Design and evaluation of biorefinery concepts

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 evaluation, process modelling
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 processrutiner från ekonomisk och miljösynpunkt är begränsad.

I detta arbete utvecklades en modelleringss metod och bedömningsmetod, som effektiverar processutveckling eftersom mera informerade beslut kan göras redan i processutvecklingskatedet. Först granskas 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 värmeintegrening. I beräkningarna ingick beräkning av energiutbyten av huvudprodukter och biprodukter, reduktion av växthusgaser och nettonuvarde (NPV). De valda processerna analyserades igen med noggrannare processmodeller. På första modelleringssnivån användes huvudprodukterns energiutbyte som en preliminär indikator för processens prestation med näjaktig noggrannhet. Skillnaderna mellan beräknade värdena för andra och tredje modelleringssnivån i indikatorerna som beskrev processen prestation d.v.s. utbyte av huvud och biprodukter, reducering av växthusgaser och nettonuvarde (NPV) var relativt små. Därför kunde prestationindicatoren räknade med andra modelleringssnivån processmodeller i de flesta fall användas i ett tidigt skede inom processutveckling.

Genom att använda den utvecklade modelleringssmetoden utvecklades också nya process koncept optimerad produktion av metanol, syntetisk naturgas eller kolvärme, 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 innamad värmever från omgivningen, det högsta utbytet av 72,5 % högsta minskning av växthusgaser and lästa kostnad av minskning av växthusgaser. Integrering till kombinerade eller enastående massa -och pappersbruk visade sig vara gynnsam eftersom processerna kunde använda tillgänglig värmever, bark och avsildt lignin från återvinningen av kemikalier vid cellulosaafbricker. De nya processerna kunde opereras i två tillstånd, antingen utan innamad energi från omgivningen på vintern eller på sommaren med inmatning av t.ex. solbaserad värmever eller el.

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

Nykkelord
Bioraffinaderier, teknökoekonomiska beräkningar, lignocellulosa-baserade biobränslen, processmodellering

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List of publications


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
\( C_{\text{cost}} \)  Production cost of a product
\( C_m \)  maintenance cost
\( D \)  Difference
\( FCI \)  Fixed capital investment
\( \text{GHG}_{\text{sav}} \)  GHG emission savings
\( i \)  internal rate
\( E_i \)  Produced amount of biofuel or other product by energy
\( f_s \)  una cost present value factor
\( n \)  Capacity exponent of plant
\( p \)  primary energy factor
\( S_i \)  Plant capacity
\( t_{\text{op}} \)  Annual operation time of plant

\( \alpha \)  chain growth probability or the probability in Fischer-Tropsch reaction
\( \eta \)  Energy fraction in production compared with raw material
\( \eta_p \)  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 polit 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 round wood 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 CO2 than would be the total CO2 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 spreadsheet)
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.
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 hy-
drogen, 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).](image)

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

<table>
<thead>
<tr>
<th>Process</th>
<th>Solid</th>
<th>Liquid</th>
<th>Gas</th>
</tr>
</thead>
<tbody>
<tr>
<td>Partial pyrolysis (torrefaction)</td>
<td>75 wt%</td>
<td>20 wt%</td>
<td>5 wt.</td>
</tr>
<tr>
<td>low temperature (250 -280°C)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>medium residence time (minutes)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Slow pyrolysis (carbonization)</td>
<td>35 wt%</td>
<td>30 wt%</td>
<td>35 wt%</td>
</tr>
<tr>
<td>low temperature (350-450°C)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>long residence time (hours)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fast pyrolysis (liquefaction)</td>
<td>12 wt.%</td>
<td>75 wt%</td>
<td>13 wt%</td>
</tr>
<tr>
<td>medium temperature (400 to 600°C)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>short residence time (seconds)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gasification</td>
<td>10 wt%</td>
<td>5 wt%</td>
<td>85 wt%</td>
</tr>
<tr>
<td>high temperature (750 to 1350 °C)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>variable residence time</td>
<td></td>
<td></td>
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</tbody>
</table>
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 H₂/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 H₂S of several hundred ppm, can be employed before gas cleaning (Kurkela and Simell,
Often the gas is washed in order to remove H₂S, CO₂, NH₃, 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, CH₄, CO₂ and H₂) 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 H₂S, COS, NH₃, 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.

![Modified block diagram of biomass for a gasification plant producing synthesis gas based on Simell et al. (2014).](image)

**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: H₂S, COS, NH₃, HCN, chlorides, tars etc. (Spath and Dayton, 2003).

Since the H₂/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, CO₂ 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 auto-hydrolysis 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 SO₂ 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 CO₂, CO, H₂ 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. Laaser 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, CO₂ 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.

<table>
<thead>
<tr>
<th>Component</th>
<th>Formula</th>
<th>Boiling point °C</th>
<th>Octane number</th>
<th>Cetane number</th>
<th>Vapour pressure KPa</th>
<th>Flash point °C</th>
<th>Lower heating value MJ/kg</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gasoline</td>
<td>C₄-C₁₂</td>
<td>30-190</td>
<td>95-98</td>
<td></td>
<td>45-90</td>
<td>&lt;0</td>
<td>43</td>
</tr>
<tr>
<td>Diesel</td>
<td>C₁₂-C₂₀</td>
<td>170-340</td>
<td>&gt;45</td>
<td>&lt;1</td>
<td>&gt;56</td>
<td>&gt;56</td>
<td>43</td>
</tr>
<tr>
<td>FAME</td>
<td>C₁₀H₂₀O₂</td>
<td>300-340</td>
<td>&gt;50</td>
<td>&gt;10</td>
<td>&gt;100</td>
<td>&gt;100</td>
<td>36</td>
</tr>
<tr>
<td>Methanol</td>
<td>CH₄O</td>
<td>64</td>
<td>122-133</td>
<td>32</td>
<td>7</td>
<td>20</td>
<td>20</td>
</tr>
<tr>
<td>Ethanol</td>
<td>C₂H₆O</td>
<td>78</td>
<td>121-130</td>
<td>8</td>
<td>16</td>
<td>13</td>
<td>27*</td>
</tr>
<tr>
<td>Dimethyl ether</td>
<td>C₂H₆O</td>
<td>24</td>
<td>-</td>
<td>55-60</td>
<td>-42</td>
<td>27.6-28.8</td>
<td>27.6-28.8</td>
</tr>
<tr>
<td>Paraffinic diesel e.g. FT diesel</td>
<td>C₁₂-C₂₀</td>
<td>180-360</td>
<td>80-110</td>
<td>&lt;1</td>
<td>&gt;56</td>
<td>43-44</td>
<td>43-44</td>
</tr>
<tr>
<td>E85***</td>
<td>~C₂₇H₅₂O₉₅</td>
<td>30-190</td>
<td>100</td>
<td>40-80</td>
<td>29.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dibutyl ether</td>
<td>C₈H₁₈O</td>
<td>141</td>
<td>91-100</td>
<td></td>
<td>25</td>
<td>42.8</td>
<td></td>
</tr>
<tr>
<td>Diethyl ether</td>
<td>C₄H₁₀O</td>
<td>35</td>
<td>140</td>
<td></td>
<td>-45</td>
<td>34.0**</td>
<td></td>
</tr>
<tr>
<td>Diethoxybutane</td>
<td>C₆H₁₈O</td>
<td>96.6</td>
<td></td>
<td>45</td>
<td>~34</td>
<td></td>
<td></td>
</tr>
<tr>
<td>N-butanol</td>
<td>C₅H₁₀OH</td>
<td>118</td>
<td>94</td>
<td>12</td>
<td>0.7 kPa</td>
<td>37</td>
<td>33.11</td>
</tr>
<tr>
<td>Isopropanol</td>
<td>C₃H₇OH</td>
<td>82.3</td>
<td>~100</td>
<td>17</td>
<td>4.4 kPa</td>
<td>30.15</td>
<td></td>
</tr>
<tr>
<td>MTHF</td>
<td>C₅H₁₀O</td>
<td>80</td>
<td>80</td>
<td>39</td>
<td>-11</td>
<td>32</td>
<td></td>
</tr>
<tr>
<td>Methane</td>
<td>CH₄</td>
<td>-161</td>
<td>130</td>
<td></td>
<td>Not applicable</td>
<td>-188</td>
<td>50</td>
</tr>
</tbody>
</table>

* 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)

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

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, NOx 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 Has-sim (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 emery 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 CO2. For example, CH4 and N2O 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.

\[
GHG_{\text{reduction}} = 1 - \left( \frac{GHG_{\text{biofuel}}}{GHG_{\text{substituting,fuel}}} \right) \quad (1)
\]

\[
\begin{align*}
GHG_{\text{reduction}} & = \text{Greenhouse gas reduction expressed in eq. CO}_2 \text{ emissions.} \\
GHG_{\text{biofuel}} & = \text{Greenhouse gas reduction expressed in eq. CO}_2 \text{ emissions.} \\
GHG_{\text{substituting,fuel}} & = \text{Greenhouse gas reduction expressed in eq. CO}_2 \text{ emissions.}
\end{align*}
\]

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.

\[
GHG_{\text{biofuel}} = GHG_{\text{trans}} + GHG_{\text{input}} + GHG_{\text{elec}} + GHG_{\text{heat}} \quad (2)
\]

\[
\begin{align*}
GHG_{\text{trans}} & = \text{the greenhouse gas emissions caused by fossil input in the biomass transport.} \\
GHG_{\text{input}} & = \text{the GHG emissions caused by inputs of chemicals and additives used in the process.} \\
GHG_{\text{elec}} & = \text{the GHG emissions of electricity input needed for the biofuel production. Produced excess electricity is subtracted.} \\
GHG_{\text{heat}} & = \text{the emissions caused by heat production. Produced excess heat is subtracted.}
\end{align*}
\]
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,

\[
NPV = f_s \left( \sum_{i=1}^{n} C_i - \sum_{j=1}^{n} C_j \right) - C_{FCI}
\]  

(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.

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

(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
- \( \alpha r \) = 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.

\[ C_{CO₂, red} = \frac{t_{op}(C_{cost} - C_{fossil})}{GHG_{sav}} \]  

In Equation 5,  
\[
\begin{align*}
C_{fossil} & = \text{the prices of the fossil fuels in eur/h} \\
C_{cost} & = \text{the prices of the biofuels in eur/h,} \\
t_{op} & = \text{annual operation hrs of plant 8000 h/a,} \\
GHG_{sav} & = \text{the reduction of equivalent greenhouse gas emissions t/a when biofuel replaces the corresponding fossil fuel.}
\end{align*}
\]

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.

\[ \eta = \frac{(E_{gas,fuel} + E_{liq,fuel} + E_{chem,prod} + E_{elec,output})}{(E_{biomass} + E_{ext,heat} + E_{elec,input})} \]  

where

\[
\begin{align*}
\eta & = \text{the efficiency to fuels and chemicals with LHV or HHV.} \\
E_{gas,fuel} & = \text{the energy of gaseous fuel produced by the corresponding heating value.} \\
E_{liq,fuel} & = \text{the energy content of liquid-produced fuel.} \\
E_{chem,prod} & = \text{the energy content for the chemical product.}
\end{align*}
\]
\[ E_{\text{elect, output}} = \text{the excess electricity amount obtained as byproduct if all the electricity generated is not used.} \]

\[ E_{\text{biomass}} = \text{the corresponding energy of the feedstock for the corresponding heating value. Produced excess electricity or heat is subtracted.} \]

\[ E_{\text{ext, heat}} = \text{the energy of external low temperature heat fed to the process} \]

\[ E_{\text{elec, input}} = \text{the input of external electricity to the process.} \]

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.

\[ \eta_p = \frac{E_{\text{fuel, tot}}}{E_{\text{biomass}}E_{\text{biomass}} + E_{\text{elec}}E_{\text{elec}} + E_{\text{sec, heat}}E_{\text{sec, heat}}} \quad (7) \]

- \( \eta_p \) = the primary energy efficiency
- \( E_{\text{fuel, tot}} \) = the total amount of fuel produced in each process including both liquid and gaseous fuel on a higher heating value basis.
- \( E_{\text{elec}} \) = the amount of electricity needed (negative if excess electricity is produced as byproduct).
- \( E_{\text{sec, heat}} \) = 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 be 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 \( \theta \leq x \leq 1 \), 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.
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 H₂/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 C5/C6 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.
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 H₂) 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 H₂/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.

![Image of energy yields from synthesis gas into products.](image_url)

**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 $\leq 10\%$ for synthesis gas and $\leq 20\%$ for all other process routes, except $\pm 10\%$ 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.
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 ºC 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 Gambard, (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 SO2 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).

<table>
<thead>
<tr>
<th>Heat Generation</th>
<th>Heat and Power usage</th>
<th>Power Plant</th>
<th>Sold</th>
</tr>
</thead>
<tbody>
<tr>
<td>Black liquor boiler</td>
<td>Bark boiler</td>
<td>Pulp mill.</td>
<td>Paper mill</td>
</tr>
<tr>
<td>Heat MW</td>
<td>375.0</td>
<td>87.5</td>
<td>187.5</td>
</tr>
<tr>
<td>Power MW</td>
<td>41.3</td>
<td>48.8</td>
<td>90.0</td>
</tr>
</tbody>
</table>

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.

<table>
<thead>
<tr>
<th>Process</th>
<th>Input/MW</th>
<th>Output/MW</th>
<th>LHV %</th>
<th>Note</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Wood</td>
<td>Power</td>
<td>Biofuel</td>
<td>Pellet</td>
</tr>
<tr>
<td>FT alone</td>
<td>351</td>
<td>0</td>
<td>169</td>
<td>0</td>
</tr>
<tr>
<td>EtOH alone</td>
<td>372</td>
<td>0</td>
<td>122</td>
<td>120</td>
</tr>
<tr>
<td>Integrated FT</td>
<td>200</td>
<td>32</td>
<td>169</td>
<td>0</td>
</tr>
<tr>
<td>Integrated EtOH</td>
<td>300</td>
<td>22</td>
<td>122</td>
<td>120</td>
</tr>
<tr>
<td>Integrated EtOH+FT</td>
<td>300</td>
<td>23</td>
<td>190</td>
<td>0</td>
</tr>
</tbody>
</table>

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 bio-mass 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, stand-alone 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.

<table>
<thead>
<tr>
<th>Case</th>
<th>Description</th>
<th>Subcases</th>
<th>Novelty</th>
</tr>
</thead>
<tbody>
<tr>
<td>MeOH</td>
<td>Conventional methanol production by gasification and conversion of synthesis gas to methanol</td>
<td>No subcases</td>
<td>Conventional process</td>
</tr>
<tr>
<td>SNG</td>
<td>Conventional synthetic natural gas production by gasification and conversion of synthesis gas to methane.</td>
<td>No subcases</td>
<td>Conventional process</td>
</tr>
<tr>
<td>EtOH</td>
<td>Conventional bioethanol production by steam explosion pre-treatment and heat and power production by combustion of residual lignin.</td>
<td>No subcases</td>
<td>Conventional process</td>
</tr>
</tbody>
</table>
| 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) Employing 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) Employing 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) Employing 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 ENNHC. 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\textsubscript{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\textsubscript{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\textsubscript{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.

**ENHHHC 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 gas-
ification of the lignin residue. Next, water, solids and hydrocarbons are sepa-
rated and hydrocarbons are distilled. Lignin is recovered and sent to gasifica-
tion.

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 ear-
ier. 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 com-
bined to calculate the overall energy balances.

The energy content of the raw material was obtained from the excess heat cal-
culated 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 pre-heating 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.

\[
    f_S = \frac{(1+i)^n - 1}{i(1+i)^n}
\]

where

- \( f_S \) = 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.

![Performance Criteria Indicator Values](image)

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 ENHHHCb) 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 ENHHHCb 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 CO2 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 de-
sign 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 pro-
cesses 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 fea-
sible due to economic uncertainties. In addition, some of the complex opera-
tions 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 produc-
tion. The feed water and feed water make-up were pre-heated for steam produc-
tion. 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
table.

**MeOH process**

A steam level of 48 bar was chosen to allow the utilization of the heat from meth-
anol 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. Sub-
sequently the rest of the steam was expanded to 1.75 bar, and used for the re-
generation 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 sub-
case '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 produc-
tion 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&MeOH process**

In the EtOH&MeOH process, a similar product energy yield (57 %) was obtained as that found earlier in the methanol process (58 %); see Table 7. Here a consistency 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 de-watered 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&MeOH 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 pre-treatment 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.](image)

![Figure 16 Savings in GHG emissions vs. NPV for the calculated processes](image)
Table 7. Key performance data of the studied processes.

<table>
<thead>
<tr>
<th>Cases</th>
<th>Unit</th>
<th>MeOH</th>
<th>SNG</th>
<th>EtOH &amp; MeOH a</th>
<th>EtOH &amp; MeOH b</th>
<th>ENHHCa</th>
<th>ENHHCb</th>
</tr>
</thead>
<tbody>
<tr>
<td>Biomass feed input rate</td>
<td>(LHV) MW</td>
<td>300</td>
<td>300</td>
<td>300</td>
<td>300</td>
<td>300</td>
<td>300</td>
</tr>
<tr>
<td>Liquid output rate</td>
<td>(LHV) MW</td>
<td>171.9</td>
<td>-</td>
<td>167.7</td>
<td>214.8</td>
<td>137.0</td>
<td>137</td>
</tr>
<tr>
<td>Gaseous fuel output rate (LHV)</td>
<td>MW</td>
<td>0</td>
<td>210.5</td>
<td>0</td>
<td>0</td>
<td>61.9</td>
<td>101.8</td>
</tr>
<tr>
<td>Total energy flow content of fuels</td>
<td>(LHV) MW</td>
<td>171.9</td>
<td>210.5</td>
<td>167.7</td>
<td>214.8</td>
<td>198.9</td>
<td>238.8</td>
</tr>
<tr>
<td>Electricity surplus</td>
<td>MW</td>
<td>2.5</td>
<td>-1.90</td>
<td>3.3</td>
<td>-7.5</td>
<td>5.0</td>
<td>-6.0</td>
</tr>
<tr>
<td>Additional heat flow inputs as low temperature heat</td>
<td>MW</td>
<td>0.0</td>
<td>0.00</td>
<td>0.0</td>
<td>50.0</td>
<td>0.0</td>
<td>23.2</td>
</tr>
<tr>
<td>Energy yield of products with heat and power</td>
<td>LHV %</td>
<td>58.1</td>
<td>69.7</td>
<td>57.0</td>
<td>60.1</td>
<td>68.0</td>
<td>72.5</td>
</tr>
<tr>
<td>NPV</td>
<td>MEUR</td>
<td>103</td>
<td>-115</td>
<td>-38</td>
<td>102</td>
<td>121</td>
<td>182</td>
</tr>
<tr>
<td>Production cost</td>
<td>EUR/MWh</td>
<td>89</td>
<td>70</td>
<td>104</td>
<td>93</td>
<td>76</td>
<td>69</td>
</tr>
<tr>
<td>eq. GHG reduced</td>
<td>kt. CO₂/a</td>
<td>433</td>
<td>369</td>
<td>389</td>
<td>467</td>
<td>470</td>
<td>504</td>
</tr>
<tr>
<td>GHG reduction cost</td>
<td>EUR/t CO₂</td>
<td>282</td>
<td>320</td>
<td>360</td>
<td>336</td>
<td>258</td>
<td>260</td>
</tr>
<tr>
<td>The difference of GHG reduction cost and reference fuel cost¹</td>
<td>EUR/t CO₂</td>
<td>123</td>
<td>206</td>
<td>187</td>
<td>158</td>
<td>115</td>
<td>111</td>
</tr>
</tbody>
</table>

¹) 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 ENHCCa 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&MeOH\textsubscript{b} 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 ENHHC\textsubscript{a}, since low-cost waste heat and power can be utilised in case \textit{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\textsubscript{2} eq., are obtained in the ENHHC\textsubscript{a} 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 \textit{b} processes.

The GHG reduction costs when a tonne of CO\textsubscript{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 ENHHC\textsubscript{a} processes (111 and 115 Eur/t CO\textsubscript{2} 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 \textit{b} produces 1.6 times the amount of gaseous products compared to ENHHC\textsubscript{a}. 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 CH₄ and C₂H₄ 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.

<table>
<thead>
<tr>
<th>Model level</th>
<th>MOH</th>
<th>SNG</th>
<th>ETOH</th>
<th>ETOH&amp;MOH</th>
<th>ETOH&amp;MOH</th>
<th>ENHMOHa</th>
<th>ENHMOHb</th>
<th>ENHSNGa</th>
<th>ENHSNGb</th>
<th>ENHHCa</th>
<th>ENHHCb</th>
<th>Av</th>
<th>STDAV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unit</td>
<td>%</td>
<td>%</td>
<td>%</td>
<td>%</td>
<td>%</td>
<td>%</td>
<td>%</td>
<td>%</td>
<td>%</td>
<td>%</td>
<td>%</td>
<td>%</td>
<td>%</td>
</tr>
<tr>
<td>1</td>
<td>73.4</td>
<td>65.3</td>
<td>45.7</td>
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<td>84.9</td>
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<td>83.3</td>
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<td>86</td>
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<tr>
<td>2</td>
<td>61.5</td>
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<td>68.0</td>
<td>72.5</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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: (2\textsuperscript{nd} level – 3\textsuperscript{rd} level).

<table>
<thead>
<tr>
<th>Process</th>
<th>$D_{he}^1$</th>
<th>$D_{fche}^2$</th>
<th>$D_{cw}^3$</th>
<th>$D_{fgdry}^4$</th>
<th>$D_{sel}^5$</th>
<th>$D_{dist}^6$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unit</td>
<td>MW</td>
<td>MW</td>
<td>MW</td>
<td>MW</td>
<td>MW</td>
<td>MW</td>
</tr>
<tr>
<td>MeOH</td>
<td>0.0</td>
<td>-21.6</td>
<td>-3.9</td>
<td>-2.9</td>
<td>3.0</td>
<td>4.5</td>
</tr>
<tr>
<td>SNG</td>
<td>0.0</td>
<td>-0.2</td>
<td>-1.7</td>
<td>0.0</td>
<td>3.3</td>
<td>0</td>
</tr>
<tr>
<td>EtOH&amp;MeOHa</td>
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<td>12.6</td>
<td>-3.3</td>
<td>5.7</td>
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</tr>
<tr>
<td>EtOH&amp;MeOHb</td>
<td>-17.3</td>
<td>24.7</td>
<td>-17.4</td>
<td>-2.9</td>
<td>2.3</td>
<td>31.5</td>
</tr>
<tr>
<td>ENHHCa</td>
<td>0.0</td>
<td>9.1</td>
<td>3.4</td>
<td>-0.9</td>
<td>6.1</td>
<td>-2.2</td>
</tr>
<tr>
<td>ENHHCb</td>
<td>-0.4</td>
<td>-0.8</td>
<td>3.4</td>
<td>0.0</td>
<td>6.1</td>
<td>-2.2</td>
</tr>
<tr>
<td>Average value</td>
<td>11.2</td>
<td>-3.3</td>
<td>4.2</td>
<td>12.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Standard deviation</td>
<td>10.7</td>
<td>7.6</td>
<td>1.6</td>
<td>19.3</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th>Process</th>
<th>$D_{pc}^1$</th>
<th>$D_{rp}^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unit</td>
<td>MW</td>
<td>MW</td>
</tr>
<tr>
<td>MeOH</td>
<td>-6.9</td>
<td>-4.6</td>
</tr>
<tr>
<td>SNG</td>
<td>-6.8</td>
<td>-4.8</td>
</tr>
<tr>
<td>EtOH&amp;MeOHa</td>
<td>-4.9</td>
<td>-2.7</td>
</tr>
<tr>
<td>EtOH&amp;MeOHb</td>
<td>-3.5</td>
<td>-2.7</td>
</tr>
<tr>
<td>ENHHCa</td>
<td>-4.8</td>
<td>-3.4</td>
</tr>
<tr>
<td>ENHHCb</td>
<td>-6.3</td>
<td>-3.4</td>
</tr>
<tr>
<td>Average value</td>
<td>-5.5</td>
<td>-3.6</td>
</tr>
<tr>
<td>Standard deviation [%] of the absolute value of average value</td>
<td>24.4</td>
<td>25.3</td>
</tr>
</tbody>
</table>

1) $D_{pc} = $ Power consumption difference (2\textsuperscript{nd} level – 3\textsuperscript{rd} level)
2) $D_{rp} = $ Refrigeration power demand differences (2\textsuperscript{nd} level – 3\textsuperscript{rd} 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 ENHHHCb 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 2\textsuperscript{nd} level ENHHCb resulted in a slightly higher GHG reduction compared to trend, whereas the 3\textsuperscript{rd} 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.

\subsection*{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 1\textsuperscript{st} and 2\textsuperscript{nd} levels are compared with those on the 3\textsuperscript{rd} level (Table 11). On 2\textsuperscript{nd} 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 1\textsuperscript{st} level both average relative differences were about 30 \%, when the same FCI is used in the 2\textsuperscript{nd} and 3\textsuperscript{rd} 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 2\textsuperscript{nd} level 12 \% and on the 1\textsuperscript{st} level a very large 77 \%. The conclusion of the calculation is that, the 1\textsuperscript{st} 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.

<table>
<thead>
<tr>
<th>Process</th>
<th>$D_{LHV23}$</th>
<th>$D_{GHG23}$</th>
<th>$D_{FCI23}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>MeOH</td>
<td>5.9%</td>
<td>-1.4%</td>
<td>9.3%</td>
</tr>
<tr>
<td>SNG</td>
<td>-2.4%</td>
<td>32.2%</td>
<td>-6.9%</td>
</tr>
<tr>
<td>EtOH&amp;MeOHa</td>
<td>1.9%</td>
<td>-4.1%</td>
<td>8.8%</td>
</tr>
<tr>
<td>EtOH&amp;MeOHb</td>
<td>16.3%</td>
<td>12.5%</td>
<td>29.7%</td>
</tr>
<tr>
<td>ENHHCa</td>
<td>-0.6%</td>
<td>4.3%</td>
<td>-15.8%</td>
</tr>
<tr>
<td>ENHHCb</td>
<td>-2.3%</td>
<td>13.3%</td>
<td>-1.5%</td>
</tr>
<tr>
<td>Average of absolute values of differences</td>
<td>4.9%</td>
<td>11.3%</td>
<td>12.0%</td>
</tr>
<tr>
<td>Standard deviation [%] of absolute values of average value of differences</td>
<td>119.5%</td>
<td>100.2%</td>
<td>81.8%</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Process</th>
<th>$D_{LHV13}$</th>
<th>$D_{GHG13}$</th>
<th>$D_{FCI13}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>MeOH</td>
<td>26.3%</td>
<td>27.5%</td>
<td>17.0%</td>
</tr>
<tr>
<td>SNG</td>
<td>-10.8%</td>
<td>25.5%</td>
<td>-22.5%</td>
</tr>
<tr>
<td>EtOH&amp;MeOHa</td>
<td>48.9%</td>
<td>66.0%</td>
<td>129.1%</td>
</tr>
<tr>
<td>EtOH&amp;MeOHb</td>
<td>41.3%</td>
<td>37.9%</td>
<td>94.1%</td>
</tr>
<tr>
<td>ENHHCa</td>
<td>26.5%</td>
<td>38.7%</td>
<td>124.3%</td>
</tr>
<tr>
<td>Average of absolute values of differences</td>
<td>30.8%</td>
<td>39.1%</td>
<td>77.4%</td>
</tr>
<tr>
<td>Standard deviation [%] of absolute values of average value of differences</td>
<td>48.1%</td>
<td>41.3%</td>
<td>70.2%</td>
</tr>
</tbody>
</table>

1) $D_{LHV23} = (LHV_2 - LHV_3)/LHV_3$
2) $D_{GHG23} = (GHG_2 - GHG_3)/GHG_3$
3) $D_{FCI23} = (NPV_3 - NPV_2)/FCI$
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 LHV, 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. Al-
ternatively, 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.

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

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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 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. CO₂/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. CO₂/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.

<table>
<thead>
<tr>
<th></th>
<th>Level 1</th>
<th>Level 2</th>
<th>Level 3</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Description</strong></td>
<td>Simple material balance model; Paper II</td>
<td>Simplified flowsheet model; Paper III</td>
<td>Simplified flowsheet model; Paper IV</td>
</tr>
<tr>
<td><strong>Process routes</strong></td>
<td>Approximately 40 process routes based on gasification, fermentation and sugar chemical conversion</td>
<td>Fischer-Tropsch production and ethanol based on literature</td>
<td>11 cases: methanol production, SNG, ethanol with CHP, ethanol&amp; methanol, enhanced methanol and SNG, enhanced hydrocarbon production</td>
</tr>
<tr>
<td><strong>Raw materials</strong></td>
<td>pine, spruce, black alder, aspen, birch, sugarcane bagasse, larch, wheat straw and pyrolysis oil</td>
<td>spruce</td>
<td>pine</td>
</tr>
<tr>
<td><strong>Reactions</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Sugar conversions (fermentation and chemical conversion)</strong></td>
<td>100 %</td>
<td>literature yield</td>
<td>literature yield</td>
</tr>
<tr>
<td>Description</td>
<td>Level 1</td>
<td>Level 2</td>
<td>Level 3</td>
</tr>
<tr>
<td>-------------------------------------------------------</td>
<td>-------------------------------------------------------------------------</td>
<td>-------------------------------------------------------------------------</td>
<td>-------------------------------------------------------------------------</td>
</tr>
<tr>
<td>Description</td>
<td>Simple material balance model; Paper II</td>
<td>Simplified flowsheet model; Paper III</td>
<td>Rigorous flowsheet model; Paper V</td>
</tr>
<tr>
<td>Gasification</td>
<td>chemical equilibrium by Gibbs free energy minimization</td>
<td>chemical equilibrium by Gibbs free energy minimization</td>
<td>chemical equilibrium by Gibbs free energy minimization with correction for methane content</td>
</tr>
<tr>
<td>Reforming</td>
<td>chemical equilibrium by Gibbs free energy minimisation</td>
<td>chemical equilibrium by Gibbs free energy minimisation</td>
<td>chemical equilibrium by Gibbs free energy minimisation</td>
</tr>
<tr>
<td>Water gas shift reaction (WGSR)</td>
<td>WGSR: conversion reactor where the conversion is adjusted for suitable H₂/CO ratio</td>
<td>WGSR: conversion reactor where the conversion is adjusted for suitable H₂/CO ratio</td>
<td>WGSR: conversion adjusted for suitable H₂/CO ratio</td>
</tr>
<tr>
<td>Thermochemical reactions other than WGSR</td>
<td>100 % selectivity and conversion</td>
<td>FT reaction conversion specified</td>
<td>MeOH conversion lower than chemical equilibrium.</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table B. Models used at the modelling levels separations and energy integration.

<table>
<thead>
<tr>
<th>Models</th>
<th>Level 1</th>
<th>Level 2</th>
<th>Level 3</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Simple material balance model; paper II</td>
<td>Simplified flowsheet model, paper III</td>
<td>Rigorous flowsheet model, paper V</td>
</tr>
<tr>
<td>Separations</td>
<td>Acid gas removal not considered</td>
<td>acid gas removal adsorption medium (Selexol) with only pressure reduction for regeneration</td>
<td>acid gas removal adsorption medium (Selexol) with fixed duty per kg acid gas removed</td>
</tr>
<tr>
<td></td>
<td>Evaporation not considered according to literature data</td>
<td>fixed heat demand per tonne of water evaporated in the evaporator</td>
<td>multi-effect evaporator model</td>
</tr>
<tr>
<td>Drying</td>
<td>drying heat requirement not considered (biomass dried to 13 wt%)</td>
<td>heat demand not calculated</td>
<td>direct drying with hot water with a heat demand of 4 MJ/kg of water evaporated</td>
</tr>
<tr>
<td>Models</td>
<td>Level 1</td>
<td>Level 2</td>
<td>Level 3</td>
</tr>
<tr>
<td>--------</td>
<td>---------</td>
<td>---------</td>
<td>---------</td>
</tr>
<tr>
<td>Simple material balance model; paper II</td>
<td>Simplified flowsheet model, paper III</td>
<td>Simplified flowsheet model, paper IV</td>
<td>Rigorous flowsheet model, paper V</td>
</tr>
<tr>
<td>Distillation and condensation</td>
<td>ideal separation with 100% product recovery</td>
<td>reported literature data for EtOH case; separation of FT product by condensation</td>
<td>Aspen ‘Distl’ model with Edminster approach</td>
</tr>
<tr>
<td>Energy related operations</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Heat integration</td>
<td>not considered</td>
<td>maximum heat recovery based on heating and cooling demand, calculated based on literature data for ethanol case and simulation for FT case</td>
<td>maximum heat recovery based on heating and cooling demand</td>
</tr>
<tr>
<td>Heat and power production</td>
<td>not considered</td>
<td>calculated for a power plant based on heat/power ratios, no pre-heating of feed water and superheating of steam</td>
<td>steam production and power production when excess heat available</td>
</tr>
<tr>
<td>Power consumption in process</td>
<td>not considered</td>
<td>compressors and oxygen production</td>
<td>compressors and oxygen production</td>
</tr>
</tbody>
</table>
Table C. Updated data from Paper II Table 1 to thesis summary, yellow values are updated.

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

<table>
<thead>
<tr>
<th></th>
<th>CONVENTIONAL PROCESSES</th>
<th>ENHANCED PROCESS CONCEPTS</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>MEOH Case</td>
<td>SNG Case</td>
</tr>
<tr>
<td>Biomass feed (HHV) and</td>
<td>320.5/300</td>
<td>320.5/300</td>
</tr>
<tr>
<td>Liquid fuel output (HHV) and</td>
<td>197.9/174.0</td>
<td>-</td>
</tr>
<tr>
<td>Gaseous fuel output (HHV)</td>
<td>22.2/19.5</td>
<td>233.3/210.3</td>
</tr>
<tr>
<td>Furfural output (HHV) and</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>Total heating value of fuels and</td>
<td>220.2/193.5</td>
<td>223.3/210.3</td>
</tr>
<tr>
<td>Electricity surplus MW</td>
<td>-14.5</td>
<td>-10.12</td>
</tr>
<tr>
<td>External low temperature heat</td>
<td>0.0</td>
<td>0.00</td>
</tr>
<tr>
<td>Fuel &amp; chemical product effi-</td>
<td>65.7/61.5</td>
<td>70.7/68.0</td>
</tr>
<tr>
<td>Main product efficiency (HHV)</td>
<td>59.1/55.0</td>
<td>70.7/68.0</td>
</tr>
<tr>
<td>Primary energy efficiency %</td>
<td>55.4</td>
<td>60.4</td>
</tr>
<tr>
<td>Carbon footprint (g CO₂)</td>
<td>83.0</td>
<td>87.3</td>
</tr>
<tr>
<td>GHG emissions saved kt CO₂</td>
<td>427</td>
<td>488</td>
</tr>
<tr>
<td>Net present value (NPV) MEur</td>
<td>136</td>
<td>137</td>
</tr>
<tr>
<td>Fixed capital investment MEur</td>
<td>350</td>
<td>320</td>
</tr>
</tbody>
</table>

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