of sulfur compounds, nitrogen and ammonia. Methane can be further converted, with steam reforming, into synthesis gas.

Objective

The routes presented here are evaluated for both material efficiency, product heat content and product properties. Gasification, calculated by Gibbs energy minimization, gives maximum potential yields. The subsequent reactions, fermentation and digestion, are considered on the basis of chemical reactions assuming stoichiometrical yields. The maximum potential amounts of synthesis gas and of its derivatives were calculated upon gasification of the whole biomass for eight different wood and non-wood lignocellulosic feedstocks. A second case was calculated for biomass conversion to pyrolysis oil, with subsequent gasification and conversion into fuel components. In addition, the maximum potential amount of synthesis gas and conversion products that could be obtained from the lignin and extractives of pine and birch was calculated. The maximum potential amount of products should be seen as a first step in evaluating upgrading paths. Then, feasible routes can be studied in more detail, by taking into account the selectivities with particular catalysts for given chemical reactions. A comparison of the maximum potential amount with the experimental yield of synthesis gas has been made by Melin *et al.*[23] As, in some upgrading paths, hydrogen is needed, the question is whether hydrogen could be produced by gasification of both lignin and biomass extractives. Further on, the amounts of different components that could be obtained through hydrolysis and fermentation, digestion or chemical conversion of the sugars from cellulose and hemicellulose were calculated. For the products obtained through hydrogenation, the necessary amount of hydrogen was computed.

METHODS

The following raw materials were considered: Pine, Spruce, Black Alder, Aspen, Silver Birch, Eucalyptus, Larch, bagasse and wheat straw. The composition was analyzed for stem wood. The composition of bark and needles differs significantly from that of stem wood.

The raw materials used in the calculation are presented in Table 1. The ultimate analysis and composition obtained after hydrolysis was used as a basis in the calculations. The lower heating value was either calculated or obtained directly from the references shown. For the sake of comparison, pyrolysis oil was also included as a feedstock. The composition of pyrolysis oil was in accordance with IEA.[24] According to IEA, for pyrolysis, the typical yield of liquid hydrocarbons is of 75%, on an anhydrous basis. For lignin, the composition of the remaining liquor was calculated by subtracting the cellulose and hemicellulose amounts from the original feedstock. The lignin heating values were assumed for both lignin and extractives.

For products and intermediates, the material efficiencies were calculated, *i.e.* mass of product (fuel components or chemicals), compared to the mass of the raw material on dry basis. In addition, the amount of heat in the products (fuel components) based on lower heating values were compared with the lower heating value of the raw material. The mass of carbon and hydrogen in the product was also calculated and compared with that of the raw material. This is important, since the rest of carbon is generally lost as carbon dioxide during processing.

For biofuel components, the important fuel properties, such as vapor pressure, flash point, octane or cetane number, water solubility and corrosiveness, were obtained from literature. Different fuel components were evaluated as to their use in conventional diesel and gasoline cars and as to their storage. The material and energy efficiency of a small number of petrochemicals that could be obtained in biofuel production as intermediates or bioproducts were also considered in this study. The application of these chemicals was also discussed.

Gasification

Due to the endothermic nature of the gasification process, one should take into account the enthalpy balance when calculating the yield of product from syngas, since the required heat is produced by the partial combustion of the raw material. The composition of the synthesis gas was calculated by Gibbs energy minimization, with a simulation software. The Gibbs energy minimization determines the reaction equilibrium and the maximum theoretical conversion under given conditions.

Methane, acting as an inert gas in many refining processes, was further reformed by autothermal reforming into CO and H_2. Both gasification and reforming were simulated by minimization of Gibbs energy. Solid carbon, CO, H_2O, O_2, CO_2, S, SO_2, N_2, CH_4 and C_2H_4 were selected as reacting components. Ash was modeled as CaO and it was assumed that it does not react, even though in reality it may react with carbon dioxide. In most feedstocks, the amount is so small that it can be neglected. The product gas contained only CO, H_2O, N_2, CH_4 and SO_2 in significant concentrations. For wood and non-wood biomass, it was assumed that the biomass feedstocks contained 50 wt% water and 50% biomass. The biomass feedstock was dried to 15 wt% water with hot gases after gasification, so that the hot exhaust gas temperature was of at least 200 °C. The evaporated water was fed to the gasification stage with the biomass. Pyrolysis oil was assumed to contain 25 wt% water and the lignin part was assumed to be in a solution containing 60 wt% lignin and 40 wt% water.

Gasification was performed at 800 °C, at 5 bar. Sufficient oxygen was added to raise the temperature of the feed to 800 °C. After the gasification stage, the gas mixture was reformed to convert residual methane into synthesis gas by heating to 950 °C. Reforming was modeled with Gibbs energy minimization and enough oxygen was added to raise the temperature from 800 to 950 °C.

Gasification with oxygen at 5 bar was preferred in this study because Kurkela *et al.*[25] concluded that the gas produced from such a process is suitable for all known fuel and chemical production processes. In addition, the reformation of synthesis gas produced with indirect gasification by steam is more challenging. They reported that only limited benefit can be obtained by increasing the gasification pressure beyond about 5 bar in methanol synthesis.

FT synthesis was calculated by assuming that the chain growth follows the Anderson-Schulz-Flory distribution with a chain growth probability $\alpha = 0.87$,[26] giving mainly diesel range products. The product distribution as a function of α is provided in literature.[27]

Subsequent upgrading reactions

The potential material efficiencies were calculated for reactions (1) to (7). The ratio between CO and H_2 was first adjusted for the synthesis gas, by the gas shift reaction. Reaction 1 was also considered to be employed in hydrogen production.

Shift reaction $$CO + H_2O \leftrightarrow H_2 + CO_2 \quad (1)$$

Methanol synthesis $$CO + 2H_2 \rightarrow CH_3OH \quad (2)$$

Methanol carbonylation into ethanol $CH_3OH + CO + 2H_2 \rightarrow C_2H_5OH + H_2O$ (3)

Methanol carbonylation to acetic acid $CH_3OH + CO \rightarrow CH_3COOH$ (4)

DME synthesis $3CO + 3H_2 \rightarrow CH_3OCH_3 + CO2$ (5)

The synthesis reaction represents the total reaction, when methanol synthesis (2) and the gas shift reaction (1) occur simultaneously.

MTO to olefins from DME $\frac{n}{2}CH_3OCH_3 \rightarrow C_nH_{2n} + \frac{n}{2}H_2O$ (6)

where n is 2, 3 and 4.

Hydration of olefins into alcohols $C_nH_{2n} + H_2O \rightarrow C_nH_{2n+1}OH$ (7)

Methanisation $CO + 3H_2 \rightarrow CH_4 + H_2O$ (8)

FT synthesis $nCO + (2n+1)H_2 \rightarrow C_nH_{2n+2} + nH_2O$ (9)

The weight fractions of the fraction with different chain lengths can be estimated with Eq. 10. The weight fraction of different hydrocarbons with n carbons in Ft synthesis is:

$$W_n = n(1-\alpha)^2(\alpha-1)^{n-1} \qquad (10)$$

where W_n is the weight fraction of hydrocarbons with n carbons.

Fermentation and oxygen removal from sugars by hydrogen

Since the aim of this study is to establish the total amount of the components that can be produced by various routes, the hydrolysis of both cellulose and hemicellulose was considered. It was also calculated how much biogas could be produced from the sugars obtained through total hydrolysis. It was assumed that lignin is not degradable by methane-producing bacteria. Ethanol fermentation of the hexose sugars was calculated according to Eq. 11.

The conversion of ethanol into butanol was calculated according to Eq. 12. The total reaction involves the combination of dehydrogenation of ethanol into acetaldehyde, aldol condensation into crotonealdehyde and subsequent hydrogenation into butanol. The further dehydration of the alcohol into ether (dibutylether and diethylether) was calculated according to Eq. 13. The dehydration of the alcohol into alkene ethylene and propylene was calculated according to Eq. 14.

Eq. 15 involves the reaction of two molecules of ethanol with one molecule of butyraldehyde. Butyraldehyde is produced from ethanol by dehydration into acetaldehyde, aldol condensation to crotonaldehyde and hydrogenation into butyraldehyde, which also gives one mole of hydrogen as by-product. Acetic acid is produced by anaerobic fermentation of glucose, according to Eq. 16, and pentose – according to Eq. 17. The acetic acid is esterified with ethanol to ethyl acetate (Eq. 18) and the ethyl acetate is hydrogenated into ethanol (Eq. 19).

ABE fermentation involves many reaction products, their dependence on the others being indirect. The assumed ABE fermentation yields were of 0.42 g ABE/g sugar[28] for C6 sugars and of 0.28 g/g sugar[29] for xylose. The fermentation gas was assumed to consist[32] of 40 mol% H_2 and 60 mol% CO_2, in the final stage of fermentation.

The hydrogenation of acetone into isopropanol was calculated according to Eq. 20. Methanol can be also obtained from carbon dioxide, according to Eq. 21.

Sugar can be also upgraded by hydrogenation, for example, by the reaction presented by Huber *et al.*[19]

Pentose sugars can be reacted into, for example, methyl tetrahydrofuran (MTHF) shown in Eq. 22 by dehydration of sugar into furan and subsequent hydrogenation *via* methylfuran. Hexose sugars can be reacted, for example, into C12 alkane type of products, according to Eq. 23. Hydrogenation involves dehydrogenation of hexose into HMF hydromethylfurfural, hydrogenation and aldol condensation of two C6 molecules into one larger molecule producing C12 hydrocarbon.

Digestion

The digestion of the organic substance is represented by Eq. 24. Finally, the produced methane could be steam-reformed into a synthesis gas, according to Eq. 25. The reaction is endothermic, *i.e.* the energy content of the produced syngas is larger than that of the methane gas, if the reaction heat is supplied from an external heat source.

Hexose ethanol fermentation	$C_6H_{12}O_6 \rightarrow 2C_2H_5OH + 2CO_2$	(11)
Butanol from ethanol	$2C_2H_5OH \rightarrow C_4H_9OH + H_2O$	(12)
Dehydration	$2C_nH_{n+1} -> C_n - O - C_n + H_2O$	(13)
Dehydration	$C_nH_{2n+1}OH \rightarrow C_nH_{2n} + H_2O$	(14)
Diethoxybutane reaction	$4C_2H_5OH \rightarrow CH_3CH_2CH_2CH(OC_2H_5)_2 + 3H_2O + H_2$	(15)
Hexose acetic acid fermentation	$C_6H_{12}O_6 \rightarrow 3CH_3COOH$	(16)
Pentose acetic acid fermentation	$2C_5H_{10}O_5 -> 5CH_3COOH$	(17)
Esterification	$CH_3COOH + C_2H_5OH \rightarrow CH_3COOCH_2CH_3 + H_2O$	(18)
Hydrogenation	$CH_3COOCH_2CH_3 + 2H2 \rightarrow 2C_2H_5OH$	(19)
Acetone hydrogenation	$CH_3COCH_3 + H_2 \rightarrow CH_3CHOHCH_3$	(20)
Methanol synthesis from CO$_2$	$CO_2 + 3H_2 \rightarrow CH_3OH + H_2O$	(21)
Pentose hydrogenation	$C_5H_{10}O_5 + 4H_2 \rightarrow C_5H_{10}O + 4H_2O$	(22)
Hexose hydrogenation	$2C_6H_{12}O_6 + 13H_2 \rightarrow C_{12}H_{26} + 12H_2O$	(23)
Digestion	$C_XH_yO_Z + \left(x - \frac{y}{4} - \frac{z}{2}\right)H_2O \rightarrow \left(\frac{x}{2} - \frac{y}{8} + \frac{z}{4}\right)CO_2 + \left(\frac{x}{2} + \frac{y}{8} - \frac{z}{4}\right)CH_4$	(24)
Steam reforming	$CH_4 + H_2O \rightarrow CO + 3H_2O$	(25)

RESULTS AND DISCUSSION

Gasification

The potential yields obtained, according to the methods described, for the selected raw material and for the derivatives are shown in Table 2. For the gasification reaction, it can be observed that the highest amount of energy remains in the synthesis gas, compared to the upgraded products.

The calculated potential heat content (LHV) in the synthesis gas ranges from 84 to 73% for different raw materials. For materials with a high ash content, such as wheat straw and sugar cane bagasse, the heat content remaining in the synthesis gas is the lowest. For fast pyrolysis with subsequent gasification of the pyrolysis oil, the remaining heat content of the synthesis gas is of approximately 50% of the original biomass.

For gasification of lignin+extractives, 23.5% of the heat content of pine can be transferred into the heat content of the synthesis gas. Also, for birch lignin, 13.3% of the original heat content of birch can be recovered by gasifying the lignin+extractives part.

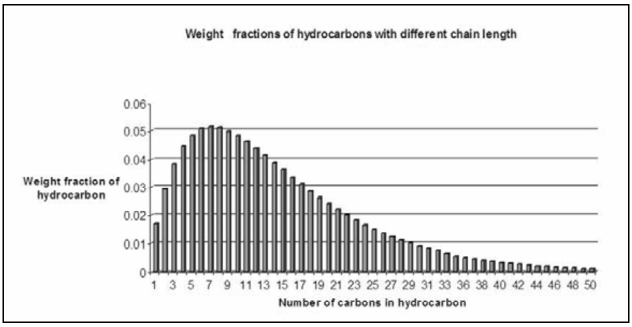

Figure 1: Distribution of hydrocarbon chain length for FT synthesis with α = 0.87

In the case of the derivatives, the remaining heat content of the product is lower than that remaining for synthesis gas. The upgrading methods studied show that the lowest amount of heat remains in the Fischer-Tropsch product, followed by methanisation. The largest amount of heat remains in the synthesis gas when this is converted into hydrogen. Second in heat conversion efficiency is methanol synthesis. Compared to the original raw material, the carbon conversion efficiency in the products ranges from above 70 to 0%.

The remaining hydrogen ranges from 0 to 200%, because the obtained carbon monoxide can be converted – according to Eq. 1 – into carbon dioxide and hydrogen with the aid of steam at a high temperature. Therefore, the hydrogen content of the product can exceed that of the raw material.

For FT synthesis, the average chain length was 14 carbons, the distribution of the molecular chain length obtained being shown in Figure 1.

Fermentation

Tables 3 to 14 list the potential yields, the material efficiencies and the carbon ratios (%) remaining in the original raw material for products obtained through fermentation, as well as through further upgrading. Ethanol, acetic acid and ABE (acetone ethanol butanol) fermentation are considered. Also, the results of the subsequent upgrading reactions are presented.

Table 4 shows that the yield of ethanol from hexose fermentation is lower than that of the raw material containing more pentose sugars, such as birch, compared to, for example, pine.

The material yield of butanol, *e.g.* for pine, is of 256 kg to 319 kg, as shown in Table 5 *vs*. Table 6. This value is significantly lower when butanol is produced from ethanol. However, in the conversion of butanol from ethanol, only approximately 2% of the liquid energy content is lost, based on LHV%.

When butanol is further converted to dibutylether, the material yield is reduced from about 256 to 225 kg, as shown for pine in Tables 5 and 6. However, the lower heating value of the fuel increases (0.2%), which indicates that the reaction should be slightly endothermic.

Anaerobic acetic acid fermentation gives a high yield because, in the reaction, no carbon is lost as carbon dioxide. Furthermore, when hydrogen is added to the acetic acid product, the material yield is decreased by approximately 200 kg from acetic acid to ethanol, while the energy content of the liquid increases from around 42 to 72% for pine, as shown in Tables 7 to 9. Also, a high amount of hydrogen (45.4 kg) is needed for pine, slightly more than it can be obtained through the gasification of pine lignin and extractives, as shown in Table 2.

The amount of energy, LHV%, in the product increases when converting ethanol into ethylene, as a result of the endothermic dehydration reaction, as shown in Table 11. It also means that external heat is needed to drive the dehydration reaction. Table 12 shows the conversion of ethanol to diethoxybutane, with hydrogen as a by-product. The amounts of energy present in the products were only slightly reduced.

The total material yield of ABE fermentation (Table 13) is lower than that for the conventional ethanol fermentation (Table 3). However, the energy content of the products is significantly higher. The *Clostridium* bacteria can also utilize pentose sugars.

When acetone is hydrogenated into isopropanol and the remaining hydrogen gas is used to hydrogenate the carbon dioxide into methanol, a slight reduction is observed in the total energy content of the products – as shown in Table 14. However, the total yield of liquid products and their usefulness increase.

Starting with the acetic acid, a high yield of butanol can be theoretically obtained. In practice, the material yield might be significantly lower, due to multiple reactions, if the selectivities in the reactions are low.

Chemical upgrading of sugars

The results of upgrading sugars through hydrogenation are shown in Table 15.

Table 1
Ultimate analysis and chemical composition of a calculated amount of raw material

Species	C, %	H, %	O, %	N, %	S, %	Ash, %	Higher heating value, MJ/kg	Lower heating value, MJ/kg	Ref.	Xylan	Cellulose	Extractives	Glucan	Mannan	Galactane	Xylane	Ref.
Pine	52.34	6.09	41.19	0.08	0.01	0.74	20.6	19.31	30	0.1	0.41	0.04	0.41	0.124	0.019	0.076	31
Spruce	52.43	5.86	40.63	0.01	0.03	1.04	20.3	19.05	25	0.11	0.41	0.02	0.41	0.136	0.028	0.056	25
Black alder	49.09	5.22	43.78	0.44	0.55	0.92	20.0	18.9	25			0.06	0.405	0.015	0.008	0.161	25
Aspen	46.21	5.77	46.40	0.15	0.55	0.92	19.9	18.7	25			0.06	0.432	0.022	0.005	0.151	25
Silver birch	47.43	5.22	46.05	0.07	0.55	0.68	19.7	18.62	25	0.33	0.4	0.03	0.407	0.017	0.007	0.2	25
Eucalyptus	57.20	5.25	36.38	0.00	0.00	1.17	20.3	19.2	25				0.523	0.011	0.01	0.16	32
Larch	48.80	6.10	44.90	0.10	0.01	0.10	19.5	18.2	25				0.46	0.11	0.02	0.063	33
Bagasse	44.8	5.35	39.55	0.38	0.01	11.2	17.33	16.2	34		0.334	0.060	0.410	0	0	0.252	35
Wheat straw	43.2	5.00	39.40	0.61	0.11	8.9	17.51	16.4	36	0.210	0.400	0.072	0.411	0.003	0.006	0.210	37
Pyrolysis oil	56	6.5	37.5	0.1					24	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A

Table 2
Potential material yield, material efficiencies for synthesis gas and its derivatives (first part)

Material heat efficiency of syngas-derived products	Type of raw material											
	Domestic softwood (Finland)		Domestic hardwood (Finland)			Foreign trees		Non-wood biomass		Biomass derivatives		
	Pine	Spruce	Black alder	Aspen	Silver birch	Eucalyptus	Larch	Sugar cane bagasse	Wheat straw	Pyrolysis oil	Pine lignin+ extractives	Birch lignin +extractives
Syngas												
H_2, kg/ton dry biomass	79.1	75.9	72.1	73.7	70.7	67.3	69.1	59.2	62.8	52.2	21.0	13.4
CO, kg/ton dry biomass	664.3	657.6	610.7	568.9	564.7	669.2	559.7	467.1	483.1	474.3	302.2	159.8
LHV, MJ/kg dry biomass	16.2	15.8	14.8	14.6	14.2	14.8	14.0	11.8	12.4	11.1	5.6	3.2
LHV, %	83.9	82.8	78.5	78.1	76.3	77.4	76.7	73.1	75.6	50.3	23.5	13.3
C material efficiency, %	54.4	53.8	53.4	52.8	51.1	50.2	49.2	44.7	48.0	36.3	21.9	13.1
H material efficiency, %	129.8	129.6	138.1	127.8	135.5	128.2	113.3	110.7	125.7	80.3	35.1	71.8
Hydrogen production												
Hydrogen, kg/ton dry biomass	126.9	123.3	116.1	114.7	111.4	115.5	109.4	92.8	97.6	86.3	42.8	24.9
LHV, MJ/kg dry biomass	15.2	14.8	13.9	13.8	13.4	13.9	13.1	11.1	11.7	10.4	5.1	3.0
LHV, %	78.9	76.6	72.2	71.3	69.2	71.8	68.0	57.7	60.7	53.7	26.6	15.5
C material efficiency, %	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
H material efficiency, %	208.3	210.4	222.3	198.8	213.3	220.0	179.4	173.5	195.2	132.8	71.4	133.4
Methanol synthesis												
Methanol, kg/ton dry biomass	672.2	653.1	614.9	607.7	590.0	611.8	579.6	491.9	517.2	457.3	226.5	132.0
LHV, MJ/kg dry biomass	14.2	13.8	13.0	12.8	12.4	12.9	12.2	10.4	10.9	9.6	4.8	2.8
LHV, %	73.4	72.3	68.6	68.5	66.8	67.3	67.2	64.1	66.4	45.3	20.1	11.5
C material efficiency, %	48.1	46.7	46.9	49.3	46.6	40.1	44.5	41.2	44.9	30.6	14.3	9.4
H material efficiency, %	138.9	140.2	148.2	132.5	142.2	146.6	119.6	115.7	130.2	88.5	47.6	88.9
Methanol carbonisation												
Ethanol, kg/ton dry biomass	483.3	469.5	442.0	436.9	424.1	439.8	416.7	353.6	371.8	328.7	162.8	94.9
LHV, MJ/kg dry biomass	13.4	13.0	12.3	12.1	11.8	12.2	11.6	9.8	10.3	9.1	4.5	2.6
LHV, %	69.4	68.3	64.8	64.8	63.1	63.6	63.5	60.6	62.7	42.9	19.0	10.9
C material efficiency, %	48.1	46.7	46.9	49.3	46.6	40.1	44.5	41.2	44.9	30.6	14.3	9.4
H material efficiency, %	86.8	87.6	92.6	82.8	88.9	91.7	74.7	72.3	81.4	55.3	29.7	55.6
Methanol carbonisation												
Acetic acid, kg/ton dry biomass	944.9	901.8	864.2	854.1	829.2	860.0	814.7	691.4	727.0	642.7	318.4	185.6
C material efficiency, %	72.21	68.80	70.42	73.94	69.94	60.14	66.78	61.73	67.32	45.91	21.48	14.17
H material efficiency, %	104.17	103.32	111.16	99.39	106.66	109.98	89.68	86.76	97.62	66.39	35.69	66.70

Table 3
Material yield, material efficiencies for synthesis gas and its derivatives (second part)

DME (dimethylether) synthesis	Pine	Spruce	Black alder	Aspen	Silver birch	Eucalyptus	Larch	Sugar cane bagasse	Wheat straw	Pyrolysis oil	Pine lignin+ extractives	Birch lignin+ extractives
DME, kg/ton dry biomass	483.2	469.5	442.0	436.8	424.1	439.8	416.7	353.6	371.8	328.7	162.8	94.9
LHV, MJ/kg dry biomass	13.9	13.5	12.7	12.6	12.2	12.7	12.0	10.2	10.7	9.5	4.7	2.7
LHV, %	72.2	71.1	67.4	67.4	65.7	66.2	66.1	63.0	65.2	44.6	19.7	11.3
C material efficiency, %	48.1	46.7	46.9	49.3	46.6	40.1	44.5	41.2	44.9	30.6	14.3	9.4
H material efficiency, %	104.2	105.2	111.2	99.4	106.7	110.0	89.7	86.8	97.6	66.4	35.7	66.7
MTO process from methanol												
Ethylene, kg/ton dry biomass	147.1	142.9	134.6	133.0	129.1	133.9	126.9	107.7	113.2	100.1	49.6	28.9
Propylene, kg/ton dry biomass	147.1	142.9	134.6	133.0	129.1	133.9	126.9	107.7	113.2	100.1	49.6	28.9
LHV, MJ/kg dry biomass	13.7	13.3	12.5	12.4	12.0	12.4	11.8	10.0	10.5	9.3	4.6	2.7
LHV, %	70.8	69.8	66.2	66.1	64.5	64.9	64.8	61.8	64.0	43.8	19.4	11.1
C material efficiency, %	48.1	45.9	46.9	49.3	46.6	40.1	44.5	41.2	44.9	30.6	14.3	9.4
H material efficiency, %	69.4	68.9	74.1	66.3	71.1	73.3	59.8	57.8	65.1	44.3	23.8	44.5
n-Propanol and ethanol through hydration of olefins												
Etanol, kg/ton dry biomass	241.6	234.7	221.0	218.4	212.1	219.9	208.3	176.8	185.9	164.4	81.4	47.5
Propanol, kg/ton dry biomass	210.1	204.1	192.2	189.9	184.4	191.2	181.2	153.7	161.7	142.9	70.8	41.3
LHV, MJ/kg	13.0	12.7	11.9	11.8	11.4	11.9	11.2	9.5	10.0	8.9	4.4	2.6
LHV, %	67.5	65.6	61.7	61.0	59.2	61.4	58.2	49.4	51.9	45.9	22.7	13.3
C material efficiency, %	48.1	46.7	46.9	49.3	46.6	40.1	44.5	41.2	44.9	30.6	14.3	9.4
H material efficiency, %	98.4	99.3	105.0	93.9	100.7	103.9	84.7	81.9	92.2	62.7	33.7	63.0
Methanisation of syngas												
Methane, kg/ton dry biomass	252.4	245.2	230.9	228.2	221.5	229.7	217.7	184.7	194.2	171.7	85.1	49.6
LHV, MJ/kg dry biomass	12.6	12.3	11.5	11.4	11.1	11.5	10.9	9.2	9.7	8.6	4.3	2.5
LHV, %	65.3	64.4	61.1	61.0	59.5	59.9	59.8	57.1	59.1	39.1	17.9	10.2
C material efficiency, %	36.1	35.0	35.2	37.0	35.0	30.1	33.4	30.9	33.7	23.0	10.7	7.1
H material efficiency, %	104.2	101.2	95.3	94.2	91.4	94.8	89.8	76.2	80.1	70.9	35.1	20.5
Once-through Ft synthesis												
Hydrocarbons, kg/ton dry biomass	268.3	257.7	244.6	250.2	239.9	228.4	234.5	200.9	213.3	177.0	71.2	45.5
Water, kg/ton of biomass	341.1	327.6	311.0	318.2	305.1	290.4	298.2	255.5	271.2	225.1	90.6	57.9
LHV, MJ/kg dry biomass	11.8	11.3	10.8	11.0	10.6	10.1	10.3	8.8	9.4	7.8	3.1	2.0
LHV, %	61.2	58.7	55.8	57.0	54.7	52.1	53.5	45.8	48.6	40.4	16.2	10.4
C material efficiency, %	43.4	41.7	42.2	45.9	42.9	33.8	40.7	38.0	41.8	26.8	10.2	7.4
H material efficiency, %	128.7	128.5	137.2	126.9	134.6	127.6	112.7	110.6	125.4	80.6	37.2	80.1

Table 4
Potential yield from hexose sugars obtained through ethanol fermentation

Ethanol fermentation (only C6 sugars)	Domestic softwood (Finland)		Domestic hardwood (Finland)			Foreign trees		Non-wood biomass	
	Pine	Spruce	Black alder	Aspen	Silver birch	Eucalyptus	Larch	Bagasse	Wheat straw
Ethanol, kg/ton dry biomass	318.6	303.2	243.1	260.2	236.0	309.0	335.0	233.0	238.6
CO_2, kg/ton dry biomass	304.3	289.6	232.2	248.6	225.5	295.2	320.0	222.6	227.9
LHV, MJ/kg dry biomass	8.8	8.4	6.7	7.2	6.5	8.6	9.3	6.5	6.6
LHV, %	45.7	44.1	35.7	38.6	35.1	44.7	51.1	39.9	40.2
C material efficiency, %	84.1	84.9	87.1	85.3	87.0	85.9	82.1	86.4	85.6

Table 5
Potential yield of butanol obtained from ethanol through hexose fermentation

Ethanol fermentation (only C6 sugars)→butanol	Domestic softwood (Finland)		Domestic hardwood (Finland)			Foreign trees		Non-wood biomass	
	Pine	Spruce	Black alder	Aspen	Silver birch	Eucalyptus	Larch	Bagasse	Wheat straw
Butanol, kg/ton dry biomass	256.3	243.9	195.6	209.3	189.9	248.6	269.5	187.4	191.9
H_20, kg/ton dry biomass	62.3	59.3	47.5	50.9	46.2	60.4	65.5	45.6	46.7
LHV, MJ/kg dry biomass	8.5	8.1	6.5	6.9	6.3	8.2	8.9	6.2	6.4
LHV, %	43.9	42.4	34.3	37.1	33.8	42.9	49.1	38.3	38.7
C material efficiency, %	84.1	84.9	87.1	85.3	87.0	88.5	82.1	86.5	86.8

Table 6
Potential yield of dibutylether obtained by hexose ethanol fermentation and subsequent dehydrogenation of butanol into dibutyether

Ethanol→butanol→dibutylether	Domestic softwood (Finland)		Domestic hardwood (Finland)			Foreign trees		Non-wood biomass	
	Pine	Spruce	Black alder	Aspen	Silver birch	Eucalyptus	Larch	Bagasse	Wheat straw
Dibutyl ether, kg/ton dry biomass	225.1	214.3	171.8	183.9	166.8	218.4	236.7	164.6	168.6
Water, kg/ton dry biomass	8.5	8.1	6.5	7.0	6.3	8.3	8.9	6.2	6.4
LHV, MJ/kg dry biomass	8.5	8.1	6.5	7.0	6.3	8.3	8.9	6.2	6.4
LHV, %	44.1	42.5	34.4	37.2	33.9	43.0	49.2	38.5	38.8
C material efficiency, %	84.1	84.9	87.1	85.3	87.0	88.5	82.1	86.5	86.8

Table 7
Potential yield of acetic acid through anaerobic acetic acid fermentation of hexose and pentose sugars

Acetic acid fermentation (both C5 and C6 sugars)	Domestic softwood (Finland)		Domestic hardwood (Finland)			Foreign trees		Non-wood biomass	
	Pine	Spruce	Black alder	Aspen	Silver birch	Eucalyptus	Larch	Bagasse	Wheat straw
Acetic acid, kg/ton dry biomass	676.3	646.2	658.3	680.4	741.0	786.0	726.6	741.9	490.4
LHV, MJ/kg dry biomass	8.0	7.7	7.8	8.1	8.8	9.3	8.6	8.8	5.8
LHV, % raw material	41.6	39.7	40.5	41.8	45.6	48.3	44.7	45.6	30.1
C material efficiency, %	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0

Table 8
Potential yield of ethyl acetate obtained through acetic acid fermentation, hydrogenation of half of it into ethanol and its esterification with acetic acid

Acetic acid fermentation (both C5 and C6 sugars)	Domestic softwood (Finland)		Domestic hardwood (Finland)			Foreign trees		Non-wood biomass	
	Pine	Spruce	Black alder	Aspen	Silver birch	Eucalyptus	Larch	Bagasse	Wheat straw
Acetic acid, kg/ton dry biomass	676.3	646.2	658.3	680.4	741.0	786.0	726.6	741.9	490.4
LHV, MJ/kg dry biomass	8.0	7.7	7.8	8.1	8.8	9.3	8.6	8.8	5.8
LHV, % raw material	41.6	39.7	40.5	41.8	45.6	48.3	44.7	45.6	30.1
C material efficiency, %	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0

Table 9
Potential yield of ethanol obtained through anaerobic acetic acid fermentation and subsequent hydrogenation;
amount of hydrogen necessary to convert acetic acid into ethanol

Acetic acid fermentation (both C5 and C6 sugars)	Domestic softwood (Finland)		Domestic hardwood (Finland)			Foreign trees		Non-wood biomass	
	Pine	Spruce	Black alder	Aspen	Silver birch	Eucalyptus	Larch	Bagasse	Wheat straw
H_2 needed, kg/ton dry biomass	45.4	43.4	44.2	45.7	49.8	52.8	48.8	49.8	32.9
Ethanol produced, kg/ton dry biomass	518.8	495.8	505.0	522.0	568.5	603.0	557.5	569.2	376.2
LHV, MJ/kg dry biomass	14.4	13.7	14.0	14.5	15.8	16.7	15.5	15.8	10.4
LHV, % raw material	74.5	72.1	74.1	77.4	84.6	87.2	84.9	97.5	63.4
C material efficiency, %	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0

Table 10
Potential yield of butanol obtained through acetic acid fermentation, hydrogenation and conversion of ethanol into butanol

Acetic acid fermentation (both C5 and C6 sugars)	Domestic softwood (Finland)		Domestic hardwood (Finland)			Foreign trees		Non-wood biomass	
	Pine	Spruce	Black alder	Aspen	Silver birch	Eucalyptus	Larch	Bagasse	Wheat straw
Butanol, kg/ton biomass	417.4	398.8	406.3	419.9	457.3	485.1	448.4	457.9	302.6
LHV, MJ/kg dry biomass	13.8	13.2	13.5	13.9	15.1	16.1	14.8	15.2	10.0
LHV, % raw material	71.6	69.3	71.2	74.3	81.3	83.8	81.6	93.7	61.0
C material efficiency, %		100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0

Table 11
Potential yield of ethylene obtained through acetic acid fermentation, hydrogenation and dehydration of ethanol into ethylene

Anaerobic acetic acid fermentation →ethanol→ethylene	Domestic softwood (Finland)		Domestic hardwood (Finland)			Foreign trees		Non-wood biomass	
	Pine	Spruce	Black alder	Aspen	Silver birch	Eucalyptus	Larch	Bagasse	Wheat straw
Ethylene, kg/ton dry biomass	315.9	301.9	307.5	317.8	346.2	367.2	339.5	346.6	229.1
LHV, MJ/kg dry biomass	13.8	13.2	13.5	13.9	15.1	16.1	14.8	15.2	10.0
LHV, % raw material	77.2	74.7	76.7	80.2	87.7	90.3	88.0	101.0	65.7
C material efficiency, %	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0

Table 12
Potential yield of diethoxybutane obtained through acetic acid fermentation, hydrogenation and conversion of ethanol and butyraldehyde produced from ethanol into diethoxybutane

Acetic acid fermentation (both C5 and C6 sugars)	Domestic softwood (Finland)		Domestic hardwood (Finland)			Foreign trees		Non-wood biomass	
	Pine	Spruce	Black alder	Aspen	Silver birch	Eucalyptus	Larch	Bagasse	Wheat straw
Diethoxybutane, kg/ton dry biomass	411.7	393.4	400.8	414.2	451.1	478.5	442.4	451.7	298.5
LHV, MJ/kg dry biomass	14.0	13.4	13.6	14.1	15.3	16.3	15.0	15.4	10.1
LHV, % raw material	72.5	70.2	72.1	75.3	82.4	84.8	82.7	94.9	61.7
C material efficiency, %	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0

Table 13
Yield of ABE fermentation based on reported yields for different raw materials

ABE fermentation (both C5 and C6 sugars)	Domestic softwood (Finland)		Domestic hardwood (Finland)			Foreign trees		Non-wood biomass	
	Pine	Spruce	Black alder	Aspen	Silver birch	Eucalyptus	Larch	Bagasse	Wheat straw
Butanol, kg/ton dry biomass	166.9	159.3	153.8	160.1	168.2	186.0	178.3	168.0	122.0
Acetone, kg/ton dry biomass	83.4	79.6	76.9	80.0	84.1	93.0	89.2	84.0	61.0
Etanol, kg/ton dry biomass	27.8	26.5	25.6	26.7	28.0	31.0	29.7	28.0	20.3
Total ABE, kg/ton dry biomass	278.1	265.5	256.3	266.8	280.4	310.0	297.2	280.0	203.3
Hydrogen, kg/ton dry biomass	12.9	12.3	13.6	14.0	16.2	16.3	14.1	16.3	8.7
CO_2, kg/ton dry biomass	352.1	334.7	371.8	381.9	442.2	445.7	385.6	444.3	237.3
LHV, MJ/kg dry biomass	10.2	9.8	9.6	10.0	10.7	11.6	11.0	10.7	7.4
LHV, % raw material	53.0	51.2	51.0	53.5	57.4	60.7	60.3	66.1	44.9
C material efficiency, %	81.6	82.5	80.6	80.1	76.9	76.8	79.9	76.8	87.6

Table 14
Potential yield of products from ABE mixture (Table 13), when acetone and carbon dioxide are hydrogenated into isopropanol and methanol

ABE fermentation (both C5 and C6 sugars)	Domestic softwood (Finland)		Domestic hardwood (Finland)			Foreign trees		Non-wood biomass	
	Pine	Spruce	Black alder	Aspen	Silver birch	Eucalyptus	Larch	Bagasse	Wheat straw
Butanol, kg/ton dry biomass	166.9	159.3	153.8	160.1	168.2	186.0	178.3	168.0	122.0
Isopropanol, kg/ton dry biomass	86.3	82.4	79.6	82.8	87.0	96.2	92.3	86.9	63.1
Etanol, kg/ton dry biomass	27.8	26.5	25.6	26.7	28.0	31.0	29.7	28.0	20.3
Metanol, kg/ton dry biomass	53.0	50.3	58.0	59.4	70.4	69.4	58.5	70.8	34.9
H_2, kg/ton dry biomass	10.0	9.5	11.0	11.2	13.3	13.1	11.0	13.4	6.6
CO_2, kg/ton dry biomass	279.3	265.6	292.0	300.3	345.5	350.3	305.3	347.1	189.4
LHV, MJ/kg dry biomass	10.0	9.6	9.4	9.8	10.5	11.4	10.7	10.5	7.2
LHV, % raw material	51.9	49.5	48.8	50.7	54.2	59.0	55.6	54.1	37.5
C material efficiency, %	85.4	86.2	84.8	84.3	82.0	81.7	84.1	81.9	90.1

Table 15
Potential yield of products from ABE mixture (Table 12), when butanol is dehydrated into dibutylether, ethanol into dethylether and acetone into isopropanol (through hydrogenation), followed by dehydration into propylene

ABE fermentation+ butanol→dibutylether; ethanol→diethylether, isopropanol→propylene	Domestic softwood (Finland)		Domestic hardwood (Finland)			Foreign trees		Non-wood biomass	
	Pine	Spruce	Black alder	Aspen	Silver birch	Eucalyptus	Larch	Bagasse	Wheat straw
Dibutylether, kg/ton dry biomass	146.6	139.9	135.1	140.6	147.8	163.4	156.7	147.6	107.1
Propylene, kg/ton dry biomass	60.4	57.7	55.7	58.0	60.9	67.4	64.6	60.9	44.2
Diethylether, kg/ton dry biomass	22.4	21.4	20.6	21.5	22.6	24.9	23.9	22.5	16.4
H2, kg/ton dry biomass	10.0	9.5	11.0	11.2	13.3	13.1	11.0	13.4	6.6
CO2, kg/ton dry biomass	279.3	265.6	292.0	300.3	345.5	350.3	305.3	347.1	189.4
LHV, MJ/kg dry biomass	10.3	9.8	9.7	10.0	10.7	11.7	11.0	10.7	7.4
LHV, % raw material	53.2	51.4	51.2	53.7	57.7	60.9	60.6	66.3	45.1
C material efficiency, %	81.6	82.5	80.6	80.1	76.9	76.8	79.9	76.8	87.6

Around 160 kg of ethers could be produced from 1 t of biomass through ABE fermentation, followed by dehydration into dibutylethers and diethylether. Due to the easy peroxide formation of the di-isopropylether, the dehydration of isopropanol into propylene is considered instead. A relatively small amount of propylene (around 50 kg) can be obtained from isopropanol dehydration. The C5 sugars are not deoxygenated fully to alkane-type product, but left at the MTHF stage, due to the undesirable high vapor pressure of pentane.

Also, when the sugars are hydrogenated to MTHF and C12 alkane, as shown in Table 15, a high amount of hydrogen is needed. The needed amount of hydrogen is however lower than that required for hydrogenating acetic acid into ethanol. In the case of pine, the hydrogen obtained through the gasification of lignin and extractives would be sufficient. The advantage is that part of the oxygen present in the biomass sugars can be removed by dehydration, when converting pentose sugars into furan and hexose sugars into HMF in the first step.

Digestion

The results calculated for sugar conversion into biogas (carbon dioxide and methane) are shown in Table 16. In Table 17, the upgrading of biogas into synthesis gas by steam reforming is considered. One possibility would be to combust non-degradable by digestion lignin and use the combustion heat to drive the steam reforming reaction of the synthesis gas. The reverse shift reaction conversion of hydrogen and carbon dioxide into water and carbon monoxide (the opposite of the shift gas reaction shown in Eq. 1) is not considered here. Due to the endothermic nature of the reverse shift gas reaction, the heat content of the product could be further increased. However, a very high temperature is needed to make the reaction thermodynamically feasible.

Table 17 shows that less than 200 kg of methane can be obtained from the digestion of pentose and hexose sugars. The energy content in the methane gas, however, is similar to that obtained with ethanol or ABE fermentation. For biogas, the separation from solution is easy, however.

By steam reforming, which is an endothermic process, the energy content in the gas could be increased to 59-77% of the raw material, as shown in Table 18. Synthesis can be viewed as a further process, according to a reaction shown in the subsequent upgrading reaction section.

Fuel properties and application of chemicals

The most important fuel properties of the different fuels here discussed are summarized in Table 19. A comparison is made between the properties of conventional fossil fuels and conventional biofuels, such as FAME (fatty acid methyl ester). The problem of both methanol and ethanol is their high water solubility and their corrosive nature. In addition, the vapor pressure of these components is high. Therefore, only low amounts of ethanol (up to 10 vol%) can be mixed, at a cold temperature. In addition, the energy content of these fuels is low, compared to gasoline, which leads to higher fuel consumption and wrong fuel–air ratio, if excessive amount of biofuel is mixed with gasoline in conventional cars. The octane numbers shown in Table 19 are however high. Other alcohols, such as butanol and propanol, are much more suitable to be used in a higher fraction in gasoline, due to their lower corrosiveness, vapor pressure and higher energy content. Ethers, such as ETBE, have been conventionally added to gasoline, to enhance clean burning. The dibutylether, diethylether and diethoxybutane have similar characteristics. These substances can be possibly blended in the existing diesel engines, to improve the cetane number of fossil diesel. However, the ethers tend to form peroxides, exposure to which may be dangerous. It should be studied whether these compounds can be safely used by adding antioxidant to the fuel mixture, for preventing peroxide formation. MTHF could be blended in larger volumes, up to 30%, in gasoline.[38]

FAME can be blended into fossil diesel fuels only in relatively low amounts (around 5%), if the mixture is used in conventional diesel engines. Possible problems refer to increased emissions and unfavorable cold properties. Below the cloud point, a part of the components present in the mixture get solidified, causing plugging of the fuel filters. The diesel range alkanes obtained through FT synthesis are similar to the components present in fossil diesel. They have very high cetane numbers, which makes them burn clean. Therefore, they can be blended into conventional diesel in very high fractions, or the diesel fuel can even be used without adding any fossil diesel. However, it is important to know that the product obtained from FT synthesis does not have sufficiently good properties. The heavy part needs to be hydrocracked to hydrocarbons with right chain length. In addition, alkanes solidify even at room temperature.

Therefore, they may be partially isomerized, to lower the cloudpoint of the mixture. Isomerization can be performed in an oil refinery, involving, nevertheless, losses, because a side reaction of isomerization assumes cracking of the diesel range hydrocarbon into smaller hydrocarbons.

DME and methane have favorable combustion properties. DME has a reasonably high cetane number and methane has a high octane number. The disadvantage refers to the storage and safety of these components. DME can be stored similarly to liquefied natural gas, requiring new infrastructure, fuel stations, etc. Methane, which cannot be liquefied at room temperature, needs to be stored under high pressure in tanks. The ether diethoxybutane and dibutylether have favorable cetane numbers. In addition, dibutylether has[39] very favorable cold properties (melting point -97.9 °C). The chemicals obtained as by-products and intermediates in biofuel production, including ethylene and propylene, appear as important raw materials for polyethylene and polypropylene. These chemicals are conventionally produced from oil or natural gas. Produced from biomass, they would have a much better carbon footprint and replace the use of oil. Ethyl acetate is commonly used as a solvent. Acetic acid is used not only in the food industry, but also as a chemical reagent.

Table 16
Potential yield of hydrocarbons and hydrogen demand
when pentose sugars are converted into MTHF and hexose into C12 alkane

Hydrogenation of C5 sugars→MTHF and C6 sugars→ C12 alkanes	Domestic softwood (Finland)		Domestic hardwood (Finland)			Foreign trees		Non-wood biomass	
	Pine	Spruce	Black alder	Aspen	Silver birch	Eucalyptus	Larch	Bagasse	Wheat straw
H_2 needed, kg/ton biomass	38.6	38.0	38.3	40.3	39.7	53.3	46.2	43.4	40.2
C12 alkane produced, kg/ton biomass	313.2	298.6	242.6	259.6	236.2	308.7	330.0	233.5	238.7
MTHF, kg/ton biomass	30.6	30.6	105.0	98.4	160.4	104.3	41.1	164.3	13.7
Total, kg/ton biomass	343.8	329.3	347.6	358.0	396.5	413.1	371.1	397.8	252.4
LHV, MJ/kg dry biomass	14.8	14.2	14.1	14.6	15.5	17.0	15.9	15.6	11.0
LHV, % raw material	76.6	74.3	74.4	78.1	83.5	88.4	87.2	96.1	66.7
C material efficiency, %	100	100	100	100	100	100	100	100	100

Table 17
Potential yield of biogas methane and carbon dioxide
when hexose and pentose sugars are digested into biogas

Digestion	Domestic softwood (Finland)		Domestic hardwood (Finland)			Foreign trees		Non-wood biomass	
	Pine	Spruce	Black alder	Aspen	Silver birch	Eucalyptus	Larch	Bagasse	Wheat straw
Methane, kg/ton biomass	180.7	172.6	175.9	181.8	198.0	210.0	194.1	198.2	131.0
CO_2, kg/ton biomass	684.7	651.7	522.5	559.3	507.3	664.2	720.1	500.8	512.8
LHV, MJ/kg dry biomass	9.0	8.6	8.8	9.1	9.9	10.5	9.7	9.9	6.5
LHV, % raw material	46.8	44.7	45.5	47.1	51.3	54.4	50.3	51.3	33.9
C material efficiency, %	64.3	66.1	70.9	67.0	70.8	68.3	59.7	69.5	67.6

Table 18
Potential yield of synthesis gas when the biogas obtained through digestion is converted into synthesis gas by steam reforming

Steam reforming of biogas	Domestic softwood (Finland)		Domestic hardwood (Finland)			Foreign trees		Non-wood biomass	
	Pine	Spruce	Black Alder	Aspen	Silver Birch	Eucalyptus	Larch	Bagasse	Wheat straw
CO, kg/ton biomass	315.4	301.4	307.0	317.3	345.6	366.6	338.9	346.0	228.7
H_2, kg/ton biomass	68.1	65.1	66.3	68.5	74.6	79.2	73.2	74.7	49.4
LHV, MJ/kg dry biomass	11.4	10.9	11.1	11.4	12.5	13.2	12.2	12.5	8.2
LHV, % raw material	58.9	57.0	58.5	61.2	66.9	68.9	67.1	77.1	50.1
C material efficiency, %	64.3	66.1	70.9	67.0	70.8	68.3	59.7	69.5	67.6

Table 19
Most important properties of different fuels
(*e.g.* vapor pressure, cetane or octane number, flashpoint, boiling point)

	Gasoline	Diesel	FAME	Methanol	Ethanol	DME dimethyl-ether	Parafic diesel, *e.g.* FT diesel	E85e	Dibutyl ether	Diethyl ether	Diethoxy-butane	n-butanol	Iso-propanol	MTHF[40]	Methane[41]
Formula	C4-C12	C12-C20	C19H34O2	CH_4O	C_2H_6O	C_2H_6O	Roughly C_{12}-C_{20}	~$C_{2.7}H_7O_{0.85}$	$C_8H_{18}O$	$C_4H_{10}O$	$C_8H_{18}O$	C_4H_9OH	C_3H_7OH	$C_5H_{10}O$	CH_4
Mol., wt g/MOL	100-105	~200	~294	32.04	46.07	46	170-280	~55	130	74	146.23	82	82.2	86.13	16.01
C/H/O, wt%	85-88/ 12-15	85-88/ 12-15	78/12/10	38/13/50	52/13/ 35			58/13/29	74/14/12	65/14/22					
Density, kg/m3	~750	~840	880	796	794	660	750-800	780	767	720				813	0.72
Boiling point, °C	30-190	170-340	300-340	64	78	24	180-360	30-190	141	35		118	82.3	80	-161
Octane number RON	95-98			122-133 (RON)	121-130 (RON)	-		100				94	~100	80	130
Cetane		>45	>50		8	55-60	80-110[42]		91-100	140	96.6	12	17		
Vapour pressure, kPa RVP, actual (blend kPa)	45-90c	<1		32 (210+)	16 (124)		<1	40-80				0.7 (at 20 °C)	4.4 (at 20 °C)	39	Super-critical
Flash point, °C	<0	>56	>100	7	13	-42	>56		25	-45	45	37	11.8	-11	-188
Heat value, MJ/kg	43	43	36	20	26	27.6-28.8	44-43	29.2	42.8		~34	33.11	30.15	32	50

CONCLUSIONS

According to the calculations, the highest amount of the original heat content in the products is retained in sugar hydrogenation and acetic acid fermentation. In the gasification of the whole feedstock biomass, also, a high amount of original heat content – up to 80% – could be converted into synthesis gas. When producing alcohols, such as isopropanol, more energy of the raw material could be retained in the products than when upgrading synthesis gas into alkanes. Therefore, it might be more feasible to convert synthesis gas into higher alcohols, such as propanol, butanol and their ethers. The alkanes produced by gasification cannot be used without isomerization as diesel or gasoline components. This further reduces the yield of the products. The pyrolysis of biomass and the gasification of only the most easily transported bio-oil convert a lower amount, around 50%, of the original biomass heat content into synthesis gas. On the other hand, in the pyrolysis stage, heat or by-products, such as charcoal, might be recovered.

In the case of acetic acid fermentation and chemical conversion of sugars, if all the needed hydrogen for upgrading cannot be produced by gasification of the lignin and extractives part of the biomass, the product heat content is misleading. According to the calculations made for pine, the necessary hydrogen could be produced through hydrogenation, when the sugars are upgraded through hydrogenation. For the hydrogenation of acetic acid into ethanol, slightly more hydrogen is needed than what can be obtained through the gasification of the lignin and extractives part of the biomass. For spruce, only approximately 50-60% of the needed hydrogen can be produced through the gasification of the biomass lignin and extractives. Therefore, fuel components that have favorable fuel properties, but do not need full oxygen removal, should be considered, such as, for example, dimehylfuran or methylfuran.[21] Alternatively, hydrogenolysis of sugars with hydrogen into ethylene glycol[20] and etherification of components, such as ethylene glycol with alcohols, might provide upgrading routes to high quality fuels needing less hydrogen than full hydrodeoxygenation.

In alcohol fermentation, the lowest amount of raw material heat content was converted into products. However, when alcohol fermentations were combined with gasification of lignin and extractives, only a slightly lower amount of energy was converted to products, as compared to the gasification of the entire biomass. It is also important to note that obtaining sugars as an intermediate product in the process enables the production of other types of valuable products, such as biopolymers and chemicals. The disadvantage of microbiological processes compared to thermochemical routes is the slow reaction. Therefore, larger reactor volumes are needed.

The digestion of biomass into biogas converts approximately an equal amount of raw material heat content into product, as compared to that converted by fermentation. In addition, the separation of the gas from the raw material is easy, compared to the separation of fermentation products from relatively dilute water solutions. Notably, the energy content of the biogas could be increased significantly by steam reforming, producing syngas in a simpler way than by gasification of solid biomass or pyrolysis oil. It could be a feasible alternative for the utilization of low-value, wet biomass.

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III

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Efficient Integration of Biofuel and Chemical Production Processes with Pulp Mills and Energy Production

Johan Kristian Melin*, Markku Hurme and Kari Parviainen

Aalto University School of Chemical Technology
P.O.Box 00076, 02015 Aalto, Finland, Kristian.Melin@aalto.fi

Biofuel production processes FT-diesel and ethanol fermentation combined with biogas and pellet production are analysed based on electricity consumption and minimum energy consumption obtained through Pinch analysis. Finally the efficiency of the integration of various processes with pulp mills and energy production is discussed. Ethanol production combined with biogas and pellet production converts a higher percentage of the biomass energy into products than FT-diesel production. Furthermore the integration of the ethanol process needing additional heat is easier that for the FT-diesel process which produces excess heat.

1. Introduction

Biofuels and chemicals made from lignocellulostic biomass can have significantly lower carbon footprint than corresponding fossil alternatives. The efficiencies of biomass refining depend both on the material and energy efficiency of technology and the efficient process integration. Usually part of the energy present in the raw material is lost as heat or converted into byproducts which significantly effects the feasibility of the production processes as well as the electric power need. Material yields and heat efficiencies were previously discussed (Melin and Hurme 2010). Another way to assess the efficiency of biofuel production is to study loss of exergy (maximum amount of work performed when system is brough to equilibrium with the surrounding.

Integration of biofuel production using excess heat in the pulp mill has been discussed previously (McKeough and Kurkela 2005). Pinch analysis gives the minimum utility consumption needed heating or cooling utilities for all temperature intervals. It is employed previously (Parisutkul and et al. 2009) for natural gas facility and synthetic natural gas production (Heyne 2010).

2. Methods

Two cases where calculated to illustrate efficiency of biomass utilization and process integration. Integration with a typical Nordic European integrated Kraft pulp mill is presented. The first case is Fischer-Tropsch -diesel production from spruce through atmospheric gasification using oxygen, low temperature FT-synthesis and hydrocracking of FT-Wax into FT-diesel and gasoline. The second case is: The

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production of cellulostic ethanol from spruce with biogas production from the distillation stillage and pellets from the water insoluble solids (lignin etc.).

2.1 Case 1: FT-diesel

Spruce with given composition and heating value (Melin and Hurme 2010) and 50 w-% moisture on total basis is dried to 15 w-% moisture on total basis. The biomass and enough oxygen preheated to 700°C is feed to gasifier operated at 800 °C and 1bar(a). Tars, methane and recycle gas from FT-synthesis with additional pre-heated oxygen is feed to the thermal reformer operated at 1163 °C producing clean synthesis gas. Both gasifier and reformer gas compositions are calculated with equilibrium models. The accuracy of such model is discussed previously (Melin and Hurme 2009). The reformer outlet the gas is cooled to 520 °C and the heat is used to generating superheated high pressure steam. Cooled reformer outlet gas and 1 bar (a) superheated steam at 300 °C obtained through biomass drying is feed to the shift reactor. A ratio of 1.7 between H_2/CO is obtained. The shifted synthesis gas is cooled to 40 °C and the pressure is increased to 20 bar by a 4 stage compressor with equal compression ratio and polytrophic efficiency of 80 % for each stage, cooling and liquid separation between each stage. Carbon dioxide is separated by absorption using a physical solvent such as Selexol regenerated by pressure reduction. FT reactor feed is heated to 200°C. In FT-reactor conversion of 0.85 and chain growth probability of (α =0.95) is assumed (Prins et al. 2004) .Outlet product is cooled to 40°C and condensed FT-Wax and Water is separated. The methane containing recycle gas is expanded in a turbine (efficiency 80 %) to 1 bar(a). A small purge stream avoids buildup of inerts in the system. The residual gas is heated to 700 °C and feed to the thermal reforming. The FT-Wax is hydrocracked in an oil refinery assuming reported yield of 85 w-% FT-diesel , 12 wt-% light gasoline range hydrocarbons (C5-C9) and 3 w-% gaseous hydrocarbons (C1-C4) (Calemma et al. 2010).A rough estimate indicates that that enough hydrogen for the hydrocracking step is obtained by steam reforming of the gaseous hydrocarbon stream.

2.2 Case 2: Lignocellulostic ethanol, biogas and pellet production

Product yields and utilities needed were calculated based on the reported data for the described process (Wingren et. al 2008) assuming that no pellets are used to generate the needed energy. Softwood with 50 w-% moisture on total basis is feed together with SO_2, LP steam and HP steam to the pre-treatment stage operated at 215 °C. Outlet product is flashed in two stages to recovered steam at 4 bar (a) and 1 bar(a) pressure. After cooling to 37 °C the mixture is feed to (SSF) Simultaneous Saccarification and Fermentation. The Water Insoluble Solid (WIS) content in the feed to SSF stage is 8.4 w-% and the distillation feed contains 3.8 w-% of ethanol. Fermented mixture containing the unhydrolysed material, biomass produced by the yeast, water and ethanol is separated by distillation. The SSF feed is split in half and LP steam is feed to the first feed stripper operated at 3 bar(a). The condenser of first feed stripper also boils the liquid in the second feed stripper operated at atmospheric pressure. The condenser in the second column also acts as a reboiler for a third vacuum column which concentrates the distillate from the first columns. Finally the ethanol is dried with molecular sieves to 99.5 w-%. WIS containing lignin, some carbohydrates and yeast are separated by centrifugation and dried to 85 w-% dry matter content and converted into pellets. The stillage from distillation is sent to anaerobic digestion for biogas production 50 % of chemical oxygen demand (COD) is removed at the anaerobic stage and the rest of the COD is removed in the final aerobic stage. Based on the data a case was calculated where no heat or electricity is produced. Instead the biogas and solids are obtained as by products. Externally produced steam and electricity are used.

3. Results

The Grand composite curve for the FT-case is shown in Figure 1. It can be seen that there is an excess of heat in all temperature intervals especially below 230 °C and no Pinch point exists. Amount and pressure of steam produced (HP steam 90 bar(a) 490 ºC), MP steam 12 bar(a) sat. steam and LP steam sat. 4 bar (a)) is shown. The flow of energy in biomass and utilities is shown in Figure 2. HP steam from the process is converted with a back pressure turbine (power output/heat output ratio 0.27 to electricity and low pressure steam. Additional Electricity is produced by combustion of additional biomass using condensing turbine with a power to heat output ratio of 0.45. For the FT -case only the synthesis gas compressor electricity consumption is considered. Totally around 51 % of the energy used as raw material for the synthesis and production of needed electricity ends up in the FT-diesel, light hydrocarbon fraction and purge gas.

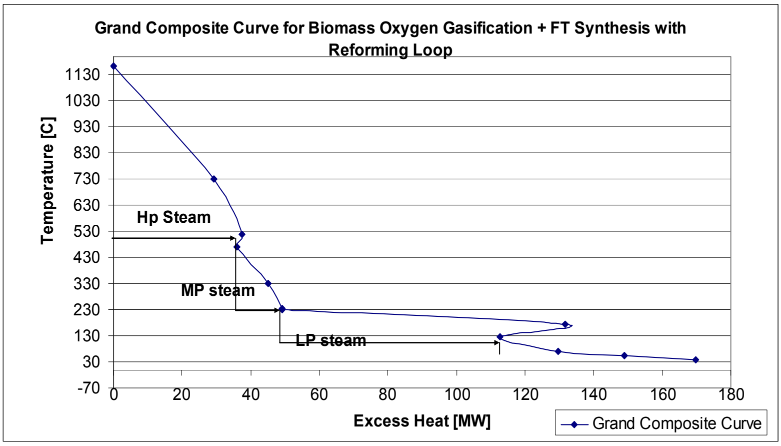

Figure 1 Grand Composite Curve for FT-synthesis. Temperature equals hot side temp. minimum temperature difference is 30 °C.

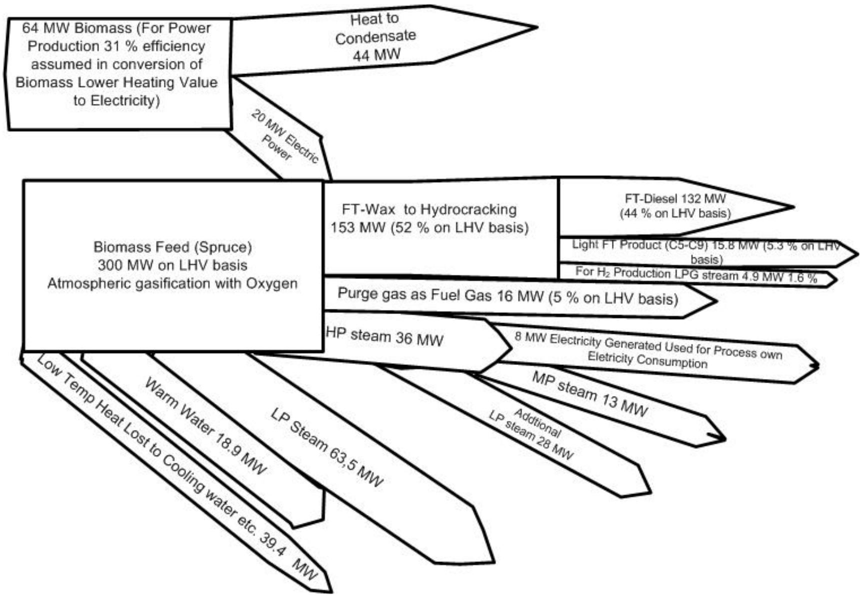

Figure 2 Energy flows of the products and utilities for FT-_synthesis case.

In the ethanol case shown in Figure 3 there is no Pinch Point. There is heat deficit in the whole temperature interval. The Steam utilities temperature levels, and amount needed are visualized in the grand composite curve. The energy flows are illustrated in Figure 4.

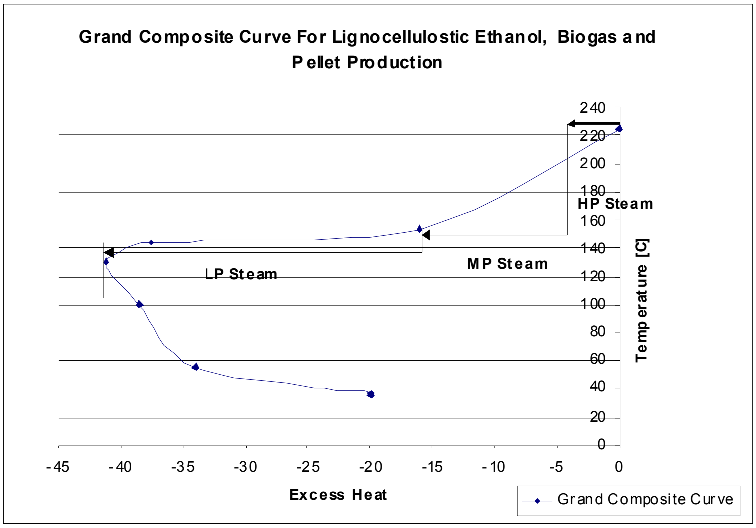

Figure 3 The Grand Composite Curve for the ethanol synthesis.

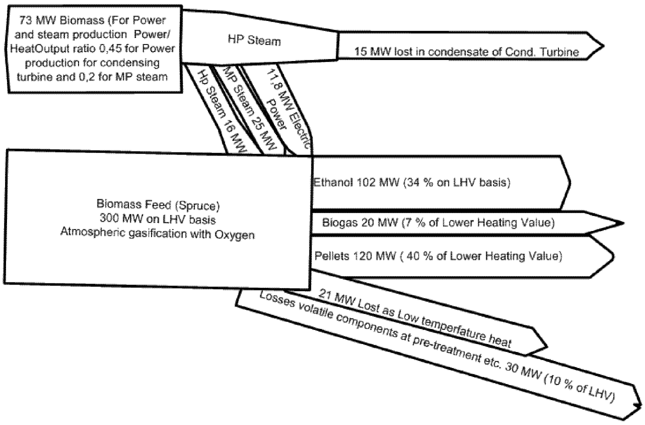

Figure 3: The heat flows illustrated for biomass and utilities.

Approximately 73 MW of additional biomass is needed shown in Figure 4 to supply the power and steam demand of the process. Due to small LP steam demand only HP and MP pressure steam is supplied to the process. Here only one high pressure level is assumed. The high pressure steam is feed through the back pressure turbine generating needed amount of MP steam with a power output/ heat output ratio of 0.20 and rest of the is feed to a condensing turbine with a power output to heat output ratio of 0.45. About 65 % of the energy content in the biomass and additional biomass 74 MW used for power and energy production can be found in the products ethanol, biogas and pellets.

Table 1: The heat and Power production calculated based on data by (Gullichen and Fogelholm 2000) for a typical Northern European Kraft Pulp Mill producing annually 600000 ton of air dried pulp with an annual operation of 8000 h. The plant is integrated to paper mill.

	Black Liq. Boiler	Bark Boiler	Pulp Mills Cons.	Paper Mill cons	Back Pressure Power	Cond. Power Production	Sold to Outside
GJ/Adt	18.0	4.2	9.0	6.5	4.4	2.3	
MW	375.0	87.5	187.5	135.4	91.7	47.9	0.0
KWh/Adt			550.0	650.0	1200.0	225.0	
MW			41.3	48.8	90.0	16.9	16.9

In Table 1 it can be concluded that normally there is no excess of LP steam in the pulp mill. About 17 MW of electricity is normally sold to outside. The amount of electricity produce could be increased if condensing turbine would be employed or a lower back pressure in the power generation. This could be done if MP and LP pressure steam produced in the biofuel process could replace steam made in the pulp mill process.

diesel case (42 %) when the electricity needed in the process is produced by combustion of biomass. Gas compression of the synthesis gas from atmospheric pressure to syngas consumes about 18 MW of electricity. Integrated combined cycle operation and pressurized gasification would significantly decrease electricity demand. FT-diesel plant integration with a pulp mill is not optimal in the case if when produced LP- steam cannot be used. For the 600 kt/a Pulp mill and 300 MW FT-plant LP steam can be used in the pulp mill when the bark boiler is not in use. For a smaller pulp mill or a non-integrated pulp mill there might be excess of low pressure steam.

The ethanol case combined with biogas and pellet production can utilize excess heat available in non-integrated mills. The integration is also easier since regardless of the size of the pulp mill and ethanol process the heat deficit can be replaced by combusting pellets to satisfy the energy balance. Utilizing available secondary heat and using a steam ejector to raise the pressure of MP- steam to the needed level could further increase the efficiency. In addition the purge gas in FT- case and the biogas from the ethanol process could most likely be used to substitute fossil fuel in the lime kiln.

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IV

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Performance of biofuel processes utilising separate lignin and carbohydrate processing

Kristian Melin [a,*], Thomas Kohl [b], Jukka Koskinen [a], Markku Hurme [a]

[a] Aalto University Finland, Department of Biotechnology and Chemical Technology, Kemistintie 1, FI 00076 Aalto, Finland
[b] Aalto University Finland, Department of Energy Technology, Finland

HIGHLIGHTS

- Separate conversion of lignocellulosic sugars and lignin to biofuels were studied.
- Several of the new processes provided better economy and a higher GHG reduction.
- Four of the processes form a Pareto curve between profitability and GHG savings.
- The new processes can utilize external low temperature heat with 100% efficiency.

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ABSTRACT

Novel biofuel pathways with increased product yields are evaluated against conventional lignocellulosic biofuel production processes: methanol or methane production via gasification and ethanol production via steam-explosion pre-treatment. The novel processes studied are ethanol production combined with methanol production by gasification, hydrocarbon fuel production with additional hydrogen produced from lignin residue gasification, methanol or methane synthesis using synthesis gas from lignin residue gasification and additional hydrogen obtained by aqueous phase reforming in synthesis gas production. The material and energy balances of the processes were calculated by Aspen flow sheet models and add on excel calculations applicable at the conceptual design stage to evaluate the pre-feasibility of the alternatives. The processes were compared using the following criteria: energy efficiency from biomass to products, primary energy efficiency, GHG reduction potential and economy (expressed as net present value: NPV). Several novel biorefinery concepts gave higher energy yields, GHG reduction potential and NPV.

1. Introduction

Biofuels can be produced from either first- or second-generation sources by various processes, as reviewed by Naik et al. (2010). The second-generation biofuels produced, e.g. from wood and straw have many advantages compared to first-generation biofuels made from food-related resources: here there is no competition with food production, the greenhouse gas emissions are potentially lower, and less land area is required due to the higher yields of the biomass per cultivated area (Kajaste, 2014). However, the investment costs of the second-generation processes are typically higher, although the lignocellulosic feedstocks are less expensive than first-generation feedstocks. The technological risk of second-generation routes is also higher since the processes are less mature: for example, no full-scale synthetic liquid fuel plants based on biomass gasification have yet been built.

Because of the large number of feedstocks and process alternatives available and the high investment cost involved, the wise selection of process concept is a key challenge. The concept selection is complicated, not only by the large number of alternatives but also by the lack of knowledge available in the early design stages of a project. This is sometimes called 'the design paradox' (Hurme and Rahman, 2005), because the route selection needs to be made at the early stage of design without full knowledge of the process, yet in later stages, when there would be much more knowledge about the process to make the

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* Corresponding author.
E-mail addresses: Kristian.Melin@aalto.fi (K. Melin), Thomas.Kohl@aalto.fi (T. Kohl), Jukka.Koskinen@aalto.fi (J. Koskinen), Markku.Hurme@iki.fi (M. Hurme).

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selections, as changes in design are much more costly or even impossible as far as the process concept is concerned. Therefore, it is essential to be able to make wise conceptual design decisions as early as possible and concentrate efforts on the one with the most potential.

Many researchers such as (Cherubini and Stroemmaner, 2010) and (Voll and Marquardt, 2012) have evaluated biorefining routes by considering yield and income from products, for example. Melin and Hurme (2010) compared production routes in terms of maximum energy yield from raw materials to products. They found out that methanol, synthetic natural gas (SNG) and dimethyl ether (DME) can be produced with high selectivity and with a higher yield compared to Fischer–Tropsch diesel. Economic studies of gasification-based biofuel production processes have been done by determining production costs, see Hannula and Kurkela (2013). Forest residues based pyrolysis processes were analysed by Wright et al. (2010) and bioethanol production by Gnansounou and Dauriat (2010) and Sassner and Zacci (2008). In an earlier study, McKeogh and Kurkela (2008) found that an optimal size of a gasification-based biofuel plant is around 200–300 MW feed for forest residues in Finland. The heat integration in lignocellulosic ethanol concepts from wheat straw has been studied by Lassmann et al. (2014) using Pinch analysis.

The economy of biorefining can be improved e.g. by increasing product yields. These are limited by various factors. According to Prins et al. (2007) and Ptasinski et al. (2007) in the gasification of wood or other oxygen-containing feedstocks the biomass needs to be over oxidised in order to reach the gasification temperature, which results in production of carbon dioxide. This reduces the conversion efficiency to products. A higher yield would be obtained if a material with higher energy content would be gasified. So by gasifying lignin rich residue instead of wood a higher yield is expected. So converting the sugars part first for example into ethanol with low energy loss at low temperature and gasifying the lignin residue has a synergistic effect that should result in a high conversion efficiency to fuel product.

Another aspect is whether all the biomass fractions are actually utilised for the product desired. For example, when biomass is hydrolysed to sugars and those are converted into e.g. ethanol, theoretically not more than 35–51% of the energy present in the biomass can be converted to energy in the ethanol product if the hexose fermentation is used, as stated in Melin and Hurme (2010). Thus, combining lignin residue gasification with the conversion of sugars would result in a higher yield route to biofuels. The gasification been demonstrated for lignin from wood residue (Koido et al., 2013) and for corncob hydrolysis residue (Chen et al., 2015). Only a few studies exist on the routes combining lignin residue gasification with ethanol fermentation: for instance, Laser et al. (2009) evaluated combined ethanol production and synthetic fuel production from switchgrass by gasification of the lignin residue. For ethanol production Ammonia Fibre Explosion (AFEX) pre-treatment was used. A high-energy yield of biofuel was obtained. Also, chemical conversion to sugars by aqueous phase reforming or aqueous phase hydrogenation has been studied by Wei et al. (2014) and Zhang et al. (2014). However, no studies of combined aqueous phase reforming and lignin residue gasification for hydrogen production were found in the open literature.

In this paper, novel biofuel production pathways based on separate lignin and sugar processing are evaluated: both the fermentation of sugars to ethanol and chemical conversion by aqueous phase reforming and hydrogenation are studied and compared with conventional processes, which do not include lignin processing. The evaluation is based on the flow sheet simulation employed in the conceptual design phase.

2. Methods

2.1. Raw materials

In all cases, the raw material is softwood (pine) logging residue. The element and chemical species composition, heating values and moisture content of the feedstock are presented in Table 1. The reference state is 25 °C and 101 kPa. The sugar composition refers to the content of sugars in the non-hydrolysed form.

2.2. Process concepts studied

In this study the following biomass based process concepts are studied using process flow sheet model:

- MeOH case: Conventional methanol production by gasification and conversion of synthesis gas to methanol.
- SNG case: Conventional synthetic natural gas production by gasification and conversion of synthesis gas to methane.
- ETOH case: Conventional bioethanol production by steam explosion pre-treatment and heat and power production by combustion of residual lignin.
- ETOH&MEOH case: Enhanced ethanol and methanol production from biomass by steam explosion pre-treatment and conversion of residual lignin to syngas and methanol.
- ENHMEOH case: Novel enhanced methanol production by one-step biomass conversion to sugars, hydrogen production from sugars by aqueous phase reforming and residual lignin gasification with methanol production from hydrogen-enriched syngas.
- ENHSNG case: Novel enhanced methane production by one-step conversion to sugars for hydrogen production from sugars by aqueous phase reforming and residual lignin gasification with methane production from hydrogen enriched syngas.
- ENHHC case: Hydrocarbon production by aqueous phase hydrogenation of biomass based sugars by hydrogen obtained from gasification of lignin residues.

The MEOH, SNG and ETOH cases are conventional lignocellulosic biorefinery processes which are compared with the enhanced processes, ETOH&MEOH, ENHMEOH, ENHSNG and ENNHC; the material and energy balances are calculated for the same raw material in all of the processes. Based on the material and energy balances, the efficiencies of the processes are calculated. In addition, the carbon footprint and economic feasibility of the processes are studied based on the material and energy balances, additional investment cost and green house gas emission data. The processes ETOH&MEOH, ENHMEOH, ENHSNG and ENHHC are chosen because they are expected to give a higher yield and possibly a higher economic and environmental performance.

Two sub-cases, A and B, are considered in ETOH&MEOH, ENHMEOH, ENHSNG and ENHHC. In sub-case A, the process is adjusted so it is self-sufficient on process heat.

For example as reported for a similar case than ETOH&MEOH the heat demand of the process can be satisfied with extra fuel (coal or wood) input to a boiler that produces heat and power needed in the bioethanol process (Halladay et al., 2007). In case B, the deficiency of low temperature heat used for drying, distillation and acid gas medium regeneration is replaced by transferring heat from a nearby plant. This increases the biofuel yield since the product is not combusted in order to satisfy the process heat demand. The inputs and outputs to the processes are shown in Fig. 1. Here all the heat is used in the process, no district heat is exported and power production is maximised. Only in the ETOH and ETOH&MEOH cases, a relatively small amount of furfural is obtained. It can also be converted into a fuel product but it is not

Table 1
Properties of the pine feedstock.

	Carbon	Hydrogen	Oxygen	Nitrogen	Sulphur	Ash	References
Ultimate composition wt%	52.34	6.09	41.19	0.08	0.01	0.74	Nurmi (2000)
Chemical species	Extractives and others	Glucan	Mannan	Galactan	Xylan	lignin	
wt%	4.0	42.4	11.8	1.9	4.7	27.0	Melin and Hurme (2010)
	Higher	Lower	Moisture content as received on total basis wt%				
Heating values MJ/kg based on dry weight	20.6	19.3	50				Melin and Hurme (2010)

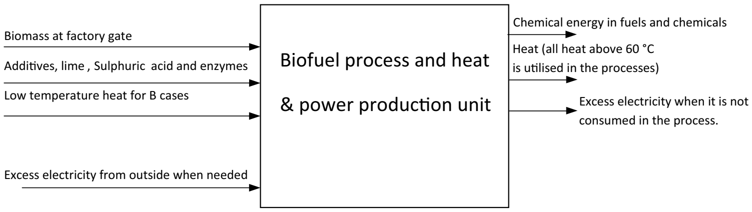

Fig. 1. The inputs and outputs from the processes considered here as well as the boundary of the calculations.

done here because an additional process step would be needed which and furfural could be sold on as a feedstock for chemicals production. The ETOH&MEOH, ENHMEOH, ENHSNG and ENHHC processes are enhanced cases which were compared with the traditional MEOH, SNG and ETOH cases.

2.3. Simulation models and assumptions

The processes of each case are briefly described in the following and the assumptions in modelling are discussed.

2.3.1. MEOH case: Methanol production from pine

Biomass is first chipped and dried at the mill (see Fig. 2). The moisture content is reduced from 50 wt% to 13 wt%. Biomass is then gasified at 800 °C and 1 MPa together with steam and oxygen. Oxygen is produced in an ASU (air separation unit) from air, requiring electricity for compression. After the gasifier ash has been filtered, more steam is fed to prevent carbon formation. Next, the mixture is fed to a reformer with additional oxygen to increase the temperature to 950 °C and to convert the tar components and methane into carbon monoxide and hydrogen by steam, according to Eq. (1).

$$CH_4 + H_2O \leftrightarrow CO + 3H_2 \tag{1}$$

Subsequently, the gas is cooled to 300 °C and fed to a shift reactor where the H_2/CO ratio is adjusted to approx. 2.1 which is suitable for methanol synthesis. Then the gas is cooled down to 25 °C and acid gases H_2S, COS and most of the carbon dioxide are removed by scrubbing with Selexol, which is a physical solvent. In the Acid Gas Absorber Regenerator (AAAR), the solvent is regenerated by using low-pressure steam. After the acid gas removal, a low level of hydrogen sulphide remains in the gas which is removed in a zinc oxide bed, as reviewed by Cheah et al. (2009).

The purified synthesis gas is compressed to 6.1 MPa by a two-stage compressor to the methanol synthesis where the synthesis gas reacts according to Eqs. (2) and (3).

$$CO + 2H_2 \leftrightarrow CH_3OH \tag{2}$$

$$CO_2 + 3H_2 \leftrightarrow CH_3OH + H_2O \tag{3}$$

After the methanol reactor, the gas is cooled to 25 °C in order to separate the methanol at the reactor pressure. The unreacted gas is recycled back to the reactor by circulation gas compressor. A small purge stream is taken out to avoid build-up of inerts. The condensed methanol water mixture is sent to methanol distillation where the methanol is purified to a purity of at least 99 wt%. The non-condensables are sent to combustion.

2.3.2. SNG case: Synthetic natural gas production from pine

The process is similar as the MEOH case, except for the synthesis section and product separation (see Fig. 2). The reformer uses a catalyst which catalyses not only tar but also methane decomposition. A higher ratio of H_2/CO of approx. 3.1 is required for the methane synthesis occurring at 31 bar according to Eqs. (4) and (5).

$$CO + 3H_2 \leftrightarrow CH_4 + H_2O \tag{4}$$

$$CO + 4H_2 \leftrightarrow CH_4 + 2H_2O \tag{5}$$

In the synthesis reactor there are 5 catalytic beds. The temperature is kept between 300 and 600 °C by cooling the reaction mixture after each stage, in a heat exchanger. Finally, the gas is cooled down to 25 °C and water is separated by condensation. The gas is compressed to 6 MPa and dried with tetra ethylene glycol.

2.3.3. ETOH case: Bioethanol production from pine with combined heat and power steam production

In case 3, pine chips, SO_2 and steam are fed to the steam explosion stage at 205 °C during 5 min (see Fig. 2). In steam recovery, the product is flashed to 0.5 MPa and the vapour is condensed to recover furfural and water condensate. After the recovery, the liquid is cooled and is sent together with additional water to simultaneous fermentation and saccharification (SSF) at $\geqslant 40$ °C up to 72 h, operated at 20 wt% solid consistency. The saccharification of hexoses and pentoses is represented by Eqs. (6) and (7) and the fermentation of hexoses and pentoses sugars into ethanol by Eqs. (8) and (9).

$$C_6H_{10}O_5 + H_2O \rightarrow C_6H_{12}O_6 \tag{6}$$

$$C_5H_8O_4 + H_2O \rightarrow C_5H_{10}O_5 \tag{7}$$

$$C_6H_{12}O_6 \rightarrow 2CO_2 + 2C_2H_5OH \quad (8)$$

$$2C_5H_{10}O_5 \rightarrow 3CO_2 + 3C_2H_5OH \quad (9)$$

Next, the fermented mixture is split in half and sent to a high-pressure column at 3.5 bar and atmospheric column at 1.3 bar. In the columns the ethanol is separated from the fermentation broth and the concentrated ethanol water mixture is sent further to the product column. Multiple columns achieve a more energy efficient separation of alcohol from water where the condenser of the column with the highest pressure acts as a reboiler for the column at 1.3 bar, as described by Sassner and Zacchi (2008). In final drying, the mixture from the product column is dehydrated to approximately 99 wt% purity with a molecular sieve.

The bottom product from high- and low-pressure column still contains unhydrolysed fibres and unfermented sugars. Next, the fibre part is separated by mechanical dewatering and the liquid is sent to evaporation which employs six stages. The furfural- and hydroxymethylfurfural-containing condensate is also sent to evaporation. The solids and the strong evaporated liquid from the evaporator are used as a fuel in the biofuel boiler. The high-pressure steam is used for cogenerating steam and power for the bioethanol plant. Any excess power is sold.

Fig. 2 The ETOH case is illustrated as a block diagram.

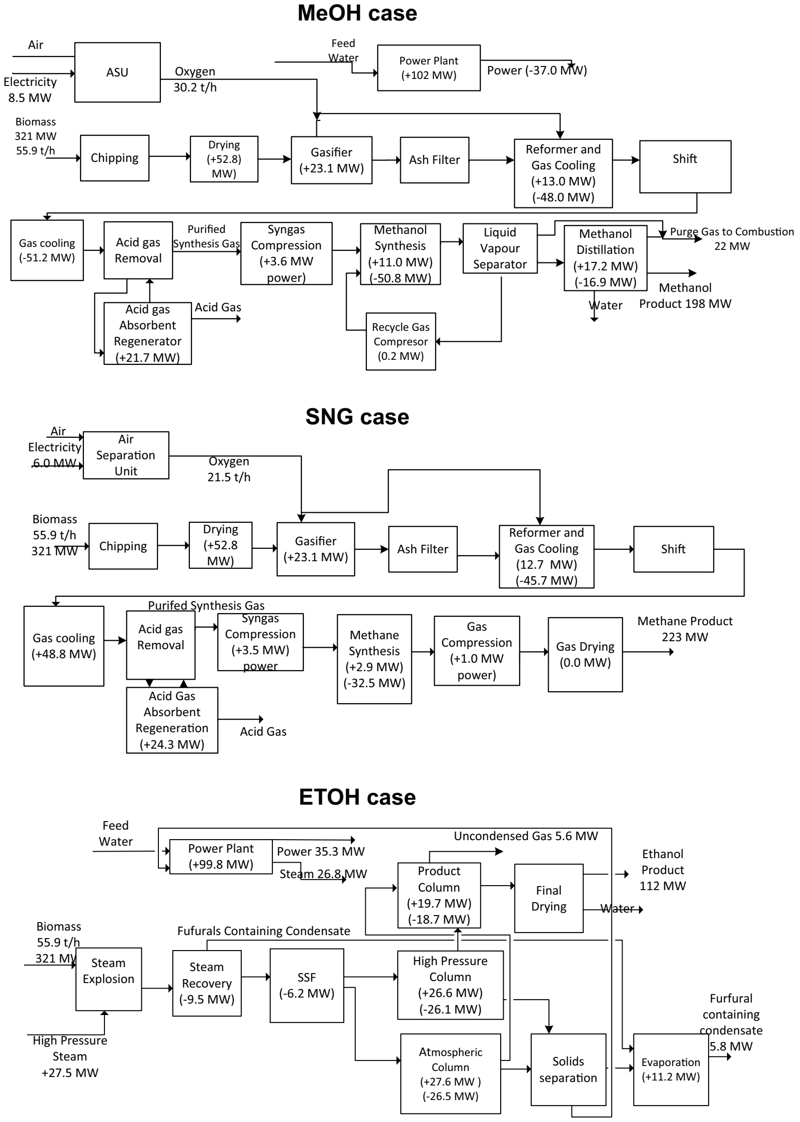

Fig. 2. Block diagrams including material and energy balance information (not complete) of the following cases: MEOH, SNG, ETOH&MEOH, ENHMEOH, ENHSNG, ENHHC. Heat and Power input (+) and output (−) for main blocks. Biomass and products energy content shown based on dry higher heating value basis.

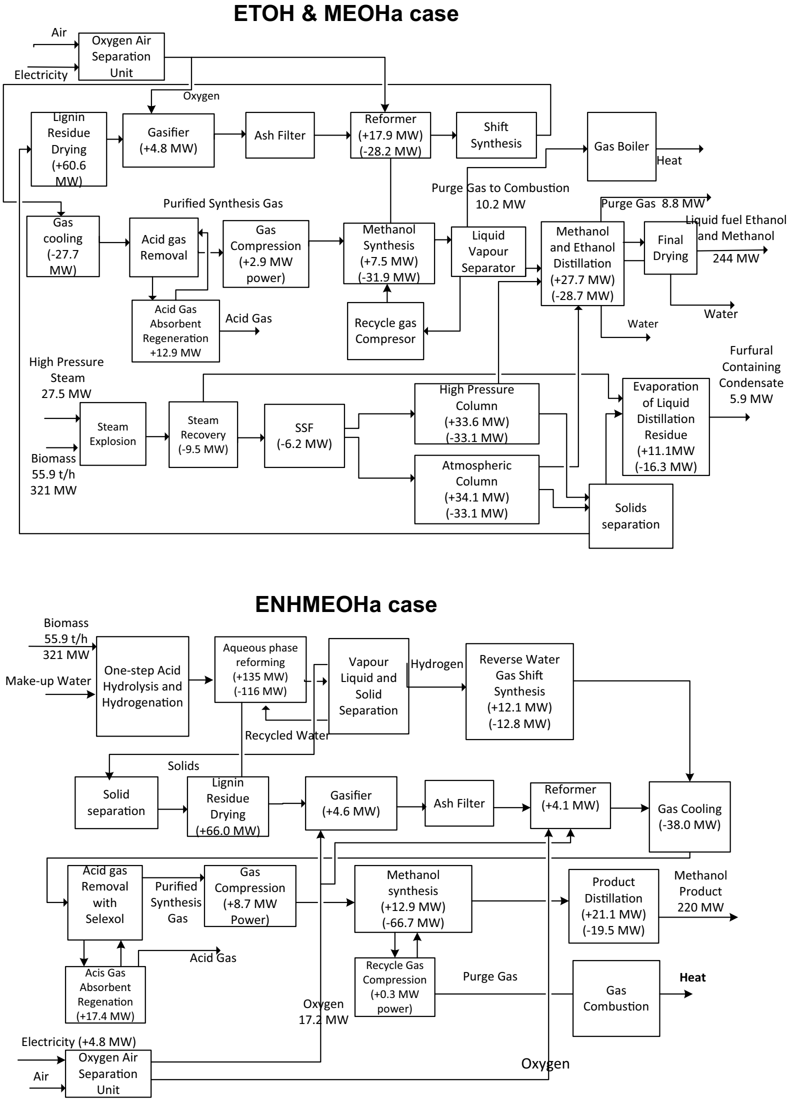

Fig. 2 (*continued*)

2.3.4. ETOH&MEOH case: Combined ethanol and syngas based methanol production from pine

In this process, ethanol is fermented from hydrolysed biomass and the lignin and other residues are converted to methanol via syngas (see Fig. 2). The process is similar to the ETOH case, except for the treatment of the lignin and residual liquid after fermentation. The concentrated liquid remaining from the evaporation and lignin residue is sent to lignin drying and dried with a belt dryer to 13 wt% moisture. Then, the dried residues are fed to a gasifier. The methanol plant is similar to the one described in the MEOH case, except that the capacity is significantly smaller. The production of methanol takes place according to Eqs. (2) and (3). The methanol and ethanol are distilled finally in the same column at 20–30 kPa.

2.3.5. ENHMEOH case: Methanol production from pine with aqueous phase reforming of sugars and lignin gasification

Pine biomass is fed to combined hydrolysis and hydrogenation step together with an acid catalyst at 160°and 50 bar in the presence of heteropolyacids with an Ru catalyst, according to Palkovits et al. (2010) (see Fig. 2). The biomass is hydrolysed (Eqs. (6) and (7)) to sugars (glucose, mannose, xylose) which are simultaneously hydrogenated to sugar alcohols (Eqs. 10–13). The advantage of simultaneous hydrolysis and hydrogenation is the higher stability of sugar alcohols. Therefore, the further degradation reactions are avoided compared to traditional sugar hydrolysis.

$$C_6H_{12}O_6 + H_2 \rightarrow C_6H_{14}O_6 \qquad (10)$$

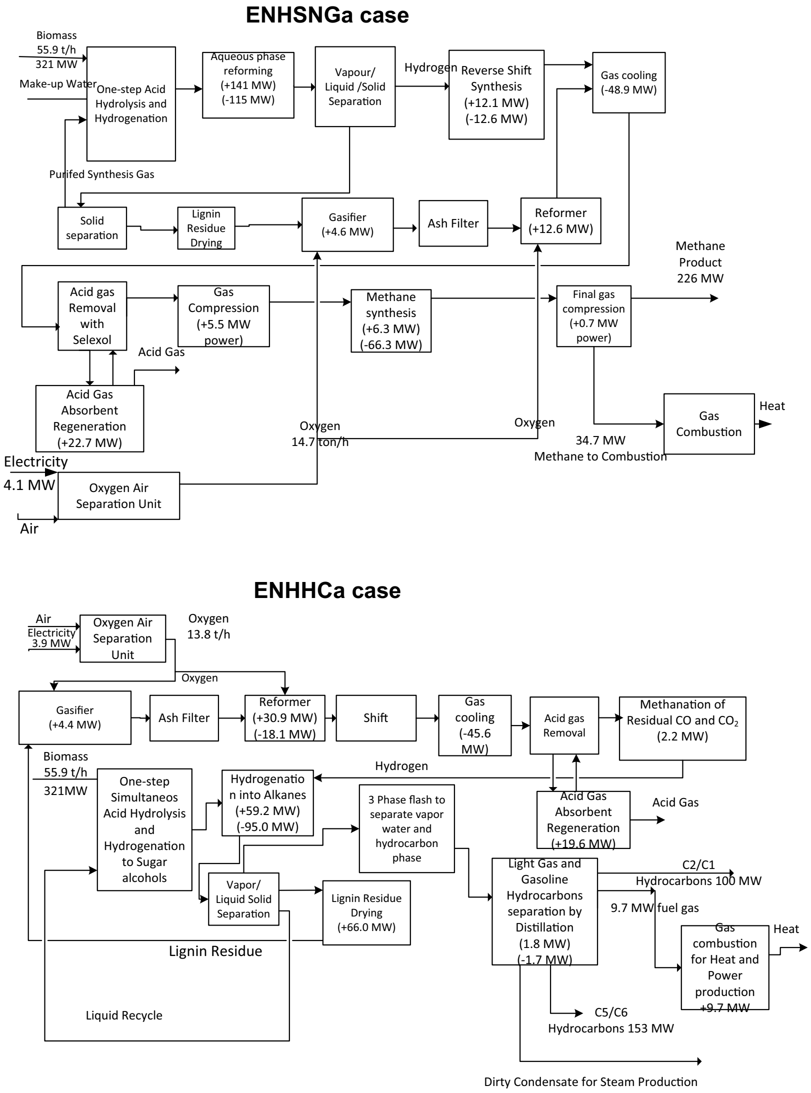

Fig. 2 (*continued*)

$$C_5H_{10}O_5 + H_2 \rightarrow C_5H_{12}O_5 \tag{11}$$

$$C_6H_{12}O_6 + 3H_2 \rightarrow 3C_2H_6O_2 \tag{12}$$

$$2C_5H_{10}O_5 + 5H_2 \rightarrow 5C_2H_6O_2 \tag{13}$$

Subsequently, the sugars and alcohols are reformed by aqueous phase to hydrogen, according to Eq. (14).

$$C_xH_{2x}O_x + xH_2O \rightarrow 2xH_2 + xCO_2 \tag{14}$$

where x is the number of carbon atoms in sugar alcohol molecule. In this case, x is 6, 5 and 2. The aqueous phase reforming reactor operates at 240 °C instead of the 250 °C reported by Meryemoglu et al. (2010) and 6 MPa to avoid excess evaporation of water. After aqueous phase reforming, the gas phase is separated from the solid and liquid in a phase separator. Subsequently, the gas phase is cooled and the condensed liquid is combined with the liquid separated earlier. Solid lignin residue is separated from the liquid by mechanical dewatering and dried to 13 wt% moisture content with a belt dryer. The specific heat consumption for the dryer is estimated to be 4 MJ/kg of evaporated water (Fagernäs et al., 2010). The solids are gasified similarly to the MEOH case. The gas containing hydrogen and carbon dioxide from aqueous phase reforming is heated to 490 °C and sent to a reverse shift reactor where the ratio H_2/CO is adjusted, according to Eq. (15).

$$H_2 + CO_2 \leftrightarrow CO + H_2O \tag{15}$$

In this case, some of the hydrogen and carbon dioxide is consumed and carbon monoxide is generated so that the mixed gas from the reformer and the outlet gas from the reverse water gas shift reaction are mixed to have the desired H_2/CO ratio. The subsequent syngas purification and methanol synthesis are identical to the MEOH case, except that the amount of carbon monoxide and hydrogen is higher than in the MEOH case, so more methanol is obtained.

2.3.6. SNG case: Production from pine with aqueous phase reforming of sugars

The ENHSNG case is identical to the ENHMEOH case except that methane is produced from the synthesis gas, instead of methanol (see Fig. 2). The methane production was described in the SNG case. In this case, the yield of carbon monoxide and hydrogen is also higher than in the SNG case.

2.3.7. ENHHC case: Hydrocarbon production from pine with aqueous phase hydrogenation with hydrogen produced by gasification of lignin residue

The carbohydrate part of the biomass is hydrogenated into sugar alcohols as in the ENHMEOH and ENHSNG cases. The sugars are hydrogenated into alkanes by aqueous phase hydrogenation, according to Eqs. (16) and (17) (see Fig. 2). Make-up and recycled water are fed to the process together with the biomass. The hydrogen required is obtained through the gasification of the lignin residue and further conversion of the synthesis gas. A product distribution in hydrogenation according to Zhang et al. (2014) is assumed.

$$C_xH_{2x}O_x + (x+1)H_2 \rightarrow C_xH_{2x+2} + xH_2O \qquad (16)$$

$$C_xH_{2x+2} + (x+1-y+1)H_2 \rightarrow (y/x)C_yH_{2y+2} \qquad (17)$$

Next, the outlet product is sent to 1st vapour/liquid separator where the evaporated water and the hydrocarbons are separated in the vapour phase and sent further to a three-phase flash to separate the gas, liquid hydrocarbons and water. In hydrocarbon distillation light hydrocarbons (methane and ethane) are separated from the heavier hydrocarbons (pentane and hexane).

The liquid part from the 1st separation consisting of water and unhydrolysed fibres is sent to liquid–solid separation and the liquid is mainly recycled back to the process in order to keep the solid concentration around 10 wt% in simultaneous acid hydrolysis and hydrogenation. From the purge water, the unhydrolysed fibres are separated by mechanical dewatering. The remaining dirty water can be vaporised as steam in the synthesis gas production. The solids are dried in a belt dryer using hot air heated with hot water. This lignin residue is sent to a gasifier as in the SNG case. To enhance the hydrogen production, more steam is fed to the shift reactor so that a high H_2/CO ratio is obtained. The gas is treated as described earlier. After cleaning the gas, the purified hydrogen-rich gas is fed to CO and CO_2 is methanated. This technology was employed earlier in hydrogen production plants. This way, the separation of hydrogen from CO by membrane is superfluous.

2.4. Methods for process analysis and evaluation

2.4.1. Material and energy balances

The material and energy balances were calculated for each case using the Aspen Plus simulation program with an add-on calculation in Excel. The simulated energy balances were checked by calculating energy inputs and outputs in the following way: the input was chemical energy by a higher heating value of the feedstock and heat above 25 °C or electricity to the process. The output was all products with a higher heating value and the residual heat after subtracting the heating demand for the process. The error in energy balance was found to be less than 2% in all the cases. In order to satisfy the energy balance, it was found necessary to use the heating values back- calculated from the heat of formation for the components in Aspen.

2.4.2. Heat and power demands

The heat integration was made based on maximum heat recovery; i.e. minimum heating and cooling demand. For this purpose, the heating and cooling demands were summed to construct a grand composite curve to check whether there was an excess or deficit of heat in the process at each temperature interval. If there was a deficit of heat, it was assumed that some of the product had been combusted with an efficiency of 89% by higher heating value in order to satisfy the heat demand.

If there was excess heat in the process, it was used for generating steam at 85.5 bar and 510 °C which was used for cogenerating heat and power. Middle- and low-pressure steam and hot water were generated and fed to the process. The temperature levels were 200 °C, 150 °C, 90 °C and 65 °C. The power production was estimated by assuming a turbine efficiency of 89%.

Lignin drying, in particular, requires lot of energy. In this work, the lignin is assumed to contain approximately 34 wt% of solids after mechanical dewatering. The lignin residue is dried in a belt dryer, utilizing heat above 65 °C. The specific heat consumption is of 4 MJ/kg water evaporated (Fagernäs et al., 2010).

The electricity consumption in the process was estimated by summing the power consumptions of compressors and pumps The power consumption in oxygen production was assumed to be 280 kWh/t for pure oxygen, the value of which is somewhat higher compared to 245 kWh/t stated by Hong et al. (2009), because the oxygen required must have higher than 95% purity.

2.4.3. Efficiency indicators

2.4.3.1. Energy yield. Efficiency to fuels by lower (LHV) or higher heating value (HHV) is presented by Eq. (18). In this work, both the lower and higher heating value efficiency are calculated.

$$\eta = (E_{\text{gas,fuel}} + E_{\text{liq,fuel}} + E_{\text{chem,prod}} + E_{\text{elec,output}})/(E_{\text{biomass}} + E_{\text{ext,heat}} + E_{\text{elec,input}}) \qquad (18)$$

where η is the efficiency to fuels and chemicals by LHV or HHV at 25 °C and 101 kPa.

$E_{\text{gas, fuel}}$ is the energy of gaseous fuel by the corresponding heating value.

$E_{\text{liq,fuel}}$ is the energy content of liquid fuel in MW.

$E_{\text{chem,prod}}$ energy of furfural by corresponding heating value for the ETOH and ETOH&MEOH cases.

$E_{\text{elect,output}}$ is the excess electricity obtained as byproduct if all produced electricity is not used. E_{biomass} is the corresponding energy of the feedstock for the corresponding heating value. $E_{\text{ext, heat}}$ is the energy of eternal low temperature heat feed to the process in B cases for the corresponding heating value. $E_{\text{elec,input}}$ is the input of external electricity to the process if the produced amount is not sufficient.

2.4.3.2. Primary energy efficiency. Different types of energy and fuel streams have different "values" in terms of their energy usability. For example, heat and power cannot be directly compared by energy value. Also, heat inputs, produced from different fuels such as wood or gas, have different conversion efficiencies. One possibility to account for the different forms of energy is to use the primary energy approach. In this case, the process boundaries are widened so that all the energy input used in the generation process is retraced to its primary sources and all energy needed to deliver the final energy product is expressed in terms of total primary energy consumption, according to Kohl et al. (2014).

The primary energy efficiency was calculated according to Eq. (19).

$$\eta_P = (E_{\mathrm{fuel,tot}})/(p_{\mathrm{biomass}}E_{\mathrm{biomass}} + p_{\mathrm{elect}}E_{\mathrm{elect}} + p_{\mathrm{sec,het}}E_{\mathrm{sec\ heat}}) \quad (19)$$

where

η_p is the primary energy efficiency.

$E_{\mathrm{fuel,\ tot}}$ is the total amount of fuel produced in each process including both liquid and gaseous fuel on a higher heating value basis.

E_{elect} is the amount of electricity needed (negative if excess electricity is produced as byproduct).

$E_{\mathrm{sec\ heat}}$ refers to secondary heat feed from an integrated process.

p_x is the primary energy factor, which is the inverse of energy efficiency by a higher heating value when a particular input is produced from primary fuel.

The primary energy factors used are the following: The primary energy factor for electricity is 3.11 (Dones et al., 2007), for biomass 1.1 European committee for standardisation (2008) and for Secondary heat from a process 1.05 Euroheat & Power (2006).

2.4.3.3. Greenhouse gas emission calculation. The fact that the greenhouse gas emissions produced during the life cycle of biofuel use are lower compared to fossil fuel is a key reason for the production of biofuels. Therefore, greenhouse gas emissions are a key performance criterion. According to sustainability criteria in the EU (2015), it is required that biofuels offer a reduction in life cycle greenhouse gas emissions of at least 35% compared to fossil fuel. In 2017, this figure will rise to 50%, and in 2018 to 60% in respect of plants that are commissioned after 1 January 2017. It is important to know that the unfavorable economics of lignocellulosic biofuel processes can be improved by co-feeding fossil inputs, for example, coal or natural gas to the extent that the sustainability criteria are fulfilled. Also, how much it is feasible to pay extra for using biofuels should also depend on the savings gained in greenhouse gas emissions. The purpose of greenhouse gas (GHG) reduction calculation is to study the effect of the process routes and the various inputs on greenhouse gas reduction when 1 MJ of product substitutes for 1 MJ of petrol. Here the greenhouse gas emissions are calculated as equivalents of carbon dioxide. For example, methane emissions are transformed to equivalents of carbon dioxide by the GWP factor, according to Biograce (2015) for each substance which compares the relative greenhouse gas potential of each compound to carbon dioxide. The actual greenhouse gas reduction is a complex issue that depends on the time horizon and land use change studied, for example, studied by Soimakallio (2012). However, the effect of the process route on greenhouse gas emissions is much more straightforward. In this case, the equivalent GHG emissions were compared to petrol according to the values based on Eq. (20) (BioGrace, 2015) on an LHV basis. The equivalent carbon dioxide emissions for each item are shown in Table 2.

Table 2
Inputs for carbon footprint calculation.

Item	Value	Unit	Ref
Wood raw material	3.89	g CO_2 eq./MJ	European committee for standardisation (2008)
Electricity	129.2	g CO_2 eq./MJ	Biograce (2015)
SO_2	268.8	g CO_2 eq./kg	*Biograce (2015)
Ammonia	2554.7	g CO_2 eq./kg	Biograce (2015)
Added low temperature heat	4.37	g CO_2 eq./MJ	**
Petrol	92.33	g CO_2 eq./MJ	Biograce (2015)

The contribution of GHG emissions is assumed to be negligible for water make-up, make-up triethylene glycol and enzymes.

$$\mathrm{GHG}_{\mathrm{reduction}} = [1 - (\mathrm{GHG}_{\mathrm{biofuel}})/(\mathrm{GHG}_{\mathrm{substfuel}})] \quad (20)$$

(*) SO2 not found in Biograce (2015) therefore an equal value to H_2SO4 is assumed. (**) It is assumed that the secondary heat is derived from the same raw material (pine chips) and the conversion efficiency for 1 MJ of biomass to 1 MJ of heat is 89%.

2.4.3.4. Economic calculation. In order to estimate the economics of the processes, the net present value (NPV) was calculated according to Eq. (21) and with the values shown in Table 3.

$$\mathrm{NPV} = f_s\left(\sum\nolimits_i^C - \sum\nolimits_j^C\right) - C_{FCI} \quad (21)$$

where C_i is the price of each item expressed for each product and C_j input (raw materials and utilities) per lower heating value, e.g. eur/MWh. The inputs and product has been calculated for 15 years. CFCI is the fixed capital investment in eur. f_s is the unacost present value factor, in this case 6.67, used to convert the sum of the cash flows into present time. The unacost present value factor corresponds to 13% internal rate and 15 years lifetime of the investment. The Fixed Capital Investment is assumed here to take pace at year 0 and all other costs and incomes are equal each year. No salary costs are included at this stage because they are expected to be of same magnitude for all the routes and do not affect the economic feasibility to a large extent. The Fixed Capital Investment was calculated by the capacity exponent method shown in Eq. (22), from the reported costs for a similar plant or process unit and the assumptions are reported in Appendix B.

$$\frac{C_1}{C_2} = (S_1/S_2)^n \quad (22)$$

where

C_1 = capital cost of plant

C_2 = capital cost of reference plant

S_1 = plant capacity

S_2 = reference plant capacity$n$ = capacity exponent, here 0.7 is used (Henrich et al., 2009).

3. Results and discussion

Appendix A presents the results of the material & energy balance calculations of the process cases studied and the indicators evaluated. A summary is given in Fig. 3 and saved GHG emissions vs. NPV are presented in Fig. 4.

Sub-cases A refer to the case without external heat input and sub-cases B with extra low temperature heat being added from outside. As indicators the primary energy efficiency, carbon footprints and NPVs are shown.

It can be seen from Appendix A that the total product HHV and LHV efficiencies for two of the novel processes (both cases of ETOH&MEOH and ENHHC) are higher than in any conventional process (MEOH, SNG and ETOH). The characteristics of the new processes are however different to the conventional ones: all of

Table 3
Cost values used in economic evaluation.

Cost	Value	Unit
Raw material	25	eur/MWh by LHV
Electricity	45	eur/MWh by LHV
Liquid fuel	100	eur/MWh by LHV
Furfural as chemical by-product	100	eur/MWh by LHV
Gaseous fuel	60	eur/MWh by LHV
Added extra heat	32	eur/MWh by LHV
Enzymes	15	% of wood raw material cost
Unacost present value factor	6.67	

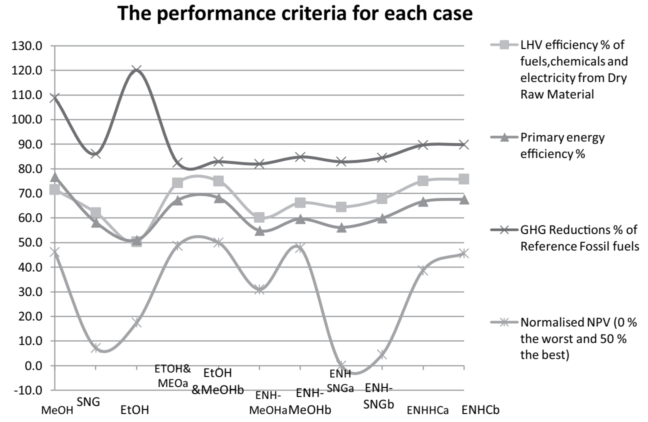

Fig. 3. Summary of the performance criterion for each process.

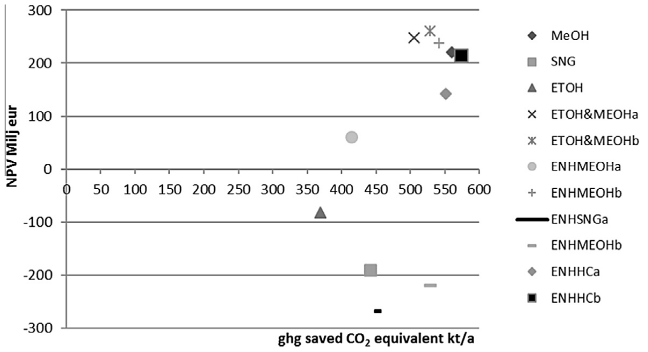

Fig. 4. GHG emissions saved as CO_2 equivalent expressed as kton per year vs. net present value per year of the process concepts.

the new processes are power deficient (i.e. electricity net consumers from 8 to 16 MW) whereas the conventional ones are mostly power producers between 21 and 35 MW (apart from the SNG process). The new process concepts are also capable of using external low temperature heat (>60 °C) as a heat source (from 9 to 47 MW) e.g. for biomass drying. This low-temperature heat can be secondary heat, for instance, from a pulp mill or a power plant nearby. The benefit is that this heat, which is usually wasted, can be utilised to 100% LHV efficiency to produce liquid or gaseous fuels. On the other hand, these processes can be run in a heat self-sufficient mode. In this case, no external heat is needed but some electricity is still required. In this mode, the HHV and LHV efficiencies are reduced by a few percentage points.

The most energy efficient processes in producing liquid and gaseous fuels (i.e. HHV and LHV% from feedstock to products) are the new ENHETOH&MEOH and ENHHC processes (best 76 LHV%). From the point of view of primary energy efficiency, the most efficient is the conventional MEOH process (77%). The difference reflects the different electricity production capabilities.

When studying the GHG reduction potential of a processes, a comparison can be made by examining how much GHG emissions can be reduced by a process (as tonnes of CO_2 equivalents per year) by producing biofuels and electricity. The best processes in this respect are the ENHHCb, MEOH and $ENHHC_b$ processes, substituting 551–574 kt CO_2 eqv. per year.

Another way of looking at the decrease is to study the reduction% of CO_2 equivalents when 1 MJ of fuel produced is substituted for one MJ of diesel or petrol (Eq. (18). In this comparison, the conventional ethanol process ETOH appears to be the best. The carbon footprint reduction, for the fuel produced in the ETOH and MEOH processes from the wood feedstock used, is approximately 120% and 109%. This is because the advantage of making renewable power is calculated here on the benefit of the biofuel produced. The best of the new process concepts are the ENHHCb and ENHHCa processes (90% reduction). The value in the new processes is less than in the conventional MEOH and ETOH processes, since no electricity is produced in the new ones.

Economy is the conventional way of looking at process feasibility. In this study, the NPV is used as the economic indicator (Equation (21)). The most important terms affecting the NPV are feedstock price, product prices and capital cost. In this early stage of process evaluation, the capital cost is the most uncertain contributor in the NPV equation, since the design stage does not allow the costing of the process except by using a rough estimation based on earlier similar designs by the capacity exponent law (Eq. (22). In Appendix A, it can be seen that the capital cost of the new processes (350 to 430 MEur) is larger than that of the conventional ones (270 to 350 MEur). By comparing the NPV, it can be seen that the new ETOH&MEOHb process is the most profitable (NPV = 261 MEur). In general, four of the new processes are very profitable: the NPV is between 215 and 261 MEur. The EHSNG processes are, however, unprofitable as is the convention SNG.

The main criteria for a biofuel process are obviously the GHG reduction potential and the profitability together. This is compared in Fig. 4, where both the GHG reduction potential (kt/a) and the NPV (MEur) are presented for the processes studied. It can be seen that there are six processes in the best cluster by these indicators. Four of the processes form a Pareto curve; a compromise between NPV and GHG values. ETOH&MEOHb process has the highest NPV (261 MEur) with 528 kt/a GHG reduction. ENHHCb is the most efficient GHG reducer (574 kt/a) with a lower NPV (215 MEur). The two other processes on the Pareto curve are ENHMEOHb and conventional MEOH, which have their NPV and GHG values between of the maximum values. The two remaining processes in the cluster, but below the Pareto curve, are ETOH&MEOHa, which has a high NPV (248 MEur) and ENHHCa with a high GHG reduction (551 kt/a).

The uncertainties in the evaluation are related to the limitations of the calculations possible in a route screening or early conceptual design stage. The evaluations are, however, necessary as earlier described to screen the alternatives and to find the points that need to be analysed with better accuracy. The main shortcomings are the following: since some parts of the processes are new, the assumptions for product yields are obtained at laboratory scale, and these should be verified on pilot scale. The exact costing of the processes is not possible in the development stage since the equipment design has not yet been made. Therefore, the costing is based on the scaling of costs of existing facilities and process sections when available. Since some parts of the processes are in the laboratory stage, analogical systems were used for the costing of those sections. In this stage, the heat integration study can be based only on maximum heat recovery potential (i.e. minimum heating and cooling demand). Yet, in a real industrial-scale plant, full heat integration potential is not feasible for economic reasons. In addition, some of the complex operations were calculated with less rigorous methods available in flow sheeting programs.

4. Conclusions

New pathways including separate conversion of lignocellulosic sugars and lignin to biofuels were studied and compared with conventional methanol, methane and bioethanol processes from biomass. Better economy and a higher GHG reduction potential were obtained compared to the conventional processes. The highest NPV was obtained for combined production of ethanol and syngas based methanol from biomass (ETOH&MEOHb) and highest GHG reduction for hydrocarbon production from pine residues by aqueous phase hydrogenation with hydrogen produced by gasification of lignin residue (ENHHCb). Advantageously these new processes can utilize the external low temperature heat and convert it into fuels with 100% efficiency.

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Appendix A. Energy values and indicators of process cases Case A; describes heat self-sufficient operation, and case B; utilisation of external low temperature heat

	Conventional processes					Enhanced process concepts					
	MEOH Case	SNG Case	ETOH Case	ETOH&MEOHa Case	ETOH&MEOHb Case	ENHMEOHa Case	ENHMEOHb Case	ENHSNGa Case	ENHSNGb Case	ENHHCa Case	ENHHCb Case
Biomass feed (HHV) and (LHV) MW	320.5/300	320.5/300	320.5/300	320.5/300	320.5/300	320.5/300	320.5/300	320.5/300	320.5/300	320.5/300	320.5/300
Liquid fuel output (HHV) and (LHV) MW	197.9/174.0	–	112.5/105.0	243.6/217.0	243.6/217.0	220.0/190.0	268.6/236.1	0	0	152.7/141.3	152.7/141.3
Gaseous fuel output (HHV) and (LHV) MW	22.2/19.5	223.5/192.9	5.7/5.3	8.8/7.8	19.0/17.0	0.0	4.7/4.1	226.0/203.6	260.7/234.9	99.5/90.0	109.2/98.8
Furfural output (HHV) and (LHV) MW	0.0	0.0	5.8/5.4	5.9/5.5	5.9/5.5	0.0	0.0	0.0	0.0	0.0	0.0
Total heating value of fuels and chemicals (HHV) and (LHV) MW	220.2/193.5	223.5/192.9	124.0/115.7	258.3/230.4	268.5/239.5	220.0/190.0	273.3/240.2	226/203.6	260.7/234.9	252.2/231.3	261.9/240.1
Electricity surplus MW	21.2	−10.12	35.3	−10.2	−10.2	−15.4	−15.4	−15.9	−15.9	−8.13	−8.13

Appendix A (*continued*)

	Conventional processes					Enhanced process concepts					
	MEOH Case	SNG Case	ETOH Case	ETOH&MEOHa Case	ETOH&MEOHb Case	ENHMEOHa Case	ENHMEOHb Case	ENHSNGa Case	ENHSNGb Case	ENHHCa Case	ENHHCb Case
External low temperature heat MW	0.0	0.00	0.0	0.0	9.1	0.0	47.5	0.0	30.9	0.00	8.6
Fuel & chemical product efficiency (HHV and LHV)%	75.3/71.6	67.6/62.2	49.7/50.3	78.13/74.3	79.0/75.0	65.5/60.2	71.3/66.2	67.2/64.4	71.0/67.7	76.7/75.1	77.7/75.8
Main product efficiency (HHV and LHV)%	61.7/58.0	67.6/62.2	35.1/35.0	73.7/70.0	71.7/68.0	65.5/60.2	70.1/65.1	67.2/64.4	71.0/67.7	47.5/45.9	45.3/44.6
Primary energy efficiency%	76.8	58.2	51.1	67.2	68.2	54.9	59.6	56.2	60.0	66.7	67.7
Carbon footprint (g CO_2 eq/MJ) reduction%	108.8	86.1	120.1	82.4	82.9	82.0	84.8	82.9	84.5	89.6	89.8
GHG emissions saved kt CO_2 eqv/annum	560	442	369	505	528	414	542	449	528	551	574
Net present value (NPV) MEur	221	−191	−82	248	261	60	238	−267	−219	142	215
Fixed capital investment MEur	350	320	270	400.0	400.0	430.0	430.0	400.0	400.0	350.0	350

Appendix B. Details of the fixed capital investment calculation

	MEOH Case	SNG Case	ETOH Case	ETOH&MEOH Case	ENHMEOH Case	ENHSNG Case	ENHENHHC Case
Calculated Fixed Investment cost	350	330	250	400	400	400	350
References	Hannula and Kurkela (2013, p.54)	Hannula (2014)	Sassner and Zacci (2008)	Sassner and Zacci (2008) & Hannula and Kurkela (2013)	Sassner and Zacci (2008) & Hannula and Kurkela (2013, p.54)	Sassner and Zacci (2008) & Hannula and Kurkela (2013)	Sassner and Zacci (2008) & Hannula and Kurkela (2013, p.540)
Reference Plant capacity	300 MW Feed on LHV wet basis	100 MW LHV Feed	106 MW LHV feed				
Reference Plant Cost	350	150	130				
Year(s) of Cost Estimate	2013	2013	2008	2013 and 2008	2013 and 2008	2013 and 2008	2013 and 2008
Notes				50% of ETOH plant cost and MEOH case calculated for 150 MW feed input added	50% of the cost of case ETOH assumed for pre-treatment, Syngas plant as for case MEOH but cost of gasifier calculated for 150 MW capacity from reported cost by Hannula and Kurkela (2013)	Same as ENHHMEOH, but SNG cost used instead of MeOH plant	70% of the cost of Ethanol plant added to cost of case SNG but 150 MW feed input capacity

Appendix C. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.biortech.2015.05.022.

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Enhanced biofuel processes utilizing separate lignin and carbohydrate processing of lignocellulose

Kristian Melin[a], Thomas Kohl[b], Jukka Koskinen[a] and Markku Hurme[a]

[a]Aalto University, Department of Biotechnology and Chemical Technology, P.O. Box 16100, 00076 Aalto, Finland; [b]Aalto University, Department of Energy Technology, P.O. Box 14400, 00076 Aalto, Finland

ABSTRACT
Enhanced biofuel production routes utilizing separate lignin and carbohydrate processing of lignocellulose are analyzed and compared with two conventional routes; the methanol and methane production via syngas from biomass. The enhanced processes studied are: hydrocarbons production by hydrogenation of biomass based sugars by hydrogen obtained from lignin gasification, and ethanol production by biomass hydrolysis and fermentation and conversion of residual lignin into methanol via syngas. The analysis of processes was done by rigorous flowsheet modeling including power production calculations and realistic heat integration and evaluation based on energy yield, greenhouse gas (GHG) reduction and net present value (NPV). The enhanced processes via separate lignin and sugar processing can run in two modes: either being energy self-sufficient or utilizing external low temperature heat and power. The processes can operate with high efficiency as 'waste heat and power to gas and liquids' processes for producing liquid or gaseous fuels especially when excess energy is available e.g. in summer. Of all the processes studied the enhanced hydrocarbon production process integrated with external low temperature heat source gave the largest GHG reduction and highest NPV. External low temperature heat and electricity is converted into fuels in 136% higher heating value (116% lower heating value) efficiency.

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Biofuels; lignocellulose; energy efficiency; cost; greenhouse gas reduction

1. Introduction

Efficient production of biofuels is a key issue in implementing biorefining routes to provide low production cost, high greenhouse gas (GHG) reduction and to minimize the burden to ecosystems caused by forestry and land use change. Traditionally the biomass is either utilized as total (e.g. total gasification) or fractionated to recover the desired component (e.g. cellulose) and the rest is burned for energy. The production of motor fuels or chemicals instead of heat would be highly attractive, since their value is higher. Also the low GHG second generation biofuels are attractive in the market since they interfere less with the food chain and require less land area per energy unit of fuel compared to first generation biofuels. To attain high efficiency processing it is potentially beneficial to

CONTACT Kristian Melin ✉ kristian.melin@aalto.fi

utilize dedicated processes and conditions for each raw material fraction. Since the main components of lignocellulose (carbohydrates and lignin) are very different in their chemical character, their separate processing could be attractive to enhance the efficiency of biorefinery.

The biorefineries are not standalone units in their nature: the plants are often integrated to pulp or power plants. The integration topics are therefore a matter of consideration. Also the national energy system is under change in many countries; the German energy transition *Energiewende* is an example.[1] The problem in the new energy systems is achieving balance in variable conditions. Excess heat and power may be available especially during summer due to the larger share of solar energy but also from traditional cogeneration sources due to low heat demand in the warm season.

The aim of this paper is to therefore answer two questions: can lignocellulosic liquid biofuel production be intensified by utilizing separate carbohydrate and lignin processing to increase the yield of biofuel, and can excess heat and power potentially available be used effectively in these processes? The main criteria in this evaluation are the GHG reduction potential and the production profitability.

Our earlier paper [2] introduced three new biorefining concepts and compared them with four existing concepts in a prefeasibility study employing partly shortcut methods and ideal heat integration. The current paper elaborates the study for four selected concepts by doing a deeper rigorous flowsheet simulation based analysis with realistic (non maximum) heat integration. Two of the routes are utilizing separate lignin and carbohydrate processing and two are conventional biofuel processes; methanol and synthetic natural gas (SNG) production from lignocellulosic biomass via syngas. Since the processes are typically integrated to a larger production site or energy system, the heat and power integration aspects are included, especially the capability to utilize low temperature level waste heat and excess power. For this purpose, two different site integration cases are analyzed for two of the process concepts.

2. Existing process technology

Existing biorefining processes often represent low efficiency due to poor utilization of the feedstock biomass as a whole. For example in the processing of lignocellulose for ethanol fermentation an increased efficiency to biofuels could be potentially be achieved through gasification of the lignin residue instead of burning it as wet biomass.[2]

Lignin gasification was studied by Ferdous et al. [3] for Kraft and Alcell lignins. The syngas produced from Kraft lignin at 800 °C contained a high amount (approximately 60%) of hydrogen. Yu et al. compared tar formation in cellulose, hemicellulose and lignin gasification.[4] The amount of tar created in lignin gasification was somewhat higher than from hemicellulose and cellulose. An interesting result was also obtained by Li et al. who compared hydrolysis residue and sawdust gasification performance.[5] The hydrolysis residue gave a significantly higher yield of hydrogen and lower carbon dioxide content than sawdust.

Sugars are typically processed by fermentation but chemical conversion is faster. This results in smaller sized equipment and potentially lower production costs. Sugar alcohol hydrogenation can be combined with acid pretreatment of cellulose [6] or spruce biomass

[7] with a high yield of sugar alcohols. Interestingly no slow enzymatic hydrolysis step was needed.

Sugar alcohols [8] and biomass hydrolysate [9] can be successfully converted into hydrogen and hydrocarbons by aqueous phase reforming (APR). In APR, liquid range hydrocarbons can be produced with co-feed hydrogen (APR-H).[10] As the ethanol fermentation also APR-H efficiently retains the energy content of the sugars. Only one study of the techno-economics of APR and APR-H for lignocellulosic biomass is available. According to the study,[11] the economics of the APR-H was not favorable compared to bioethanol production. However the study was made assuming that enzymatic hydrolysis is needed as well as a separate reactor to produce hydrogen for APR-H. The dominant cost in the process was the noble metal catalysts. Yet according to a review article by Wei et al., a cheaper catalyst such as nickel could be used [12] especially when a mixture of C1−C6 hydrocarbons and hydrogen can be accepted as a product.

3. Methods

3.1 Processes studied and feedstock

Two enhanced process routes employing separate lignin and sugar processing were selected for this study:

- Ethanol production by biomass hydrolysis and fermentation and conversion of residual lignin into methanol via syngas (ETOH&MeOH)
- Hydrocarbon production by biomass hydrolysis and APR of sugars into hydrocarbons by co-feeding hydrogen from lignin gasification (ENHHC)

These are compared with two conventional processes:

- Methanol production from biomass via syngas (MeOH)
- Synthetic natural gas production from biomass derived syngas (SNG)

The feedstock in all of the processes is pine logging residue. The element composition is carbon 52.34 wt%, hydrogen 6.09%, oxygen 41.19%, nitrogen 0.08%, sulfur 0.01% and ash 0.74%.[13] The chemical composition is hexoses 56.1 wt%, pentoses 4.7 wt% and lignin 27.0 wt%. The higher heating value (HHV) of dry pine residue is 20.6 MJ/kg and the lower heating value (LHV) is 19.3 MJ/kg. The biomass moisture is 50% in the feed conditions but dried into 13% in the processes.

The processes are described below. Process details are given in Melin et al.[2]

3.1.1 MeOH process: conventional methanol production by biomass gasification via synthesis gas

Pine biomass is dried to 13 wt% moisture and fed together with steam and oxygen to a gasifier operated at 800 °C and 10 bar as shown in Figure 1. The reformer works at 950 °C. Subsequently the synthesis gas is purified, compressed and the CO/H_2 ratio is adjusted to be suitable for methanol production at 6 MPa.

3.1.2 SNG process: conventional synthetic natural gas production by gasification of biomass and conversion of synthesis gas into methane

The process in Figure 2 is similar to the methanol process except for the synthesis and product separation. The reformer uses a catalyst which does not catalyze methane but

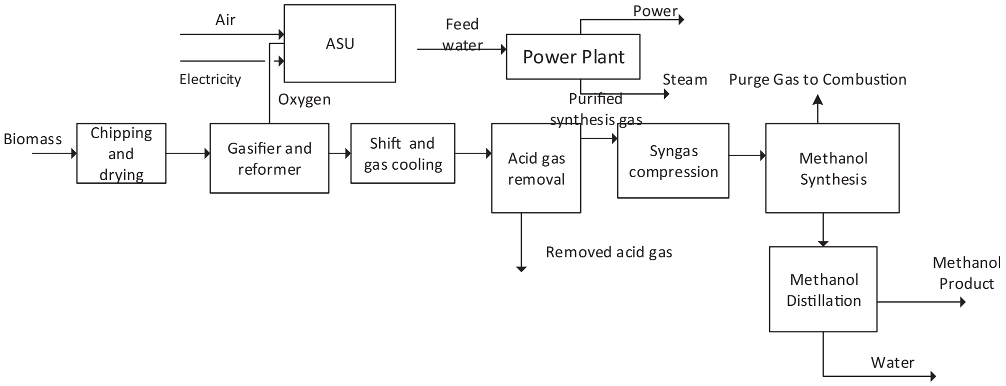

Figure 1. Block diagram of the MeOH process.

only tar steam reforming. A higher ratio of H_2/CO of approximately 3.1 is required for the methanol synthesis. Syngas is heated and fed to the methanation section where carbon dioxide and hydrogen is converted into methane at 31 bar. Methane is dried by tetra ethylene glycol (TEG) to allow SNG to be injected to the gas grid. The TEG is regenerated by distillation.

3.1.3 ETOH&MeOH process: ethanol production by biomass hydrolysis and fermentation and conversion of residual lignin into methanol via syngas

Pine chips, SO_2 and steam are fed to steam explosion at 215 °C (Figure 3). After the steam pre-treatment the liquid is cooled and sent to simultaneous fermentation and saccharification (SSF). A yield reported by Sassner and Zacci [14] has been assumed. In the pre-treatment step, 28 wt% of hexoses and 37 wt% of pentoses solubilize, whereas 9% of hexoses and 53% of pentoses are degraded to furfurals. In the SSF the ethanol yield is assumed to be 85% of the theoretical yield for hexoses (a bit more conservative than 90% reported [14] and 53% for based on Sonderegger and Sauer.[15] The solid lignin residue and remaining strong solution from evaporation is dried and processed into methanol in the gasification section as described in the MeOH process. The route has been presented in conceptual level.[16]

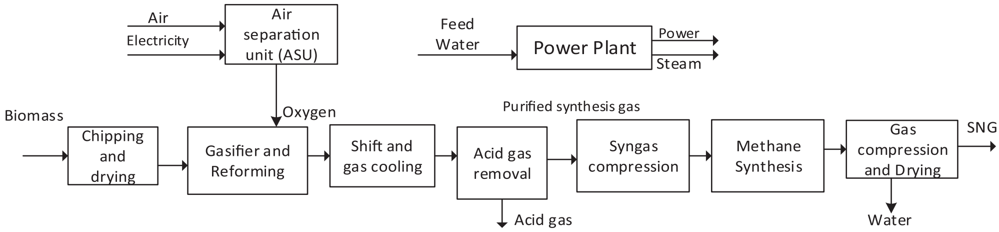

Figure 2. Block diagram of the SNG process.

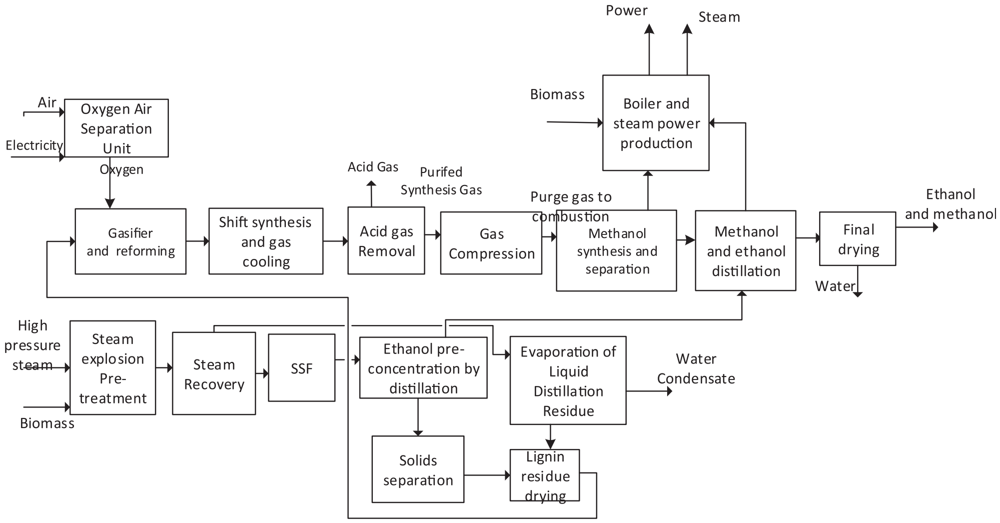

Figure 3. Block diagram of the ETOH&MeOH process.

3.1.4 ENHHC process: hydrocarbon production by biomass hydrolysis and aqueous phase reforming of sugars to hydrocarbons with co-feed hydrogen obtained from lignin gasification

This is a new route presented by Melin et al.[2] The hydrolysis sugars from hemicellulose and cellulose are hydrogenated into sugar alcohols together with an acid catalyst at 160° and 50 bar in the presence of heteropolyacids with a Ru catalyst according to Palkovits et al. [7] into 64.9 wt% C4–C6 sugar alcohols and 7.7% C1–C3 sugar alcohols. The sugar alcohols are further hydrogenated into alkanes by APR with co-feed hydrogen as shown in Figure 4. Hydrogen is obtained through gasification of the lignin residue and further conversion of the synthesis gas. A product distribution of 85% hexane, 10% pentane and 5% (C1–C3) hydrocarbon according to Zhang et al. [10] is assumed.

The methods used in the paper such as simulation methods, the heat integration approach and performance indicators employed are described as follows.

3.2 Modeling

The material and energy balances were calculated with Aspen Plus v 8.4 flowsheet simulation program. The processes were simulated including biomass feedstock drying and the power generation. The following operations were calculated with detailed Aspen models separately: gas purification and regeneration of Selexol solvent, low temperature cooling with ammonia, and gas drying in the SNG process with TEG and TEG regeneration. MS Excel models were also used: for process ETOH&MeOH dehydration of ethanol and methanol after distillation was calculated separately in Excel. Also the drying, fuel consumption in transport of biomass and the power consumption in oxygen production were calculated separately in Excel. The details of modeling are given in Appendix B.

The results from all models were compiled into an Excel model in order to calculate the overall mass and energy balances. The simulated energy balances were checked by

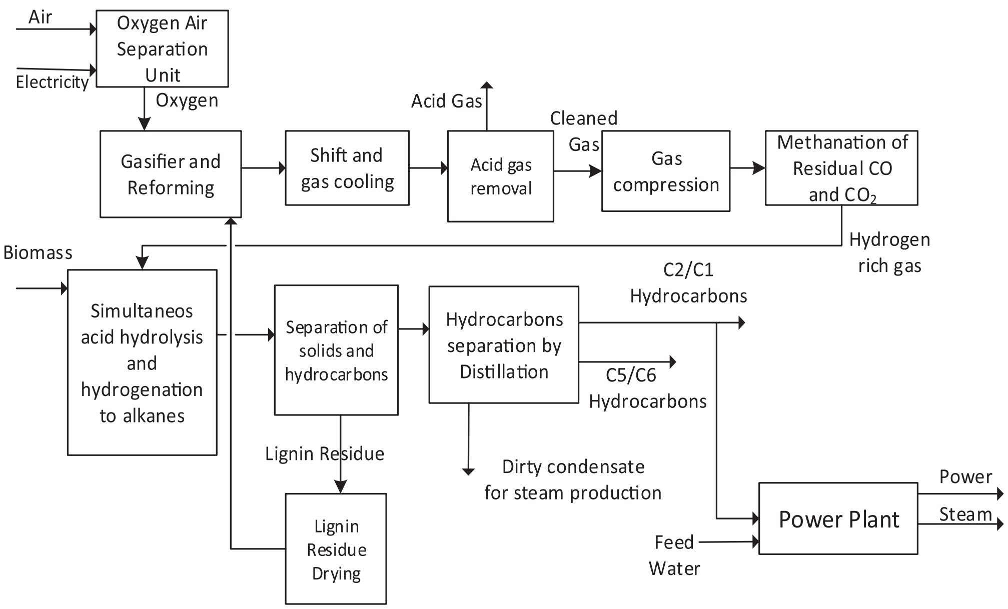

Figure 4. Block diagram of the ENHHC process.

calculating energy inputs and outputs in the following way. The inputs were chemical energy by HHV of the feedstock, heat input above 25 °C and power input to the process when needed. The outputs were all products by HHV, power excess and excess heat above 25 °C. The small errors (some percent) in the energy balances are caused by not considering heat output from oxygen separation and chipping. The accuracy in the calculations is however sufficient to compare the feasibility of the different processes.

The energy balances were presented as Sankey diagrams (Figures 5–10).

3.3 Heat integration and power production

In preliminary evaluations [2] processes are often studied by considering ideal (maximum) heat integration based on minimum heating and cooling demand. However such an approach would need too many heat exchangers and be uneconomical. Therefore here the flowsheets were integrated in a practical way, while still minimizing exergy losses that occur when high temperature heat is used for heating at lower temperatures. This is done in the following way. Hot utility (steam and hot water) or process heat with the lowest possible temperature is used for heating. The heating is done mainly with process utilities, high, middle and low pressure steam but also excess direct heat from the process ≤150 °C when it is available. The exception is that the chemical synthesis (methanation or methanol synthesis) feed is heated with the product. Also distillation columns feeds are pre-heated with their bottom product.

The feedstock and lignin residue is dried with a belt dryer using low temperature heat ≥65 °C. A specific heat consumption of 4 MJ/kg evaporated water is assumed.[17]

The high temperature heat above 250 °C is utilized for steam production. The feed water for steam production is pre-heated as much as possible. Also the feed water make-up is pre-heated. The pressure of the high pressure (HP) steam produced was adjusted to utilize the heat from the chemical synthesis. The synthesis reactor temperature in SNG and ENHHC processes was ≥300 °C and in the MeOH and ETOH&MeOH processes ≥250 °C. The superheated steam fed to a steam turbine and the lower pressure steams extracted.

3.4 Performance indicators

3.4.1 Greenhouse gas reductions and energy efficiencies

The energy yield by lower and HHV and GHG reduction are calculated. The diesel consumption in transport is included in the GHG emission of biomass. The GHG reduction (t GHG/a) is calculated according to Equation 1:

$$GHG_{\mathrm{reduction}} = (GHG_{\mathrm{fossil}} + GHG_{\mathrm{el,out}} - GHG_{\mathrm{biofuel}}) \tag{1}$$

where

GHG_{fossil} is the tons eq. CO_2 emissions per year for the fossil fuels (gasoline and natural gas) that are replaced by the biofuel produced (by same energy as LHV).

$GHG_{\mathrm{el,out}}$ is the tons eq. CO_2 emissions per year for the average grid electricity replaced by the electricity produced by the process.

GHG_{biofuel} is the tons eq. CO_2 emissions per year for biofuels produced in the process.

The equivalent GHG emissions for the feeds and fossil fuels replaced are presented in Appendix A.

The equation for LHV or HHV energy efficiency η is presented in Equation 2:

$$\eta = (E_{\mathrm{gas,fuel}} + E_{\mathrm{liq,fuel}} + E_{\mathrm{elec,output}})/(E_{\mathrm{biomass}} + E_{\mathrm{ext,heat}} + E_{\mathrm{elec,input}}) \tag{2}$$

$E_{\mathrm{gas,\ fuel}}$ is the energy of gaseous fuel by the corresponding heating value. $E_{\mathrm{elect,output}}$ is the excess electricity obtained as byproduct. E_{biomass} is the energy of the feedstock for the corresponding heating value. $E_{\mathrm{ext,\ heat}}$ is the energy of external low temperature heat used. $E_{\mathrm{elec,input}}$ is the input of external electricity to the process if the produced amount is not sufficient.

3.4.2 Economic calculation

The economic performance of the processes is assessed by net present value (NPV) calculated using Equation 3:

$$NPV = f_s \left(\sum C_i - \sum C_j\right) - C_{FCI} \tag{3}$$

where C_i is the income from a product (Eur/a), C_j is cost for each input item (raw materials, utilities, etc.; Eur/a). C_{FCI} is the fixed capital investment in Euro. f_s is the unacost present value factor for 15 years. Appendix A presents the cost for each item.

The NPV profitability measure (Equation 3) is calculated as the sum of the discounted revenues of years from present time until the last year of the economic life time of the project, here 15 years. Since the prices are dynamic, a sensitivity analysis is done later for the NPV for each route on product prices, plant investment costs, etc.

For GHG reduction cost another economic measure, the production cost, is calculated by Equation 4:

$$c_{Cost} = \left(\left(\sum \mathrm{E_j c_j} - \sum \mathrm{E}_b c_b + E_{cost,enzymes}\right) t_{op} + c_m - FCIa_f\right) \ /(E_i t_{op}) \tag{4}$$

C_{cost} is the production cost in Eur/MWh for the main product
C_j is the cost for each energy-based input item (raw material, heat and power) (Eur/MWh)
E_j is the amount used in MWh during one hour of operation
C_b is the price for each energy based by-product (electricity or biogas) (Eur/MWh)
E_b is their produced amount in MWh during one hour of operation
t_{op} is annual operation time 8000 h/a
c_m is the maintenance cost in Eur/a
FCI is the fixed capital investment of the plant in Eur
a_f is the annuity factor for 13% internal rate and 15 years payback time
t_{op} is annual operation hours h/a
Ei is the product amount (MWh/h)

The estimates for investment cost and the details of the FCI calculations are given by Melin et al.[1]

In Equation 5, the cost of reducing equivalent GHG emissions $C_{CO2,red}$ in Eur/t of eq. CO_2 is calculated when liquid biofuel substitutes regular gasoline and gaseous biofuel substitute natural gas. C_{fossil} and C_{cost} are the prices of the fuels in Eur/MWh, t_{op} is annual operation hours h/a, $GHG_{reduction}$ is the reduction of equivalent GHG emissions t/a when biofuel is substituting the corresponding fossil fuel.

$$c_{\mathrm{CO2,red}} = \left(c_{\mathrm{fossil}} - c_{\mathrm{cost}}\ \right) t_{\mathrm{op}} / GHG_{\mathrm{savings}} \tag{5}$$

The cost and GHG values [17] are given in Appendix A Table A1.

4. Results and discussion

The process integration, energy and material balances of the processes are presented. Finally the various performance indicators are discussed.

4.1 Energy integration

4.1.1 Process MeOH

More heat is liberated than consumed in the process. Heat was obtained from cooling of the following streams: reformed synthesis gas, water gas shift synthesis product, methanol synthesis product and flue gas from gas combustion. The high temperature heat from cooling of reformer, flue gas from gas combustion, heat from methanol synthesis cooling and part of the heat from the shift outlet could be used to generate superheated steam from feed water. A steam level of 48 bar was chosen to allow the utilization of the heat from methanol synthesis (≥270 °C) to be used for steam generation. The steam generated (48 bar and 485 °C) was fed to turbine and steam for reforming and gasification extracted at 10 bar. The low pressure steam was extracted at 1.6 bar for methanol distillation and regeneration of the Selexol solvent. The lowest pressure steam (≥65 °C) obtained from turbine is used for the methanol column together with 1.6 bar steam and for drying the feedstock. The heat integration is shown in Appendix B Table B2.

4.1.2 Process SNG

In the SNG process the heat integration could be done in a similar way as in the methanol process since excess heat was available for steam production. No gas was combusted so only the heat from reformer outlet, shift and methanation was used to generate steam. A higher pressure steam (80 bar) was generated because of the higher temperature of the methanation (≥300 °C). The heat not used for steam production was used for the dryer. A small amount of HP steam was used for regeneration of triethylene glycol. The steam was expanded to 10 bar and the steam for gasification and drying was extracted. Subsequently the rest of the steam was expanded to 1.75 bar which was used for regeneration of Selexol. The hear integration is presented in Appendix B Table B3.

4.1.3 Process ETOH&MeOH

In the ETOH&MeOH process not enough heat is available in case a and therefore extra biomass is combusted. In case b the excess heat is obtained from an external source. The heat integration is shown in Appendix B Table B3 for both cases.

In the ETOH&MeOH a process steam is generated by cooling the product streams from reforming, shift outlet, methanol synthesis and flue gas from combustion. The HP steam (48 bar) is generated from heat of methanol synthesis. The steam was extracted as follows: 21 bar for pre-treatment, 10 bar for gasification and reforming, 5 bar for ethanol HP distillation and evaporation, 1.75 bar steam for Selexol and product distillation and the turbine exit steam for drying.

The secondary heat obtained from steam explosion treatment was utilized in the first stage of the evaporator together with the 5 bar steam. The heat demand of the stillage evaporation was significantly reduced by compressing the vapor condensate and preheating the feed with it. The hot streams after the evaporator were used both in the product column reboiler and for drying. All heat in the process above 65 °C could be fully utilized.

The atmospheric column was run with the heat from the HP column condenser. The atmospheric column condenser heat was partly used in the product column as well as for drying.

In case b the heat for drying, all steam for Selexol regeneration and part of the heat for the product column was obtained from an external source as waste heat.

It was found that the heat demand of the ETOH&MeOH process depended most on the level of heat-integration in the process.

4.1.4 Process ENHHC

As in the ETOH&MeOH process there was not enough heat to satisfy the process’ own heat demand. Therefore in the a process product gas is combusted and in the b process external heat was added. The detailed integration is shown in Table B4 in Appendix B. In case a, steam was generated by heat from reformer outlet, after shift reactor, heat from methanation and from combustion of product gas. The make-up to the process water was heated to 55 °C with heat from the process below 65 °C. The hydrogenation reactor aqueous feed could be pre-heated with the reactor product. Subsequently the heat from cooling the reactor product vapor and liquid could be used for drying. The bottom product of the hydrocarbon distillation column was used to pre-heat the distillation column feed. The turbine exit and unused heat above 65 °C was used for the drying of lignin. HP steam (80 bar 510 °C) was generated to take advantage of the higher temperature in methanation. Steam was extracted at 10 bar and 2 bar levels and as turbine exit steam. In the gas combustion air was pre-heated by cooling the flue gases from 300 °C to 120 °C.

In case b, external low temperature heat was needed for lignin drying and Selexol liquid regeneration.

4.2 Energy balances

4.2.1 MeOH process

In the methanol production process (Figure 6) it can be seen that the significant amount of heat liberated in conversion can be utilized for steam and power production in the power plant. In this process, the largest consumer of energy is the drying of feed biomass

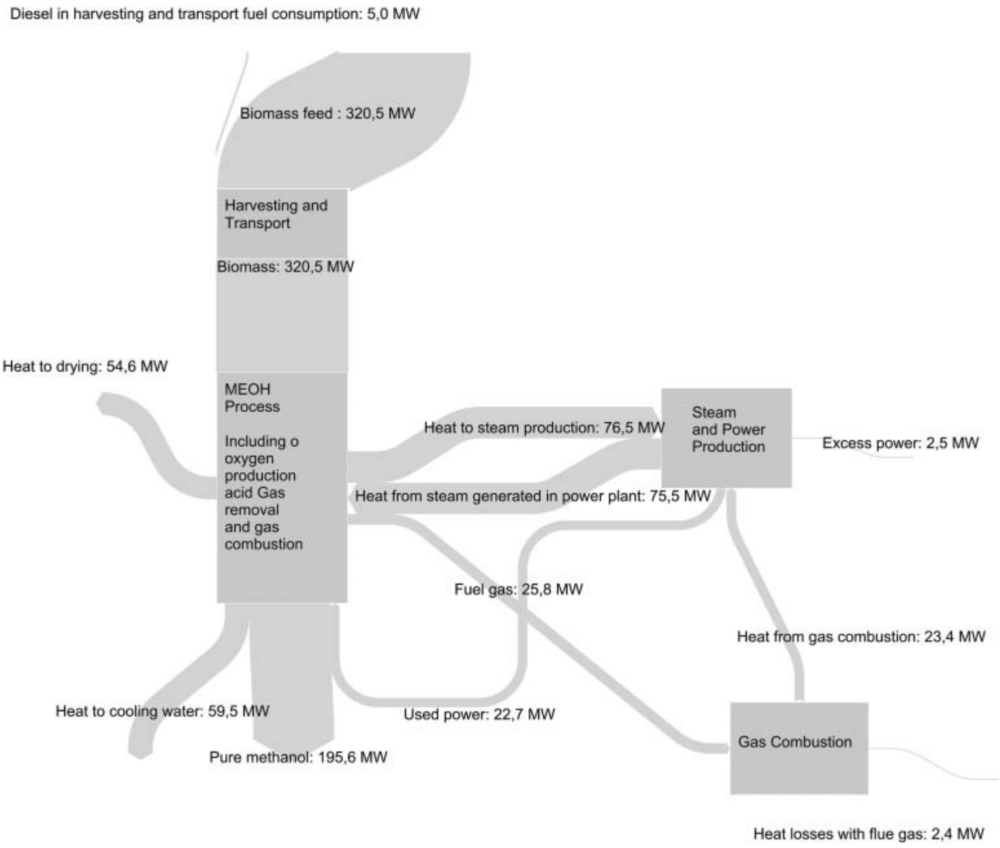

Figure 5. Methanol synthesis Sankey diagram (HHV based).

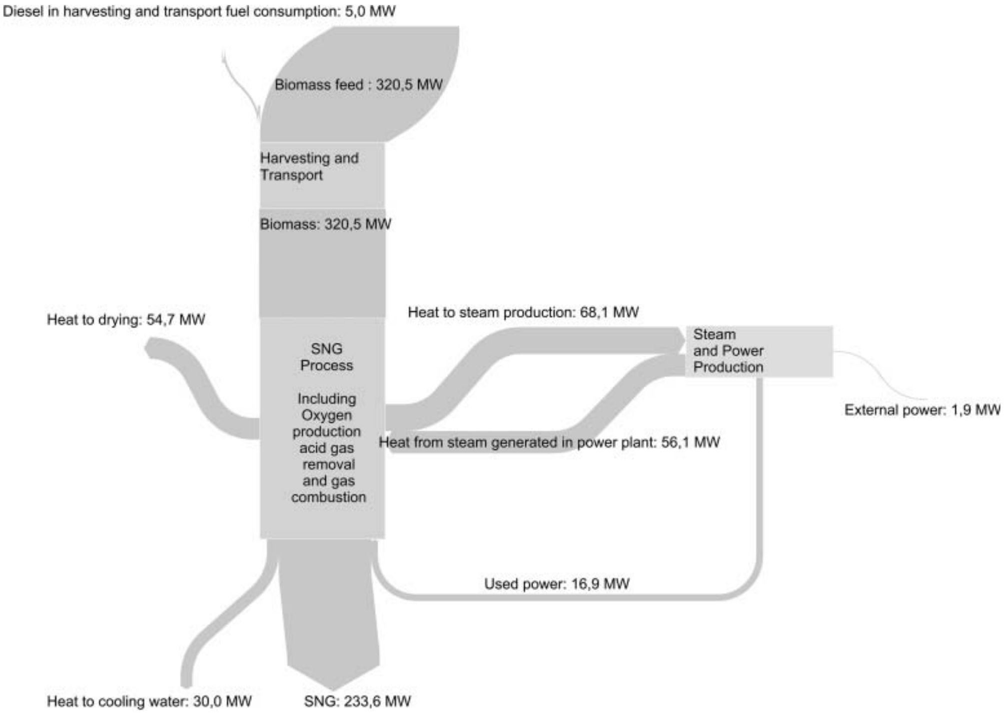

Figure 6. Methane synthesis Sankey diagram (HHV based).

and the distillation of methanol. The process produces 2.5 MW of excess power. A similar energy yield of methanol was obtained compared to Hannula and Kurkela.[19] When the efficiencies are compared on equal basis for dry biomass, Hannula and Kurkela [19] obtained 56% LHV into methanol for dry biomass in case 1 and 61% in case 3 compared to 58% obtained in this study. Case 1 in their work with cooling of synthesis gas before filtration gave similar excess power 2.5 MW vs. 2.6 MW in this study. Both in their case 1 and in our work, no district heat was produced. In our study, a higher pressure gasification (10 bar) was used compared to 5 bar in their work. This results in lower electricity consumption in gas compression for the methanol synthesis. However, the cooling of synthesis gas before filtration increases somewhat the heat production in the process. Here the acid gas removal was done at low pressure before the synthesis gas compressor at approximately 8 bar. It resulted in almost 30% lower electricity consumption in the synthesis gas compression. Acid gas removal is at low pressure due to lower partial pressure of acid gas components. A higher circulation rate for Selexol is needed, and therefore more steam is required to regenerate the Selexol. The electricity consumption of pumps (except the feed water pump) has not been taken into account in this study; their effect to the overall power consumption is relatively small.

4.2.2 SNG process

The main difference of the SNG process compared to methanol is that the product yield is higher, and heat is liberated at higher temperature from methanation. The results are illustrated in Figure 7. Due to the higher product yield, not enough power

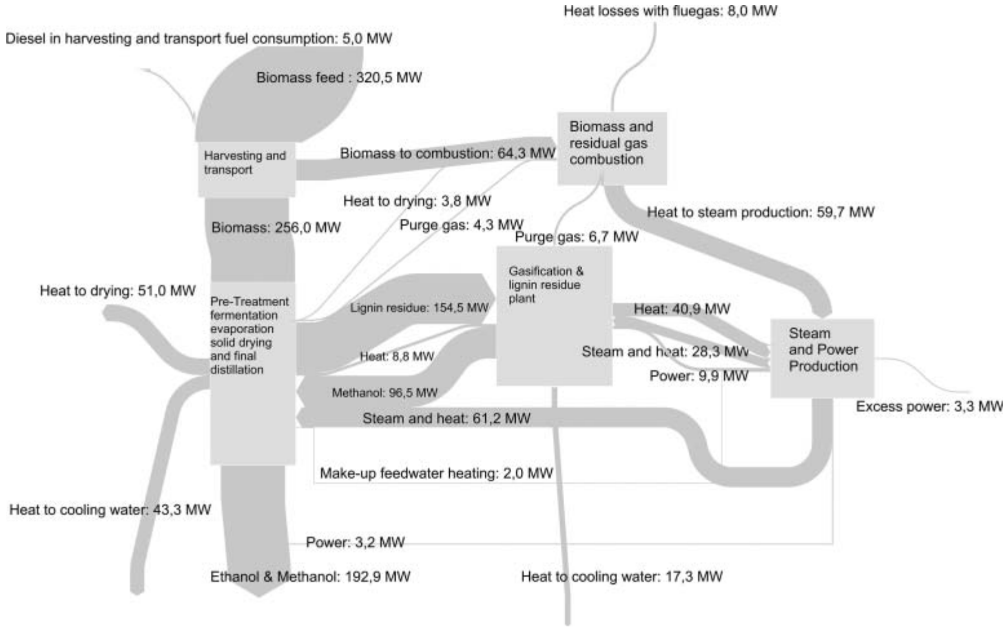

Figure 7. Energy flow diagram of process ETOH&MeOH a (HHV based).

can be generated for the process demand and extra electricity is imported from the grid. The higher yield depends also, in the reforming step, that the catalyst is only reforming tar components not the methane. Therefore a lower conversion in the methanation is needed which results in a lower loss of the synthesis gas chemical energy content into heat. The energy yield of SNG here (70%) is slightly higher than the 62% biomass to chemical energy yield reported for the Güssing plant.[20] Yet their simulation based energy yield was 66%. The reason is that here the gasification is done at HP 10 bar which results in high initial methane content and also the tars are converted into synthesis gas. In addition, the gasifier type here was direct gasification and not internal fluidized bed gasifier as in Güssing. However the SNG product yield might be slightly optimistic here.

4.2.3 *ETOH&MeOH a process*

In the ETOH&MeOH process shown in Figure 8, a nearly similar product energy yield was obtained as in the methanol process presented earlier. Here in the simultaneous saccharification and fermentation the consistence of 20 wt% is assumed. With a lower consistence the energy needed for product recovery would be significantly higher. In this process, which does not utilize external energy, about 71 MW of wood and the residual gas from the product distillation and methanol synthesis is combusted in order to produce heat and power for the process demands. The drying of lignin is the largest consumer of power. Here the lignin was dried from approximately 66 wt% water content obtained by mechanical dewatering to approximately 13 wt% water content. If the gasification was done at higher water content a lower part of the raw material energy content would be

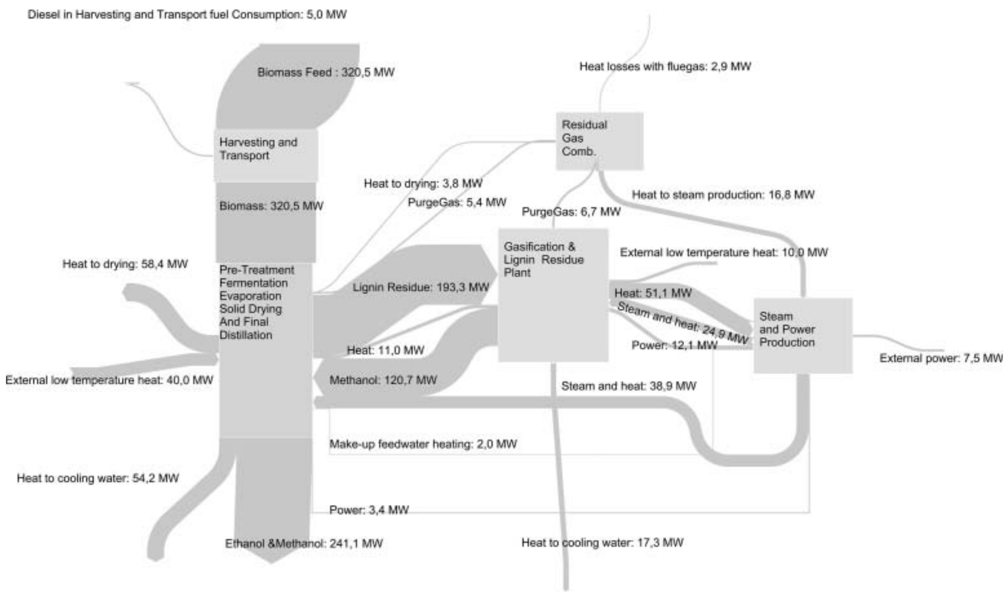

Figure 8. Energy flow diagram for process ETOH&MeOH b (HHV based).

converted into chemical energy in synthesis gas. This was not attempted here but the yields from lignin residues have been calculated for 40 wt% moisture content.[21] Laser et al. [22] also reported LHV efficiency close to 80% for separate sugar and lignin residue gasification for switchgrass. They did not report the deficient amount of heat for the process, however due to raw material with lower lignin content and ammonia fiber explosion pre-treatment the process heat requirement was significantly lower.

In this study the energy consumption in evaporation was significantly reduced by compressing back the vapor after the evaporator to a higher pressure and exchanging the heat to the evaporator feed. The power consumption of the bioethanol part may be somewhat underestimated since the power consumption of mechanical dewatering, pumps and stirring in other vessels except SSF was not considered. The results indicate that in process ETOH&MeOH a the bottle neck for the biofuel yield in the biofuel production is not the conversion efficiency from raw material to fuel but the heat demand of the process.

In the gasification of lignin the tar amount remaining in the synthesis gas naturally affect the feasibility of lignin gasification. This is not predicted reliably by the equilibrium model of gasification. Removing tars to the required level for the subsequent catalytic reactions is crucial.

4.2.4 *ETOH&MeOH b process*

Since part of the feed biomass energy was used in the ETOH&MeOH a process for low temperature heat production, an analysis was done to find out how much utilization of external low temperature heat would increase the process yield. It was found out that the biofuel yield could be increased significantly by utilizing external low temperature heat in the process ETOH&MeOH b as shown in Figure 9. In fact the process can act as a 'waste heat and power to gas and liquids' process for producing liquids in 89% HHV efficiency for the added low temperature heat and some power. This has also a significant benefit to

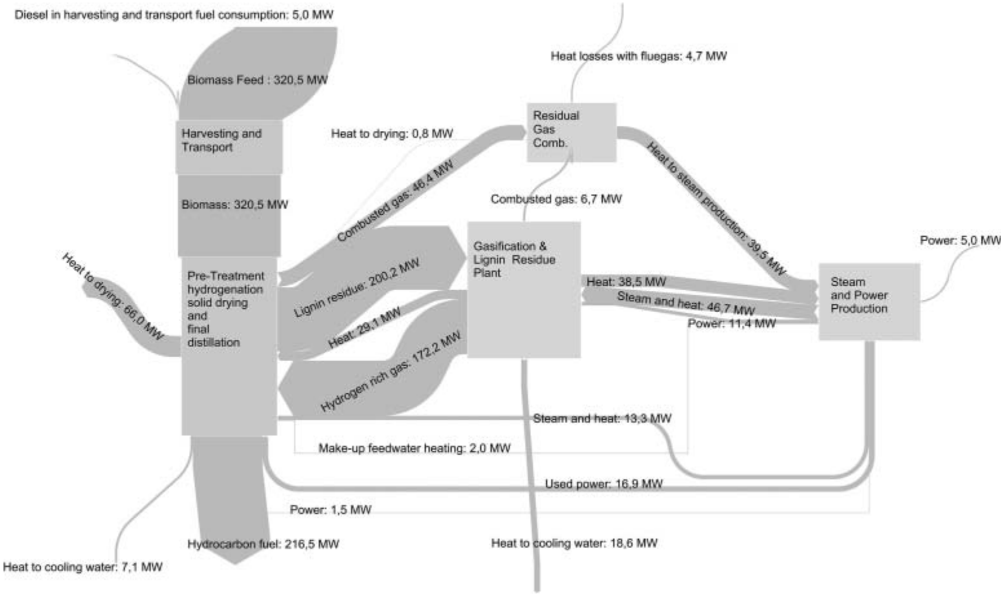

Figure 9. Energy flow diagram for process ENHHC a (HHV based).

the economics as seen in Table 1 when comparing processes a and b of ETOH&MeOH. Low temperature heat would be available from power plants or pulp mills especially in summer time. The process could run in summer in b mode to utilize excess heat and power available to produce motor fuels, and during winter in a mode to also produce some biopower.

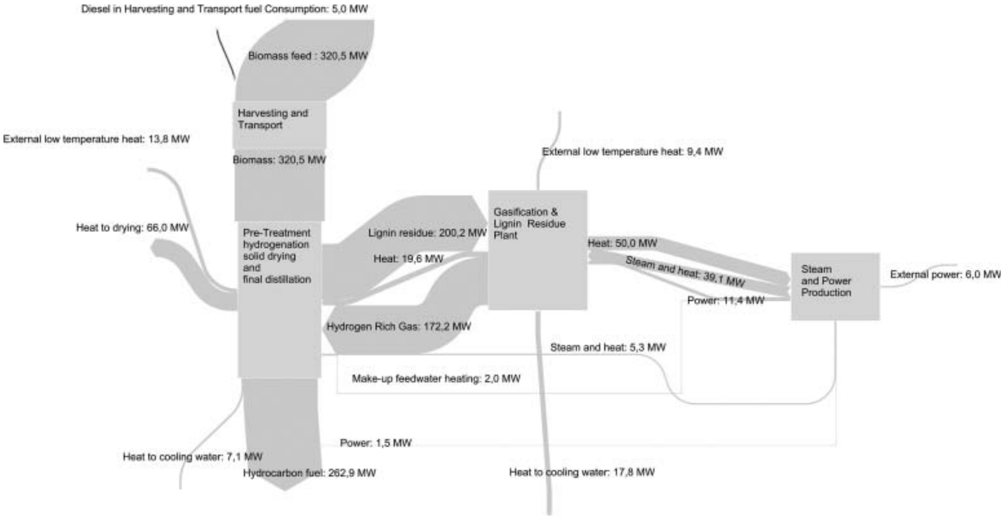

Figure 10. Energy flow diagram of process ENHHC b (HHV based).

Table 1. The energy inputs and outputs of the processes and the performance indicators calculated.

	MeOH	SNG	Ethanol & MeOH a	Ethanol & MeOH b	ENHHC a	ENHHC b
Biomass feed (HHV/LHV) MW	320.5/300	320.5/300	320.5/300	320.5/300	320.5/300	320.5/300
Liquid output (HHV/LHV) MW	195.6/171.9	–	186.8/167.7	241.1/214.8	150/137	150.0/137
Gaseous fuel (HHV/LHV) MW	0	233.6/210.5	0	0	66.3/61.9	112.7/101.8
Total heating value of fuels and chemicals (HHV/LHV) MW	195.6/171.9	232.9/210.5	186.8/167.7	241.1/214.8	216.3/198.9	262.9/238.8
Electricity surplus MW	2.5	−1.90	3.3	−7.5	5.0	−6.0
Additional heat as low temperature heat MW	0	0	0	50.0	0	23.2
LHV % with heat and power	58.1	69.7	57.0	60.1	68.0	72.5
Fixed capital investment milj Eur	350	320	430	430	350	350
NPV milj Eur	103	−115	-38	102	121	182
Production cost Eur/MWh	88.8	70.2	104.2	91.1	76.2	68.6
GHG reduction kton/a	433	369	388	467	470	504
GHG reduction cost Eur/t CO_2	282	320	360	336	258	260
GHG reduction cost - ref. fuel cost Eur/t CO_2	123	206	187	151	115	111

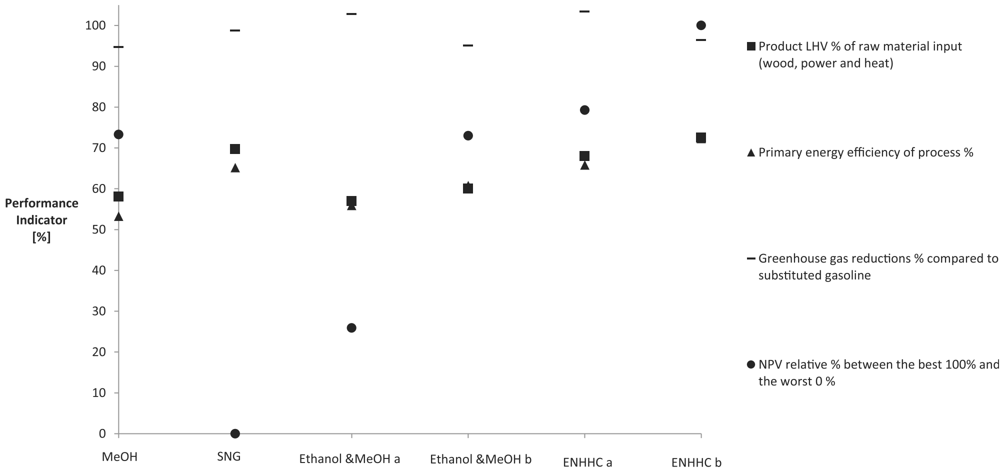

Figure 11. The main performance criteria of the processes.

4.2.5 ENHHC processes

In process ENHHC the APR is performed at 10 wt% solid concentration so that 72% of the sugars are hydrolyzed and hydrogenated into sugar alcohols as reported by Palkovits et al.[7] Compared to ETOH&MeOH, significantly less energy is needed for product recovery. However, slightly more energy is consumed when drying the lignin residue, since the amount of lignin residue is larger than in ETOH&MeOH. A product distribution of

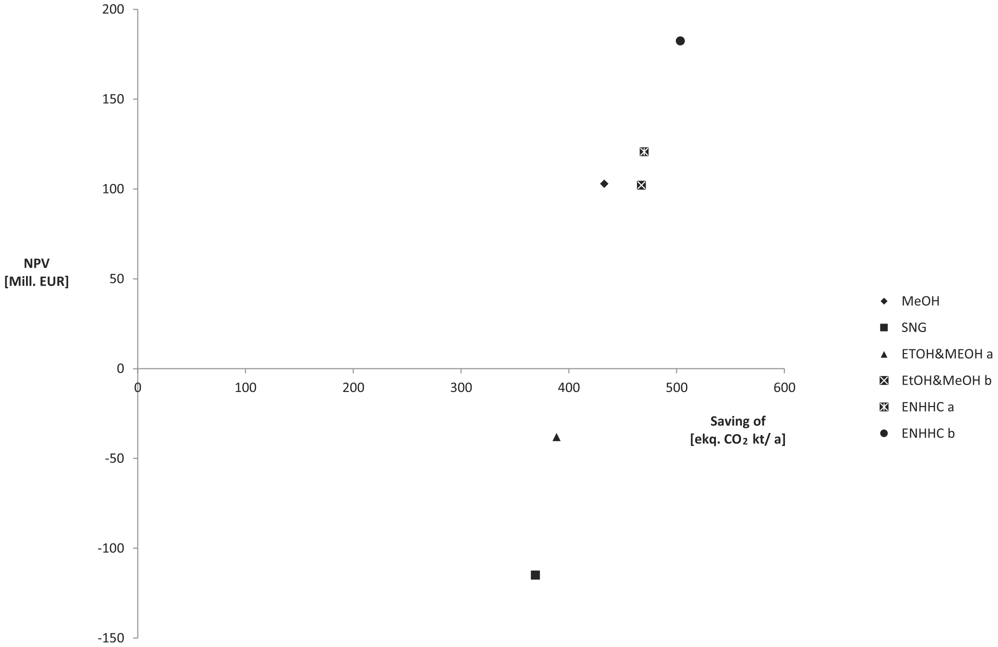

Figure 12. Savings in GHG emissions vs. estimated NPV for the process.

hydrocarbons according to Zhang et al. [10] obtained in the laboratory is assumed. If the hydrolysis yield can be increased further the yield of liquid hydrocarbons would be significantly increased. A study done by Cragnell et al. [11] reports higher conversion, yet they employed first enzymes to hydrolyze the cellulose and hemicellulose into sugars which were further converted into sugar alcohols, which might be less economical. Also in process ENHHC the bottle neck for fuel yield is the low temperature heat available for lignin drying and regeneration of Selexol solvent. Therefore this process is also capable of running in two modes; the b-mode utilizing external low temperature heat and power, and the a-mode being energy sufficient but producing less fuels and some power.

The product yield in process ENHHC in b-mode (Figure 11) is even higher than in other processes. The high performance of the process is based on the general high yield of this process but also on the availability of low temperature waste heat and some power. The assumptions made include that the main part of the water can be recycled back to the simultaneous pre-treatment and hydrogenation and no evaporation of the water phase is needed for solids separation.

4.3 Performance indicators

Several energy, economic and GHG indicators were calculated for the processes based on the balances presented in Figures 5—10 and cost and GHG factors given in Appendix A. The main indicators presented in Table 1 are LHV efficiency, NPV, production cost, GHG reduction, GHG reduction cost and GHG reduction cost compared to gasoline (or natural gas for gas products). The estimates for investment cost (FCI) come from Hake et al.[1]

Figure 11 presents some indicators graphically, Figure 12 gives NPV vs. the equivalent carbon dioxide savings (kt/a) for the processes and Figure 13 details the sensitivity analysis of NPV.

5. Discussion

It can be seen from Table 1 and earlier process descriptions, the product of processes vary being liquid (methanol, ethanol, their mixture or hydrocarbons), gas (SNG or mixture of C1s and C2s) and power. Three of the processes are energy self sufficient (or excessive) producing power, other three are power deficient, and two also heat deficient in the low temperature range. These two (ETOH&MeOH b and ENHHC b) are in fact operation modes utilizing external heat and power if available; the processes can be run also in energy sufficient mode (case a).

Since the processes have various product (and also inputs), they are here compared based on energy yield, economics and GHG reduction mainly.

Process energy yields (LHV% including heat and power) in Table 1 vary between 57 and 72.5%. The highest energy yields are in ENHHC b, SNG and ENHHC a processes (approximately 73, 70 and 68%). The others are in the range 57—60%. All of the three high LHV% processes also produce gas products.

In the *economic analysis* process, ENHHC b and ENHHC a give the highest NPV (182 and 121 MEur) with the prices presented in Appendix A. This is because of the high product yields and low investment costs. Two other profitable processes are ETOH&MeOH b and

MeOH (NPV $\approx$ 100 MEur). The SNG process is the most unprofitable (NPV $= -115$ MEur), since the product is gas has a much lower price compared to liquid biofuels.

Process ENHHC b gives higher profit and energy yield than ENHHC a, since low cost waste heat and power can be utilized in case b with high efficiency. Both the ENHHC and ETOH&MeOH can be run either in a or b mode depending on the availability of waste heat and low cost power (e.g. in summer). If the cost of low temperature heat would be still lower, the NPV would be even higher. This is quite possible when the waste heat does not have any alternative use and it would be dumped.

The lowest *production cost* processes are ENHHC b and SNG (68.6 and 70.2 Eur/MWh). This does not make the SNG process profitable, since the gas product is cheaper.

The *GHG reductions* gained by the processes vary between 369 and 504 kt/a. The ENHHC b process has the highest GHG reduction (504 kt/a). This is because of the high energy yield efficiency (LHV%) and large usage of excess heat, which has a low GHG value. A slightly lower GHG reduction cost is however with the ENHHC a process 258 Eur/t CO_2 eq. since the share of high value liquid fuels produced is higher than in ENHHC b (260 Eur/t CO_2 eq.). The GHG emissions depend on several variables: the yield of product which substitutes fossil fuel, the type of product substituted (gasoline or natural gas), the amount of power used / produced and the usage amount of excess heat. For electricity the average EU emission factor was used [18]; see Appendix A. Greener electricity would favor case b processes. An electricity with higher GHG emission factor (e.g. coal) would favor the processes which produce excess electricity (case a).

The GHG reduction cost can be expressed also as replacement costs (the last line in Table 1); i.e. as *additional* cost compared to a fossil reference fuel (gasoline or natural gas) when a ton of CO_2 eq. is reduced. The lowest replacement cost is gained by the ENHHC b and ENHHC a processes (111 and 115 Eur/t CO_2 eq.).

Since fuel and other cost vary, a sensitivity analysis on the NPV is presented in Figure 13. The variables are product price, raw material price and product yield. In Figure 13 the step size on the x-axis corresponds to 20% change. It can be seen that the NPV of all the processes is most sensitive to the product price. This is understandable since product revenue is the largest term in NPV. The raw material price and product have a slightly lower influence. The enzyme cost, electricity price and price of external heat were found to affect the NPV less and are not shown in Figure 13. Since the prices of all of the fuel products are all expressed per energy unit (Eur/MWh), large changes in their relative pricing are less common. Therefore the NPV ranking of the processes (i.e. relative profitability) is much less sensitive to the price changes than the NPV.

When analyzing the two enhanced processes further, the following characteristics can be found. The ETOH&MeOH and ENHHC processes can be operated either in energy self sufficient mode (a) or heat and power deficient mode (b). When comparing the ENHHC modes, it can be seen from Table 1 that both modes produce the same amount of liquid fuel but mode b produces 1.6 times gaseous products compared to ENHHC a. In fact the low temperature heat (with some power) is transformed to gaseous fuels by 116% LHV efficiency by the ENHHC b process. In the MeOH&ETOH process the product increase from utilizing waste heat and power is not gas but liquid fuel (alcohol mix), which may be more convenient. The transformation efficiency for the waste heat and power added is less (77% LHV), which is good in comparison to the total LHV efficiency (in 60% range).

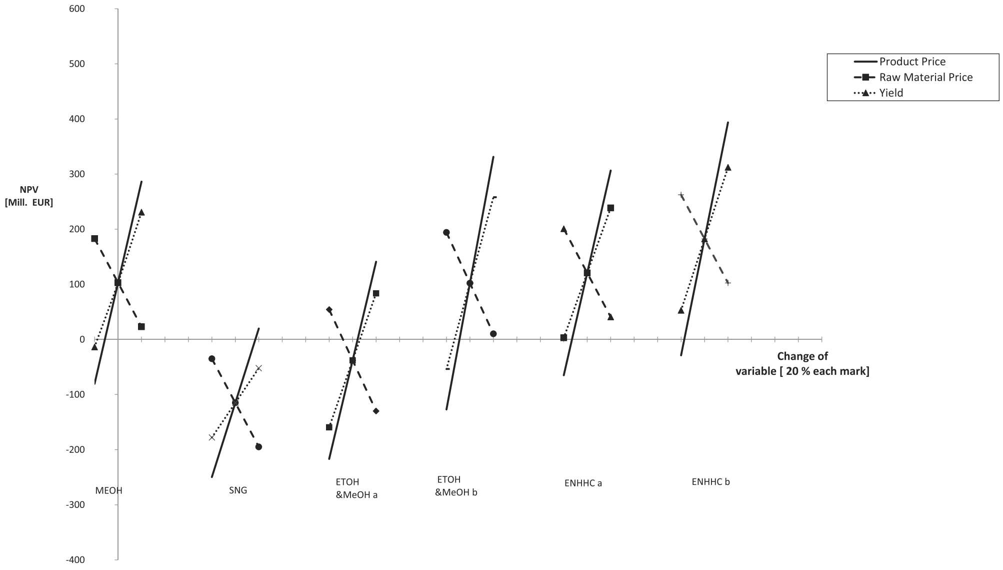

Figure 13. The sensitivity analysis of NPV vs. change in each variables with +— 20% on x-axis.

Processes ETOH&MeOH and ENHHC utilize separate lignin and carbohydrate processing in contrast to the MeOH and SNG processes, where all fractions are processed in a similar way through gasification. A research question was if the separate processing is more efficient. Comparing the cases it can be seen that ENHHC is better in all criteria. ETOH&-MeOH a, which is closest to the MeOH process (partly similar product, no external heat used, about same power excess) is worse than MeOH in LHV%, GHG and economic terms. If the comparison is made between lignocellulosic ethanol plants and ETOH&MeOH process the latter (i.e. separate processing) was better in the preliminary study.[2] Therefore by these cases the separate lignin and carbohydrate processing can in some cases be beneficial (compared to lignocellulosic ethanol process) but not always (the results vary when compared to gasification).

The uncertainties of ENHHC processes are related to uncertain knowledge of the route in a larger scale, since the study is based on laboratory scale yields for the individual steps, which should be verified on a larger scale and for a process working with several steps combined. Also certain processing assumptions were made as described in Section 4.2.5, which should be checked in pilot runs.

6. Conclusions

Enhanced lignocellulosic biorefining routes employing separate processing for the lignin and carbohydrate part have been analyzed by rigorous flowsheet models and by including realistic heat integration. A comparison to convention routes such as methanol and SNG production from biomass was made.

Processes ENHHC b and ENHHC a presented the best NPV values, highest GHG reduction tons, lowest GHG reduction costs and lowest additional GHG reduction costs vs. fossil fuels as shown in Figures 12 and 13.

It was found that the routes employing separate processing for lignin and carbohydrate part (ENHHC and ETOH&MeOH) are heat deficient in the low temperature area but produce some excess power. Therefore it is beneficial to integrate these processes with other process having excess of low temperature heat (e.g. power plants or pulp mills). In fact both the ETOH&MeOH and ENHHC processes can be operated efficiently as 'waste heat and power to gas and liquids' processes. ENHHC process can in b-mode utilize low temperature heat (and some power) with 116% LHV efficiency to increase gaseous fuel yield and ETOH&MeOH process in 77% LHV efficiency for increased alcohols yield. This is an important aspect as excess heat and power may be available especially during summer not only from traditional cogeneration sources but also from solar energy sources as the energy transition goes on. Therefore in summer the processes can run in b-mode to produce fuels with good energy efficiency, and during winter to run in a-mode to produce also biopower. Both processes can also utilize lignin from outside e.g. from pulping processes, which may separate lignin with the LignoBoost process.[23] Lignin can also be stored for use during the winter period. The yield of the processes could be increased by adding to syngas extra hydrogen obtained for example from water electrolysis (available in the power to hydrogen economy).

It should be noted that the 'enhanced' processes produce different products. The ENHHC processes produce hydrocarbons as product which resemble their fossil counterparts and are therefore suitable for existing car engines in a wide blend. The down side is that part of the products is gas (80% methane), whereas the ETOH&MeOH processes produce only liquids (alcohol mixture). The hydrocarbons produced from C6 sugar alcohols such as sorbitol can be converted according to Zhang et al. [10] mainly into C5 and C6 hydrocarbons. These hydrocarbons can be blended particularly if isomerized to increase octane number with existing gasoline or E-85 fuel. The sugar 'cleavage' product obtained as byproduct (light sugar alcohols such as ethylene glycol) forms light hydrocarbon such as ethane. These can be mixed in limited amounts in SNG or used as a renewable feedstock for an ethylene cracker to produce polyolefins and other petrochemicals.

As a conclusion the answers to the two research questions presented earlier are: lignocellulosic liquid biofuel production can be intensified compared to lignocellulosic methanol production by utilizing separate carbohydrate and lignin processing (by ENHHC) but not by the ETOH&MeOH process to increase the biofuel yields. However compared to conventional lignocellulosic ethanol production the enhancements are possible by this approach in both cases. Secondly, the excess heat and power from outside can be utilized effectively in these processes (in ENHHC with 136% HHV / 116% LHV) efficiency an in ETOH&MeOH with (89% HHV / 77% LHV) efficiency. Therefore, enhanced processes utilizing separate processing for the lignin and carbohydrate parts, especially the ENHHC, seem quite promising.

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Disclosure statement

No potential conflict of interest was reported by the authors.

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Appendix A

Table A1. The inputs for economic and GHG calculations.

Cost	Value	Unit
Raw material	25	Eur/MWh LHV
Electricity	45	Eur/MWh
Liquid biofuel produced	100	Eur/MWh LHV
External heat used	32	Eur/MWh
Gaseous biofuel produced	60	Eur/MWh LHV
Fossil gasoline	50	Eur/MWh LHV
Fossil natural gas	25	Eur/MWh LHV
Enzymes	15	% of biomass cost
Maintenance	3	% of fixed capital investment
Unacost present value factor	6.67	
Annuity factor	0.15	GHGHG
GHG feed wood biomass	3.89	eq. CO_2 g/MJ
GHG electricity used	129.2	eq. CO_2 g/MJ
GHG low temperature heat used	4.37	eq. CO_2 g/MJ
GHG fossil gasoline	92.33	eq. CO_2 g/MJ
GHG fossil natural gas	67.6	eq. CO_2 g/MJ
GHG SO_2g	268.8	eq. CO_2 g/kg
GHG ammoniag	2554.7	eq. CO_2 g/kg

Appendix B

Table B1. MeOH process heat duties.

Stream	Temperature	Pressure (bar)	Heat duty (MW)	Used for
Heat sinks/demand				
Reheating prior to MeOH reactor	82–230		16.3	
Process steam	220	10	55.6	–
Oxygen preheating	25–200		1.4	–
Distillation		1.6	23.5	–
Selexol regeneration	92–106		18.2	
Dryer	65–95		52.8	–
Methanol column feed preheating	25–31		0.2	
Heat sources				
Waste gas combustion	1839–260		21.8	Steam generation
Syngas reformer out	950–300		47.9	Steam generation
Methanol reactor cooling	270		21.6	Steam generation
Syngas after WGS out	339–125		21.3	Methanol column reboiler
Syngas after WGS out	125–118		5.2	Feed water preheating
Syngas after WGS out	118–65		19.4	Drying
Syngas after MeOH reactor	270–116		16.3	Reheating prior to MeOH reactor
Waste gas combustion	260–120		1.6	Drying
Syngas compressor intercooling	172–65		2.1	Drying
Methanol reactor outlet	116–65		14.0	Drying
Methanol column bottom product cooler	105–35		0.2	Preheating of feed

WGS: water gas shift.

Table B2. SNG process heat duties.

Stream	Temperature (°C)	Pressure (Bars)	Heat duty (MW)	Used for
Heat sinks				
Upgrading	510	80	0.1	–
Oxygen preheating	25–170		0.8	–
Process steam	177	10	33	–
Reheating prior methanation	160–230		14.0	
Selexol regeneration	106		19.8	
Dryer	65–95		52.8	–
Heat sources				
Syngas reformer out	950–300		45.7	Steam generation
Methanation reactors	600–250		22.1	Steam generation
Syngas after WGS out	350–135		15.2	Feed water preheating
Syngas after methanation	250–169		14.0	Reheating prior to methanation
Gas compressor	135–65		0.7	Drying
Syngas after WGS out	135–65		6.6	Drying

Table B3. ETOH&MeOH process heat duties.

Stream	Temperature (°C)	Pressure (Bars)	Heat duty case a (MW)	Heat duty case b (MW)	Used for
Heat sinks/demand					
Process steam	372	21	19.8	24.7	Steam explosion
Process steam	235	10	19.3	24.1	
Reheating prior to MeOH reactor	98–230		8.8	11	
Oxygen preheating	25–200		0.6	0.7	
MeOH distillation	120		9.3	11.7	
Stillage evaporation	128		11.8	14.8	
Product distillation	78		23.6	29.5	
Selexol regeneration	106		8.4	10.6	
Dryer	65–95		51.0	58.4	
Heat sources					
Waste gas combustion	1700–189		9.7	12.1	Steam generation
Biomass combustion	1324–189		50.0	0	Steam generation
Fluegas from biomass and gas combustion	189–101		3.8	0	
Syngas reformer out	950–300		22.3	28.0	Steam generation
Methanol reactor	270		10.1	12.6	Steam generation
Syngas after WGS out	330–128		8.5	10.6	Steam generation
Syngas after MeOH reactor	270–109		8.8	11	Reheating prior to MeOH reactor
Syngas after WGS out	124–98		8.2	10.3	Product column
Gas compressor	172–65		1.8	2.2	Drying
Syngas after MeOH reactor	97–79		2.9	3.7	Vacuum distillation
Syngas after MeOH reactor	79–65		2.2	2.8	Drying
MVR vapor condensation	113–78		6.9	8.7	Preheat of feed
Evaporation liquid condensate at 1 bar	99–65		2.7	3.3	Drying
MVR evaporation condensate 1 bar	78–65		3.3	4.4	Drying
Steam explosion recovery	148–138		7.1	8.9	Evaporation
Cooling before enzymatic hydrolysis	84–65		3.7	4.3	Drying
Condensate atm. distillation	100–84		6.2	7.7	Evaporation
External heat	106		–	10.6	Selexol
External heat	65		–	40	Lignin drying

Table B4. ENHHC process heat duties.

Stream	Temperature (°C)	Heat duty case a (MW)	Heat duty case b (MW)	Used for
Heat sinks/demand				
Process steam	177	4.0	4.0	Hydrocarbon distillation
Process steam	177	34.5	34.5	Gasification and reforming
Reheating prior methanation reactor	160–290	2.1	2.1	–
Oxygen preheating	25–177	0.6	0.6	–
Dryer	65–95	66.0	66.0	–
Selexol regeneration	106	13.5	13.5	
Feed water preheating	15–55	1.4	1.4	
Water circulation heating before hydrogenation	25–200	68.3	68.3	
Air preheating for gas combustion	25–230	4.0	NA	
Heat sources				
Gas combustion to steam	1700–300	39.4	NA	Steam generation
Gas combustion to air preheating	1700–189	4.0	NA	Air preheating
Gas combustion to drying	189–89	0.8	NA	Drying
Syngas reformer out	950–300	19.2	19.2	Steam generation
I Shift stage outlet cooling	453–300	7.7	/.7	Steam generation
II Shift stage outlet cooling	300–197	5.6	5.6	Steam generation, feed water preheating
II Shift outlet cooling	197–65	29.1	29.1	Drying
Partial methanation	600–300	5.8	5.8	Steam generation
Syngas after MeOH reactor	300–162	2.1	2.1	Reheating prior to MeOH reactor
Hydrogenation reactor cooling	250	1.8	1.8	Distillation
Liquid and vapor after hydrogenation reactor	250–124	68.3	68.3	
Liquid and vapor after hydrogenation reactor	124–65	18.0	18.0	
Hydrocarbon distillation condenser	124>65	2.2	2.2	
External heat for Selexol	106	–	9.4	
External heat for drying	>65	–	13.8	

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