THESIS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

Process integration studies on Kraft pulp-mill-based biorefineries producing ethanol

RICKARD FORNELL

Heat and Power Technology
Department of Energy and Environment
CHALMERS UNIVERSITY OF TECHNOLOGY

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Department of Energy and Environment
Chalmers University of Technology
SE-412 96 Göteborg
Sweden
Telephone + 46(0)31-772 1000

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ABSTRACT
Large scale, sustainable production of biofuels will require commercialization of processes using lignocellulosic feedstocks. These processes are still not competitive with existing pathways, however. The competitiveness of lignocellulosic biofuel production plants could potentially be improved if they were integrated with already existing facilities. One such example being explored currently is connected to the fact that the pulping industry is showing a growing interest in expanding their product portfolio, namely the complete or partial conversion of pulp mills into biorefineries for production of transport fuels.

The objective of the work presented in this thesis has been to study different potential biorefinery concepts connected to chemical pulping, and more specifically the Kraft pulping process. Three different process combinations have been assessed in the project; a process where a Kraft pulp mill is repurposed to ethanol production (no pulp is produced), a process where ethanol and di-methyl-ether is produced in a repurposed Kraft pulp mill, and finally a process where an ethanol plant is co-located with a modern Kraft pulp mill.

The findings from the studies reveal that an increasing degree of heat integration leads to a lower production cost of ethanol both if the ethanol plant is based on a repurposed mill and if the plant is co-located with a modern mill. In the ethanol- and di-methyl-ether process, which has much higher conversion efficiency from feedstock to biofuel than the other processes, it was shown that the process could be competitive with the other combinations in terms of production cost, if the biofuel price is high and if the biorefinery is perceived as a low risk investment.

Keywords: Biorefinery, Process integration, Ethanol, Kraft pulp mill, Energy efficiency, Biofuels

The thesis is based on the following papers:

I. Rickard Fornell, Thore Berntsson. Techno-economic analysis of energy efficiency measures in a pulp mill converted to an ethanol plant. *Nordic Pulp and Paper Research Journal, 24(2); 183-192; 2009.*

II. Rickard Fornell, Thore Berntsson. Process integration study of a Kraft pulp mill converted to an ethanol production plant – Part A: Potential for heat integration of thermal separation units. *Applied Thermal Engineering, 35, 81-90, 2012.*

III. Rickard Fornell, Thore Berntsson, Anders Åsblad. Process integration study of a Kraft pulp mill converted to an ethanol production plant – Part B: Techno-economic analysis. *Article in Press, Applied Thermal Engineering.*

IV. Rickard Fornell, Thore Berntsson, Anders Åsblad. Techno-economic analysis of a Kraft pulp mill based biorefinery producing both ethanol and DME. *Submitted for publication.*

V. Rickard Fornell, Thore Berntsson, Anders Åsblad, Anna von Schenck. Heat integration opportunities for a combined lignocellulosic ethanol and Kraft pulping process. *Submitted for publication.*

Papers not included in the thesis:

Rickard Fornell, Thore Berntsson. Possibilities for lignin extraction versus maximized power production in a process integrated pulp mill converted to ethanol production plant. *11th Conference on Process Integration, Modelling and Optimisation for Energy Saving and Pollution Reduction PRES, 24-28 August 2008, Prague, Czech Republic.*

Rickard Fornell, Thore Berntsson. Heat integration analysis of thermal separation units in a pulp mill converted to an ethanol production plant. *Proceedings 22nd International Conference on Efficiency, Cost, Optimisation, Simulation and Environmental impact of Energy Systems ECOS 2009, Aug 31 – Sep 3, Foz do Iguacu, Brazil.*

Rickard Fornell, Karin Pettersson, Thore Berntsson. Preliminary Design and Energy Efficiency Analysis of a Kraft Pulp Mill Converted to a Biorefinery Producing Ethanol and DME from Softwood. *Chemical Engineering Transactions, 21, 2010*

Statement of the author's contribution

Rickard Fornell has been the main author of all papers. Thore Berntsson (all papers) and Anders Åsblad (Papers III-V) supervised the work. Anna von Schenck contributed with the introduction in Paper V.

TABLE OF CONTENTS

1 Introduction

The International Panel on Climate Change (IPCC) states that if society only focuses on adaptation to the impacts of climate change during the next century, this would come with a very high cost to both society and the environment. Only focusing on mitigation of greenhouse gas emissions would also not be enough, however. Both these issues (i.e. adaptation and mitigation) would most likely need to be addressed to reduce the hazards of climate change. Mitigation efforts can, according to the IPCC, be implemented by using technologies that are either currently available or expected to be commercialised in the near future. Figure 1.1 shows the results of different mitigation measures from four different climate models (IMAGE, MESSAGE, AIM, IPAC) that aim at stabilizing the CO_2 concentration at 650ppm or 490-540ppm [1].

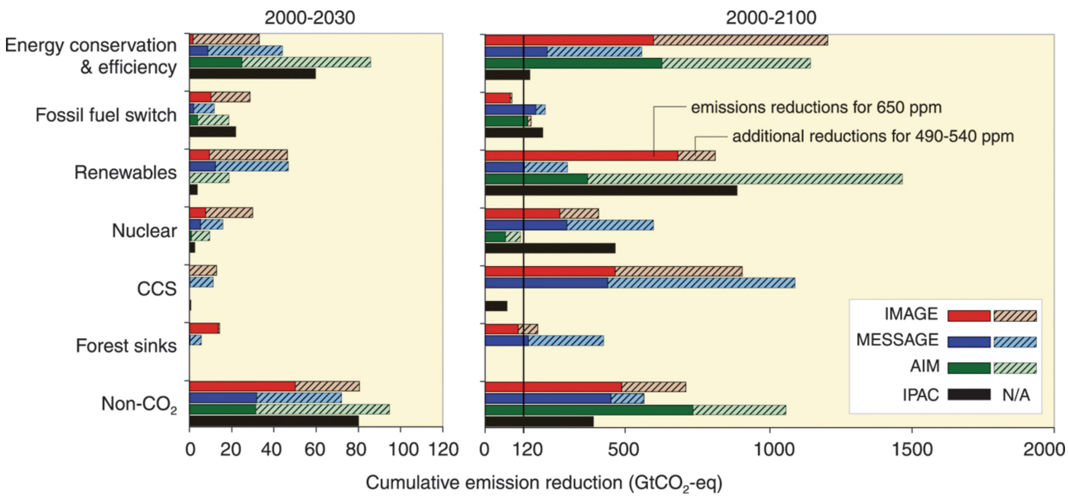

Figure 1.1. Cumulative Greenhouse gas emission reductions due to mitigation measures according to different forecast models (Figure 3.23 in IPCC AR4 WG III [2]).

As can be seen in Figure 1.1, improving the efficiency in which energy is used in all sectors of society can play a critical role in issues of energy security, environmental impact, and achieving sustainability. According to the International Energy Agency (IEA) improving energy efficiency is a priority for all countries. The IEA has produced a number of recommended actions ranging over a multitude of priority areas, which it has estimated to potentially save about 7.6 Gt CO_2 / year by 2030 (1.5 times current US annual CO_2 emissions) [3]. Within the European Union (EU) work on improving energy efficiency has intensified in recent years. For example, a project called the Energy Efficiency Watch Project was initiated in 2006. It focuses on promoting energy efficiency across Europe, and in 2007-2008 National Energy Efficiency Plans (NEEAPs) were published by member states [4].

In the industrial sector there is great potential to improve energy efficiency. Since the industrial sector accounts for one-third of the total global primary energy supply and 36% of global CO_2 emissions these potential improvements will make a difference if implemented [5]. Actions needed according to the IEA are, e.g., improving the energy performance of electric motors, and improving energy management in industry at different levels of the energy system. The IEA says that it is important to coordinate policies in order to address barriers to energy efficiency that include high initial capital costs, discount rates, and difficulties in quantifying external benefits.

This thesis presents studies of energy efficiency measures related to the pulp and paper industry and biorefineries that produce transport fuels. The central theme is the focus on 2nd generation ethanol production and the integration of this process concept with a Kraft pulp mill. The following part of this chapter includes a short introduction to the two industrial branches that are merged in this project.

Kraft pulping – yesterday, today and tomorrow

The Kraft pulping process was patented in 1884 in Germany. In 1890 the first Kraft pulp mill started in Sweden. When the Tomlinson boiler was invented in the 1930´s the Kraft process grew in strength since this boiler led to the possibility to recover and reuse the inorganic pulping chemicals in the process. Since then the Kraft process has become the leading chemical pulping process.

In a global context, a shift in the capacity for Bleached Hardwood and Softwood Kraft Pulp has occurred in recent years. The traditionally strong pulping countries in North America and northern Europe are experiencing a decrease in capacity for these pulps (Figure 1.2).

Figure 1.2. Capacity closures (including idled plants) in northern Europe and North America 2007-2009 (green = Hardwood, brown = softwood). [6]

Modern pulp mills that use low cost raw materials are being built in other parts of the world and give these countries an edge in terms of production cost. The difference in raw material cost is substantial; in a presentation by Jokinen (2009) the softwood prices in Scandinavia are the highest in the world. A pulp mill in South America had to pay less than one third of the price in Scandinavia for the raw material. In North America the price was about 50% lower than in Scandinavia, but due to other costs the Bleached Softwood Kraft Pulp price in North America was similar to Scandinavia. The pulp price for the "best mills" in South America was 50% lower than in North America and Scandinavia [6]. This is one of the reasons why traditionally strong pulping countries have begun to focus on finding new ways of processing forest material into profitable products. Since it is difficult to compete with the price of raw material and labour, other products than pulp are currently being explored.

If new ideas were implemented the benefit would be large; for example, the synergetic effects of using existing infrastructure, process units and knowledge could be an important factor for the commercialisation of 2nd generation biofuel production.

Ethanol production – yesterday, today and tomorrow

Ethanol is not a new transport fuel. Early in the beginning of the automotive era cars were built to run on this alcohol. During the First World War ethanol was used as fuel in the US, and before tetraethyl lead was introduced by the automotive industry, ethanol played an important role as an octane enhancer. Lead-enhanced gasoline was shown to be cheaper and easier to produce than ethanol, however, and in the aftermath of the Second World War ethanol was disregarded while the use of fossil fuels began to dominate the transport sector.

When tetraethyl lead was phased out in the US in the mid 80´s MTBE dominated the market as an octane enhancer. In the early 21st century ethanol production and use in the US began to grow rapidly. The main reasons for this were that MTBE was banned in many states, and that the Energy Policy Act of 2005 stated an oxygen requirement in reformulated gasoline, which could be met by blending in ethanol [7].

In Brazil ethanol has been blended in gasoline since the early 20th century. As early as 1931 a compulsory blend of 5% was implemented by the government in order to reduce dependence on foreign petroleum fuels, as well as to make use of excess production in the sugar industry. Until 1975 the blend of ethanol in gasoline in Brazil was fairly constant at 5%. Due to the oil crisis Brazil started up a program in order to increase the amount of indigenous automotive fuel used in its car fleet. Sugar cane ethanol was subsidized and the production in Brazil increased rapidly. In 1985 approximately 8 billion litres of ethanol was being produced. In the 90´s the ethanol industry in Brazil experienced tougher times and much of the subsidies and governmental influence on prices that helped the industry thrive were removed. The blend of anhydrous ethanol in gasoline decreased from 20% to 10%, but rose slowly during the 90´s and is today 25%. In 2003 the flexible fuel car was introduced in Brazil. This affected the demand for ethanol, increasing the use of hydrated ethanol which had diminished to virtually zero in the 90´s [8].

In Sweden ethanol was produced from sulphite pulp in the early 20th century. This ethanol was used in cars for a period of time, but then other areas of use (mainly alcoholic beverages) became dominant in the following decades [9]. Ethanol from sulphite pulp was used in the transport sector again in the 90's, and a pilot plant on lignocellulosic ethanol was built in 2004 [10]. In 1998 a wheat-to-ethanol plant integrated with a combined heat and power plant was granted a building permit. This plant started production in 2001, and is currently producing about 210 000 m3 ethanol annually [11]. The development of alternative fuel in Sweden started as early as the 70´s, however, when the global oil crisis induced thoughts of decreasing oil dependence in the transport sector. The main choice at that point was methanol, and in the early 80´s the plan was to blend gasoline with 15% methanol. The interest for methanol declined in the late 80´s, and from the early 90´s focus turned to ethanol production.

The current global production of ethanol is mainly located in the USA and Brazil, where 1st generation feedstock, such as corn (USA) and sugar cane (Brazil), is processed. In Europe ethanol is produced to some extent, mainly from sugar beets, cereal and wine alcohol [12]. Many crops used in 1st generation ethanol production have limitations and uncertainties with regard to environmental performance because of the use of fossil fuels in production, the use of fertilizers and of water for irrigation, along with competition with other important uses of the feedstocks for food production (corn in the US, wheat in Europe) (cf. [13]).

In order to meet the expected demand of ethanol in the future, many new processing plants are needed. Thus new feedstocks are required. Lignocellulosic biomass accounts for about 50% of the total biomass on Earth, and a transformation from 1st to 2nd generation feedstocks, i.e., from starch/sugar to lignocellulosic feedstocks, is seen as necessary in order to manage the growing demand for environmentally benign ethanol biofuel in the near future. Nevertheless, few commercial 2nd generation ethanol plants have been erected, but there are many projects currently running with the aim of commercialization. The main problems that remain are due to the recalcitrance of the lignocellulosic material, which makes it difficult to break down and free the sugars that are fermented into ethanol [14]. The main costs in the process are investment costs in pretreatment and boiler/turbines, and the cost for raw material [14, 15]. Process integration with other types of plants, e.g. CHP-plants, 1ste generation ethanol plants, is a way of decreasing the production cost for ethanol [14, 16].

A list of some of the current and planned demonstration and commercial scale plants for lignocellulosic ethanol production is shown in Table 1.1. The information is from the European biofuels technology platform and the US Department of Energy biomass program [17, 18].

Table 1.1. Planned and current demonstration and commercial size lignocellulosic ethanol projects in the USA and Europe, more information can be found in references [17, 18].

Company	Technology	Location	Scale	Annual production
Abengoa	*Biochemical*	*Kansas, USA*	*Commercial*	*97000 m^3*
Bluefire LLC	*Biochemical*	*Mississippi, USA*	*Commercial*	*74000 m^3*
Mascoma	*Biochemical*	*Michigan, USA*	*Commercial*	*155000 m^3*
POET	*Biochemical*	*Iowa, USA*	*Commercial*	*97000 m^3*
Rangefuels	*Thermo-gasification*	*Georgia, USA*	*Commercial*	*77000 m^3*
Enerkem	*Thermo-gasification*	*Mississippi, USA*	*Demonstration*	*40000 m^3*
INEOS	*Hybrid*	*Florida, USA*	*Demonstration*	*30000 m^3*
Lignol	*Biochemical*	*Washington, USA*	*Demonstration*	*9700 m^3*
Verenium	*Biochemical*	*Louisiana, USA*	*Demonstration*	*5400 m^3*
Chemtex	*Biochemical*	*Crescentino, Italy*	*Commercial*	*50000 m^3*
Inbicon	*Biochemical*	*Kalundborg, Denmark*	*Demonstration*	*5400 m^3*
Abengoa	*Biochemical*	*Salamanca, Spain*	*Demonstration*	*5000 m^3*

Objectives

The primary objective of the PhD project presented in this thesis has been to increase knowledge of how synergetic effects of the integration of biofuel production processes into Kraft pulp mills might affect the feasibility of 2nd generation biofuel production for the transport sector.

Another objective has been to increase the understanding of process integration issues related to the studied processes.

Appended Papers

The work done in this PhD project has culminated in 5 different papers that are attached at the end of the thesis. A short description of the papers is included in this section.

Paper I is a preliminary study of the potential for by-products export in a conceptual ethanol production plant. A typical Scandinavian Kraft pulp mill is assumed to have been repurposed to ethanol production, and different levels of energy efficiency measures are investigated and compared with a base case where only investments in ethanol production, i.e., no energy efficiency measures, are made. The results are also compared to a similar study of the Kraft pulp mill, in order to see if the conclusions drawn differ when ethanol is produced instead of pulp.

Paper II is a detailed study of the possibilities for integration into a Kraft pulp mill repurposed to an ethanol plant. A number of different designs of the process are investigated to observe the potential for steam savings in the process, as well as to determine if there are differences in process design possibilities.

Paper III is an economic assessment of the results in Paper II. The different designs are investigated in more detail, and the economic feasibility of different levels of energy efficiency measures are assessed, the robustness of the process economics is studied in a scenario analysis and compared to other 2nd generation processes.

Paper IV is a study of a repurposed Kraft pulp mill where ethanol is produced instead of pulp, and the recovery boiler is replaced with a black liquor gasification process for the production of di-methyl-ether, another transport biofuel. The process is designed and assessed from an energy and economic viewpoint.

Paper V focuses on the potential for process integration in an ethanol process that is integrated with a modern state-of-the-art Kraft pulp mill. This mill is much larger in size than the ethanol process, which opens up for interesting possibilities for integration. Different energy efficiency measures are suggested, designed, and assessed both from an energy and economic perspective.

2 The Kraft pulping process

The different studies included in this thesis are all based on biorefineries connected to a Kraft pulp mill. Therefore a short description of the Kraft pulping process is included. A block flow diagram of a Kraft pulp mill is shown in Figure 2.1.

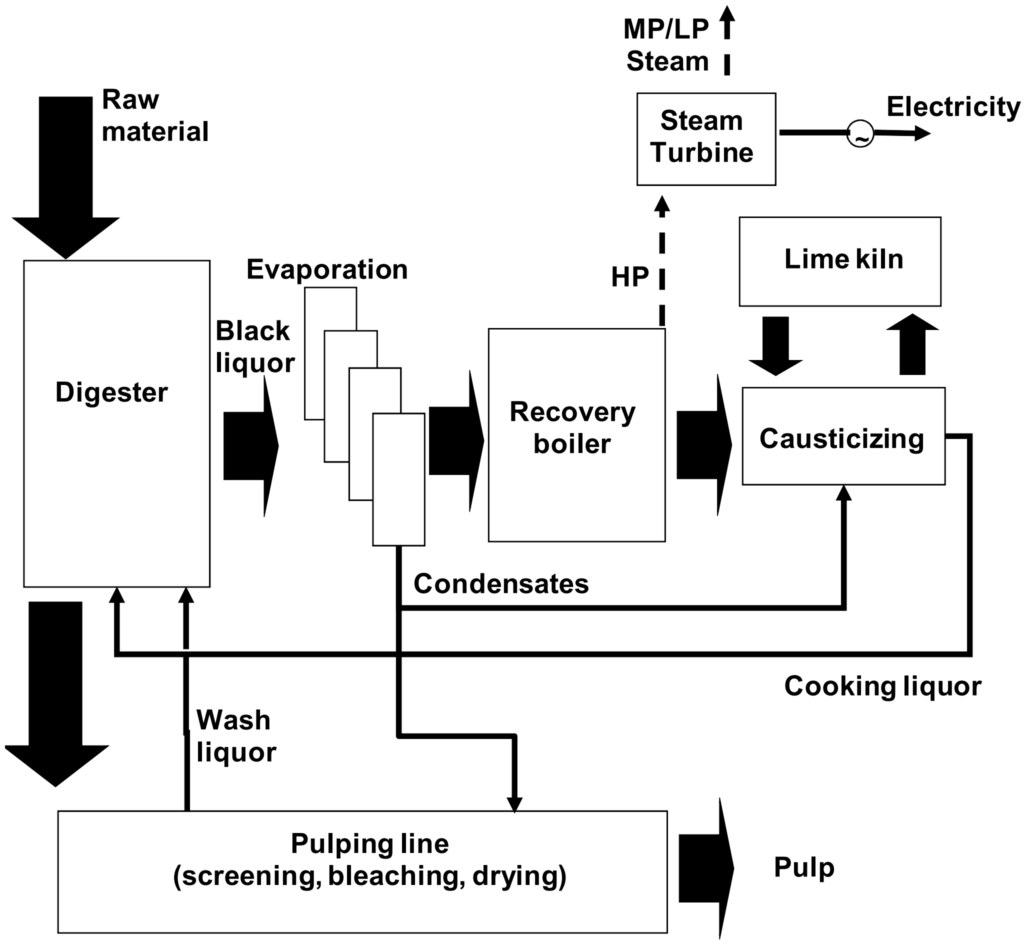

Figure 2.1. Block flow diagram of the Kraft pulp mill process.

Digester

The wood entering a Kraft pulp mill is first debarked, chipped, and screened. It is then sent to the digester where steam and cooking chemicals (Na_2S and NaOH) are introduced in order to break the lignin seal in the wood and separate a pulp (mainly cellulose) from black liquor (mainly lignin, hemicelluloses and degradation products from carbohydrates). The main reactions in the Kraft digester are the degradation and solubilisation of lignin and the degradation and hydrolysis of carbohydrates (that form carboxylic acids and fragmented carbohydrate chains) [19-21].

Evaporation

The black liquor, which consists mainly of cooking chemicals, degraded carbohydrates and solubilised lignin, is sent to an evaporation plant where it is concentrated to a high dry solids content (typically 70-85% DS). The evaporation is done with steam in up to 7-9 heat-integrated evaporation effects.

Recovery boiler

The concentrated liquor from the evaporation is sent to a recovery boiler where the organic components are combusted in order to produce steam and electricity. The inorganic cooking chemicals are recovered in a smelt (as Na_2CO_3 and Na_2S).

Chemical Recovery cycle

In order to recover the cooking chemicals Na_2CO_3 needs to be converted to NaOH. This is done in the causticizing plant where CaO from the lime kiln is mixed with the dissolved smelt (green liquor) from the recovery boiler producing NaOH and $CaCO_3$. The $CaCO_3$ formed is sent to the lime kiln where it is reburned to CaO at high temperatures by using external fuel, e.g., fuel oil, gasified bark.

Pulping line (washing, bleaching, drying)

The crude pulp from the digester needs to be processed further before being sold. First the pulp is washed, however, in order to separate dissolved organic and spent inorganic compounds, i.e., black liquor, from the pulp and fibres. After separating the pulp from the black liquor, knots and other solid impurities are removed by screening. Then the pulp is bleached and dried before leaving the process. Further delignification using oxygen can also be included in conjunction with the bleaching plant.

More detailed descriptions of the Kraft pulping process can be found in [22].

3 Lignocellulosic ethanol production

Compared to the production of ethanol from feedstocks rich in sugar or starch, such as sugar cane or wheat, lignocellulosic feedstock requires a more complex process. The basic steps needed in for lignocellulosic ethanol production are shown in Figure 3.1. First the lignocellulose needs to be broken down in order for the polysaccharides to be accessible. These are then hydrolysed to monomeric sugars, which then are fermented to ethanol. Finally the ethanol is concentrated and purified up to the required specifications. As can be seen in Figure 3.1 there are two different pathways that can be used, either acid catalysed-or enzymatic hydrolysis. If enzymatic hydrolysis is chosen, the feedstock needs to be pre-treated in order to make the polysaccharides accessible for the enzymes. In acid hydrolysis this is not required. A short description of the different process steps is included in this chapter.

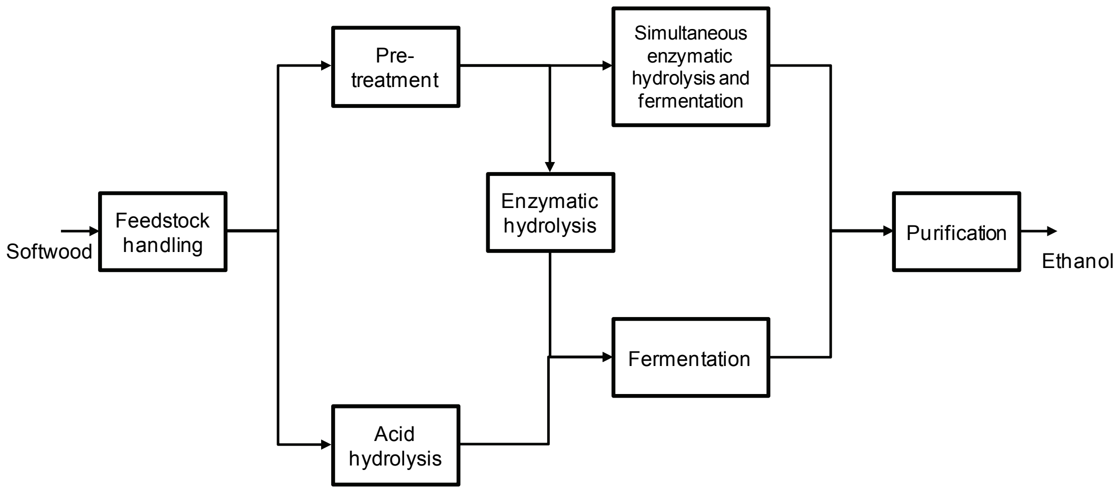

Figure 3.1. Block diagram of acid-or enzyme hydrolysed production of ethanol from lignocellulosic raw material (softwood).

Pre-treatment and hydrolysis

The most common acid used in this process is sulphuric acid. The hydrolysis can either be done with diluted or concentrated acid. The benefits of a high concentration are low temperatures and high yields, while the downsides of this alternative are the expensive recovery of the acid and corrosion issues. A dilute acid process has low consumption of acid, but high temperatures are required which increase the rates of sugar degradation to inhibitory compounds such as HMF and furfurals [23]. The dilute acid process could be done in two steps in order to decrease the degradation of sugars, but the cost would increase [16, 24].

The yield of monomeric sugars in enzymatic hydrolysis is higher than the acid hydrolysis processes due to the low temperature and the specificity of the enzymes [24]. There are a number of different ways to pre-treat the lignocellulosic raw material prior to enzymatic hydrolysis. They can be divided into acidic, neutral, and alkaline methods; some alternatives described in the scientific literature are, steam explosion with acid catalysts (H_2SO_4 or SO_2), Ammonia Freeze Explosion (AFEX), and Organosolv (C_2H_5OH) [13, 16, 19, 23-26].

Enzymes used in hydrolysis of the cellulose are called cellulases. They are normally derived from fungi, such as *Trichoderma reesei*. Today there are several companies producing and selling cellulases, The enzymes are among the highest costs in the ethanol plant, and a lot of research is conducted in order to find ways to reduce this cost, e.g., increasing the enzyme activity and reducing the loading of enzymes in the hydrolysis [27].

Fermentation

The fermentation of monomeric sugars to ethanol can be done in different ways. If the hydrolysis and following fermentation are done separately, both steps can be run at optimal conditions. The end-product inhibition in the enzymatic hydrolysis will impact this design negatively, however. Enzymatic hydrolysis and fermentation can also be carried out in one step (SSF). This will lead to a lower end-product inhibition, but some disadvantages exist such as difficulties to recycle the yeast used in fermentation. Today, commercial ethanol processes ferment only hexoses using ordinary bakers-yeast (*Saccharomyces cerevisiae)*. New microorganisms that have the ability to ferment pentose sugars as well are being developed, however. Compared to 1st generation ethanol production, the hydrolysis and fermentation in the lignocellulosic process also needs to be done at lower solids content. This affects the concentration of the ethanol into the purification section, and the water usage in the process. Finding ways to increase the yield at higher solids content could therefore both improve the energy efficiency and reduce the water demand in the process.

Ethanol purification

Ethanol and water is a non-ideal mixture that forms an azeotrope at approximately 95% w/w ethanol at atmospheric pressure. The azeotrope is pressure-sensitive; if the pressure is low enough it should be possible to reach a high purity of ethanol exclusively through distillation. The distillation sequence is normally designed as 2 to 3 heat-integrated columns. The ethanol is first removed from bulk water, dissolved solids, carbohydrates and different degradation products in a stripper (a beer column), and then purified up to close to the azeotropic concentration in a distillation column (a rectifier). To concentrate the ethanol up to the specified purity a tertiary compound such as benzene can be used in order to break the azeotrope, but a more common method is to use molecular sieves to increase the purity. The organic material entering the beer column(s) may cause fouling, and since this occurs more extensively at higher temperatures and pressures, the beer columns are normally designed at as low a pressure as possible. One reason for fouling in the columns is the presence of proteins, so when woody raw material (that does not contain much protein) is used the fouling may be expected to be lower than in current, 1st generation, ethanol processes (cf. [28]).

4 Related work

Since the project presented in this thesis is aimed at studying energy efficiency in a biorefinery that produces ethanol, albeit in connection with a repurposed Kraft pulp mill, there are numerous studies found in the literature that touch on parts of the subject. A search on the scopus database (www.scopus.com) indicated the large number of studies on ethanol as a biofuel in recent years. In 2011 approximately 820 articles were found with the search words *ethanol* and *biofuel*. For the words *ethanol* and *energy efficiency* the corresponding number was 91. In the years 2007 to 2011 approximately 15-20 articles/year were found with the search words *pulp mill biorefinery*.

Energy efficiency studies in lignocellulosic ethanol production

The importance of energy efficiency for the production of ethanol from lignocellulosic raw-material has been stated in several studies by leading experts on ethanol production [13, 24]. Studies on energy efficiency in ethanol production can be found in the literature from as early as the 1980´s. In a study by Collura (1988) the aim was to find distillation and evaporation designs that minimized the annual operating cost of these units in an ethanol production process. Heat integration between distillation and evaporation, or internal heat integration in distillation, or evaporation with the use of a heat pump, was considered. The study presents some suggestions for designing a heat-integrated ethanol plant, and also for using heat pumps in both distillation and evaporation. The study concluded that heat pumping was a good alternative due to a decrease in operating cost, but also that multiple integrated distillation columns could be interesting if the price of electricity is high or if the price of steam is low [29].

Ficarella et al (1999) have produced a study that assessed the possibilities of energy conversion in an ethanol plant with 3 alternative distillation schemes. The introduction of a heat pump was also discussed. The process energy efficiency was improved by a process integration that focussed on heat exchanger network optimization of the distillation sequence [30].

Galbe et al (2002) have discussed the importance of energy integration in order to increase the export of lignin. The conclusion was that minimizing energy demand, which in turn creates greater potential for by-product sales, is essential for process economics. Different integration aspects mentioned in the study are the integration of distillation and multi-effect evaporation, but also using the flash vapour from the pre-treatment step in other parts of the process [24].
In a study by Grisales et al (2005) an ethanol production plant was simulated in the flowsheeting software Aspen Plus. The process had two distillation columns (one stripper and one rectifier), and azeotropic distillation with benzene in order to obtain fuel grade ethanol. A process integration study was performed in order to improve the heat exchanger network, and the findings indicate that increased heat integration between distillation and evaporation is favourable [31].
Summers (2006) has presented a paper on improving the design of the distillation columns in ethanol production. In this study the distillation scheme consists of a stripper and a rectifier. The author describes the benefits of using structured packing in part of the rectifying column, which leads to a lower pressure drop over the column. This in turn leads to a lower temperature difference between the condenser and the reboiler in the column. The benefit of this is greater potential for internal and external heat integration since the temperature difference in the column is lower [32].
A few different alternative designs for distillation and evaporation in an ethanol production plant were assessed in a study by Wingren et al (2007). A base case with 3 distillation columns (2 strippers and 1 rectifier) and a 5-effect evaporation train were simulated, and then four different alternative designs (increasing the evaporation train to 8 effects, integrating one of the stripper reboilers with evaporation, increasing the internal heat recovery of the first evaporation effect by means of a heat pump, and using anaerobic digestion instead of evaporation) were suggested, investigated and compared. The results were presented both in energy terms and as total ethanol production cost. Using the parameters set in the study the authors concluded that using a heat pump in evaporation and anaerobic digestion were the most promising alternatives [33].

The study by Sassner et al (2007) was built on Wingren (2007), and added the conclusion that integration with a district heating system could increase energy efficiency and reduce production cost even further [16].

In 2007 an extensive review article was presented by Cardona et al that included information that could be applied to energy efficiency studies. A list of potential co-products in ethanol production showed that there is great potential for using internal energy efficiency measures to improve the profitability of the process. Furthermore the study mentions the potential of optimizing distillation in various ways, and using heat pumps for integration.

A study of different fermentation and distillation schemes within lignocellulosic ethanol production has also been conducted by Haelssig et al (2008). In this study 6 different alternatives were simulated in Aspen Plus. They were then evaluated for energy demand and economics. The distillation sequence was based on either one or two columns, and heat pumps were included in two of the alternatives. No integration with other process equipment was considered in the study. The authors concluded that either two heat integrated columns, or one column using a heat pump, would be the most feasible option [26].

Energy efficiency studies in Kraft pulp mills

The potential for improvements in energy efficiency in Kraft pulp mills in North America and northern Europe might be great, since many of the mills are relatively old and inefficient. In a paper by Bruce (2000) different Kraft pulp mills were benchmarked, and opportunities for energy conversion were discussed [34]. An assessment of the potential for improving energy efficiency in the US pulp and paper industry was produced by Martin et al (2000), who concluded that there was great potential for primary energy savings [35]. Lutz (2008) presented a more specific study on a Canadian Kraft pulp mill, and concluded that steam consumption could be reduced by 16% through improved thermal integration [36].

At the research group where this project was conducted a large knowledge-base for energy efficiency in Kraft pulp mills has been built up through the years. Wising (2003) has discussed several topics in her PhD dissertation, for example, redesigning the secondary heating system to release excess heat that could be used in the evaporation plant, and the energy consequences of lignin precipitation in a pulp mill setting. Together with Algehed, Wising

has presented a paper on energy efficient evaporation in pulp and paper mills [37].
In her PhD project Algehed (2002) has developed a tool for simulating black liquor evaporation plants where excess heat can be introduced. This work was furthered by Olsson (2009), who added new features to the tool, e.g., lignin extraction coupled to the evaporation plant. This tool was used in this project and will thus be described further in the methodology chapter [38].
Studies on energy efficiency measures in Kraft pulp mills continued with the PhD project by Bengtsson (2004) who has used pinch analysis tools to study process integration opportunities in the mills. In order to enhance the pinch analysis procedure, Nordman (2005) has put forth a set of new pinch curves which aid in visualizing the potential for process integration and energy efficiency measures in an existing industrial process. He has also presented a new method for designing hot and warm water systems in order to increase the availability of excess heat, which then can be used in other parts of the process [39].
Olsson collaborated with Axelsson (2008) on a series of studies where heat integration opportunities in model mills supported by the Swedish FRAM research program were assessed in different ways. In one study the resulting steam savings were transformed into sellable products (lignin and power), in order to assess the economic potential for taking energy efficiency measures in a typical average Scandinavian Kraft pulp mill [40, 41].

New possibilities for Kraft pulp mills

As discussed in the Introduction-chapter, the increased global competition in the pulp and paper industry negatively affects some of the more traditionally strong countries in this field. The current situation in these countries has lead to a growing focus on research on finding new ways of utilizing different components in the wood raw material. Here a short review of different studies focussing on issues related to this research topic is presented. The first part concerns studies from North America and then studies from Europe are discussed.
In North America Van Heiningen (2006) has presented a paper that states that bioenergy and new biomaterials, in addition to traditional pulp and paper products, are needed in order for the industry to increase its revenue and remain competitive. The paper presented the concept of an Integrated

Forest Products Biorefinery (IFBR), producing value-added products such as bio-fuels, polymers and carbon fibres besides producing pulp. The co-products are based on hemicelluloses and lignin, the cellulose should according to Van Heiningen still be used for pulp since the market price and yield are higher than that of cellulose-based ethanol [42].

Two reports investigating in more detail than Van Heiningen the potential of new products from lignocellulose were published by the National Renewable Energy Laboratory in the USA. In the first report different building block chemicals that can be co-produced from sugars and syngas in a biorefinery in order to add value to the product portfolio were identified and evaluated [43]. The second report focused on the possibility of using lignin as a resource for different products. It was concluded that in the near-term the most important potential for lignin lies within power, fuel and syngas production, while in the medium- to long-term, the production of macromolecules and aromatics and monomers hold promise as these products are expected to add more value to the product portfolio [44].

Several studies in the USA in recent years have focused on the IFBR concept. Frederick et al (2008) have investigated the potential for producing ethanol from hemicelluloses by extracting the hemicelluloses prior to pulping and hydrolysing, and fermenting the sugars to ethanol. The main conclusion of this study was that the loss of cellulose fiber in pre-extraction must be eliminated in order for the process to be competitive with other ethanol production processes found in the literature. Other conclusions drawn were that there was a strong dependence between the price of raw material and production cost, and that the small scale of the studied process resulted in a high capital cost per unit of ethanol produced [45].

Mao et al (2008) have conducted a similar study on the pre-extraction of hemicelluloses for the production of ethanol. They simulated the process in Aspen Plus as along with economic analyses in order to evaluate the process from a technical and an economic perspective. It was concluded that the rate of return of the investment varied depending on plant size and needed capital investments from a negative number up to approximately 13%. Benefits of this process were discussed, and it was stated that the positive effects of this new design were less degradation of pulp quality as well as potential for production increase if the recovery cycle was bottle-necked in the process [46].

Utilizing the spent liquor (black liquor) in a pulp mill for the production of transport biofuels through thermochemical processes has also been studied in recent years. In a project sponsored by the US Department of Energy and the American Forest and Paper Association several different designs and products in a black liquor gasification plant were assessed [47]. The study concluded that producing biofuels from black liquor could be interesting both from an economic and a societal (i.e. decreasing foreign oil dependence in the USA) point-of-view, when fully commercialized.

In contrast to the IFBR presented by van Heiningen, Phillips et al (2008) have presented a study on repurposing a pulp mill, thus producing ethanol from cellulose instead of pulp [48]. The conclusions from this paper were that this could be an interesting way of commercialising ethanol from wood due to the reduced capital costs needed, compared to Greenfield ethanol plants, and the benefit of an already existing supply chain. Several additional studies have been made regarding this concept since the first publication in 2008. An economic comparison between a repurposed pulp mill and a Greenfield ethanol process that indicates the benefits of integration and using hardwood as raw-material was made by Gonzales et al. [49]. Further studies on this concept have focused on optimizing the pre-treatment and hydrolysis of this wood-to-ethanol process in various ways (cf. [50-53]).

In 2009 Huang et al presented a study that describes how to model an integrated forest biorefinery. They used simulation tools to design a model of a biorefinery that produces ethanol, pulp, and liquid bio-fuels from syngas [54].

As in North America, Europe has seen a shift in research focus towards different pulp mill biorefinery solutions. One indication of this is the growing interest on biorefinery concepts at various branch-specific conferences in recent years. At the PulPaper 2007 Conference held in Helsinki, several topics highlighted research on pulp-mill-based biorefineries. Axegård et al (2007) presented different alternative pathways for lignin and xylan, while Holmbom (2007) discussed the possibilities of producing new high-value health promoting compounds from knots and bark [55, 56]. At the Nordic Wood Biorefining Conference (NWBC) 2009 in Helsinki Axegård (2009) presented an overview of different possibilities for Kraft pulp mill biorefineries studied by the Swedish research institute

Innventia, namely lignin separation from Kraft pulp mills, separation of hemicelluloses from wood, and ethanol production from wood-cellulose (preferably forest residues) through alkaline delignification and subsequent hydrolysis and fermentation [57].

A number of studies in Europe discuss the potential for extracting hemicellulose from wood in a Kraft pulp mill. Lundberg et al presented a study on the potential for process integration if a near-neutral hemicellulose extraction for production of ethanol and acetic acid was implemented in a Kraft pulp mill. The study concluded that the hemicellulose process did not need to imply an increase in the steam demand of the Kraft pulp mill, but that the sodium and sulphur balances of the mill would be disrupted in this process combination [58].

The effect on pulp properties when extracting hemicellulose was studied by Helmerius et al [59]. In this study it was concluded that extraction in alkaline conditions did not affect the pulp quality or yield, but led to a lower concentration of fermentable sugars in the extracted liquor. On the other hand, extraction with water showed the opposite results, high concentration of fermentable xylan but deteriorated pulp quality.

Extracting lignin for use as a biofuel or production of chemicals and materials has been studied extensively in Sweden in the past decade. The two main extraction methods are filtration or precipitation. Jönsson et al assessed the cost of extracting lignin by filtration in different parts of the Kraft pulping process. They concluded that recovering lignin from black liquor in the evaporation plant showed the lower cost than if recovered from the cooking liquor. The main reason for this was the difference in yield of lignin [60].

Precipitation of lignin from black liquor in a Kraft pulp mill was studied in a PhD project by Öhman [61]. The concept, named LignoBoost, was developed within the framework of a Swedish research programme (Future Resource Adapted Mill). The separation process was tested in a demonstration plant, and combustion trials in full scale plants were made [62].

In accordance with the IFBR concept described previously, studies on black liquor gasification have been conducted in Sweden. The goal of the BLGMF project (Black Liquor Gasification with Motor Fuel production) was to generate preliminary design and cost estimates for a BLGMF process. The conclusions were that the process could be economically feasible, with a low payback period if methanol or Di-methyl-ether (DME) was produced [63, 64]. Studies on the effects of integration on economics and CO_2 emissions were presented by Pettersson in her PhD project [65]. One conclusion from this work was that DME was the most profitable transport biofuel product from this type of biorefinery.

Producing ethanol in a process co-located with a Kraft pulp mill was studied within the framework of the Swedish research programme “Ecocyclic Pulp Mill – KAM”. The results from this study indicated that the investment cost might be decreased if co-located due to synergetic effects of sharing utilities and water-and effluent treatment [66].

The repurposing of a pulp mill for the production of ethanol from wood-cellulose was discussed by Innventia in several papers, where it was concluded that the proposed concept could potentially have low production costs. This was dependent on the assumed cost of the existing, reusable, equipment [67, 68]. This process will be discussed further in the following chapters of this thesis, since it has been used in the different process integration studies.

A summary (from a Swedish perspective) of research activities on biorefineries in pulp mills can be found in reference [69].

5 Methodology

Process integration studies can be used with various different aims, e.g., energy efficiency (heat integration), efficient raw material use, emissions reduction and improved process operation [70]. In this project heat integration studies on conceptual processes have been conducted using pinch analysis tools.

Pinch analysis was originally developed in the 70's at the ETH Zürich and at Leeds University [71]. The first centre for process integration was established in the early 1980's. From its introduction up until today the pinch methodology has been used in a wide variety of processes, and several different new areas of use have been developed. The methods have been applied to other aspects than energy efficiency, such as efficient use of water, hydrogen, and oxygen [70]. Another new development is the concept of total site heat integration (cf. [72-75]). This refers to the integration of several processes at an industrial site by using pinch analysis methods. In a similar manner, the potential for direct heat integration between different unit operations such as distillation columns and evaporation plants can be studied (cf. [70, 76]). Pinch analysis has also been combined with other methods for studying process integration, such as mathematical programming and exergy analysis (cf. [73, 77-79]). Further information on the different tools and methods included in process integration studies can be found in the books and guides written on this topic (cf. [70, 71, 76, 80]).

At the research group where this project was conducted, a lot of knowledge on process integration issues related to the pulping industry has been developed through the years. Detailed studies on the potential for process integration of black liquor evaporation plants in Kraft pulp mills have been conducted (cf. [38, 81]), and tools for assessing the heat integration potential in the pulp mill hot and warm water system, so called tank curves, have been presented (cf. [82]). Previous research projects have also suggested new pinch analysis tools such as the matrix method for retrofitting heat exchanger networks [83], and the so called advanced composite curves used for assessing the potential for heat integration and in retrofit situations (cf. [84-86]).

Pinch analysis in this project

In the project in this thesis the main investigations into heat integration were coupled to thermal separation units such as distillation and evaporation, since these comprise a large part of the hot utility demand in ethanol production. Also, in Paper IV total site analysis curves were used in order to investigate the potential for integration of two biofuel production processes.

Heat integration between a process and a few different unit operations are shown in the split Grand Composite Curves (GCCs) in Figure 5.1. The appropriate placement of distillation columns and evaporators should be above or below the process pinch. Otherwise heat would be transferred across the pinch, thus increasing both hot and cold utility demand. If a flash system is included in a process, the optimal number of flash steps can be estimated according to Figure 5.1, lower left quadrant. Finally, a heat pump, as shown in Figure 5.1, lower right quadrant, should be integrated through the pinch since removing heat from the excess region and adding it to the region where there is a deficit reduces both hot and cold utility demand.

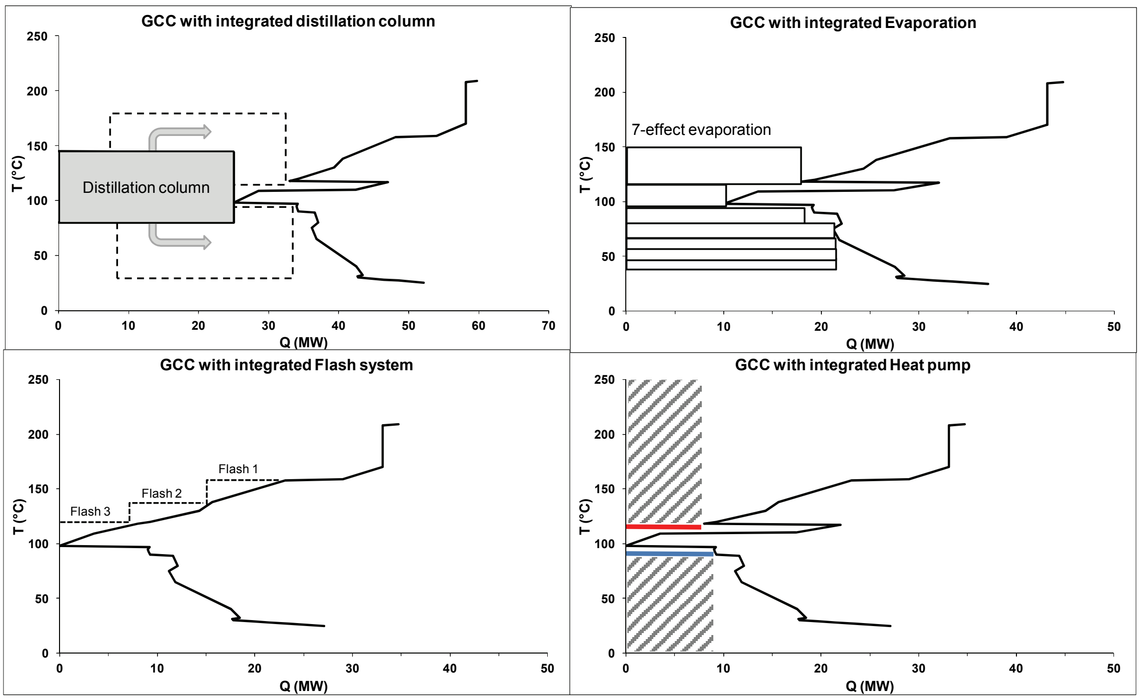

Figure 5.1. Examples of potential for integration by using split GCCs. Distillation column (upper left), evaporation plant (upper right), Flash system (lower left), and a heat pump (lower right).

Process-integrated evaporation

The dominant hot and cold streams in an evaporation plant are the latent heat loads related to vaporization and condensation. Evaporation is normally restricted to the vaporization of one component (e.g. water), which indicates that the latent heat load is located at a constant temperature. Consequently, an evaporator can be depicted as a box in a Temperature-Enthalpy diagram when making a preliminary assessment of integration potentials. An evaporation plant normally consists of several heat integrated evaporation effects. It is therefore possible to add or withdraw steam at several different temperature levels, as well as vary the heat flow in the different effects (as shown in Figure 5.1, upper right quadrant). A simple estimation of the resulting steam demand of an evaporation plant with N effects can be done by dividing the total energy required for increasing the dry solids content by the number of effects (N). This will give an estimate of the steam demand and the potential for integration for this unit operation. More detailed studies on heat integration opportunities for evaporation plants, including variations in, e.g., boiling point elevation and heat transfer coefficients with temperature and pressure, were used in this project in order to further assess the initial suggestions made by the estimations described above.

Process-integrated distillation

Similar to the evaporation plant, the dominant heating and cooling demands in distillation are vaporization and condensation. For the initial investigation into the potential for heat integration, the box-approach should be sufficient, but in distillation latent heat loads are seldom located at constant temperatures since mixtures of components are often vaporized or condensed. Changing the pressure of a distillation column will also change the shape of the "box" in the Temperature-Enthalpy diagram. This is because the thermodynamic properties of the mixture change with changing pressures. For example, the relative volatility of the components generally decreases with increasing pressure [76]. As in evaporation, the distillation sequence can be designed with multi-effect columns. This opens up for integration potential both with the rest of the process and in isolation. The multi-effect distillation sequence could also be integrated in various ways with the rest of the process, e.g., in two columns where one column is above and one below the pinch point.

Process-integrated heat pumps

Heat below the pinch point (where there is an excess) can be used above the pinch (in the deficit region) if the temperature level of the heat is raised by some type of primary energy in a heat pump. There are several heat pump cycles that could be used for this purpose, e.g., Closed Compression Cycles, Mechanical Vapour Recompression, Thermal Vapour Recompression and Absorption Cycles. A Grand Composite Curve (GCC) can be used to assess which type of heat pump is suitable for a specific process. This is dependent on the temperature lift, the heat sink and heat source temperatures, and the relative load of the heat sink and heat source. In this project Mechanical Vapour Recompression heat pumps have been deemed to be the best options for all cases studied, with reference to these parameters [87].

Process integration using advanced composite curves

Advanced composite curves are a set of pinch curves that can be used to advantage in heat integration analyses. Compared to traditional curves, such as the GCC, these curves also give information about at what temperature levels existing units are located in the heat exchanger network [84]. The curves can be used in retrofit without the need for detailed design calculations, and also for the identification of temperature levels and the amount of excess heat available in a given process [86]. In Figure 5.2 the four of these curves that have been used in this project are explained (Figures 5.2a and 5.2b) and depicted (Figure 5.2c). A set of curves depicting the actual heating and cooling load temperatures, i.e., the process side of heaters and coolers in the heat exchanger network, have been defined (AHLC and ACLC in Fig. 5.2a and 5.2c). Also included in Figure 5.2 are the theoretical heating and cooling load curves, THLC and TCLC, which depict the maximum temperature of cooling demand (TCLC) and minimum temperature of hot utility demand (THLC) in the process, if the heat exchanger network is designed accordingly. The ΔT_{HX} is set as low as possible in order to increase the potential for internal heat recovery, and the ΔT_{min} is set to determine the minimum utility requirements. Compared to the GCC, the THLC and TCLC can reveal greater potential for heat integration since these curves include the possibility of redesigning the process to increase the potential for integration for a given utility demand. This is further discussed in Papers II and III.

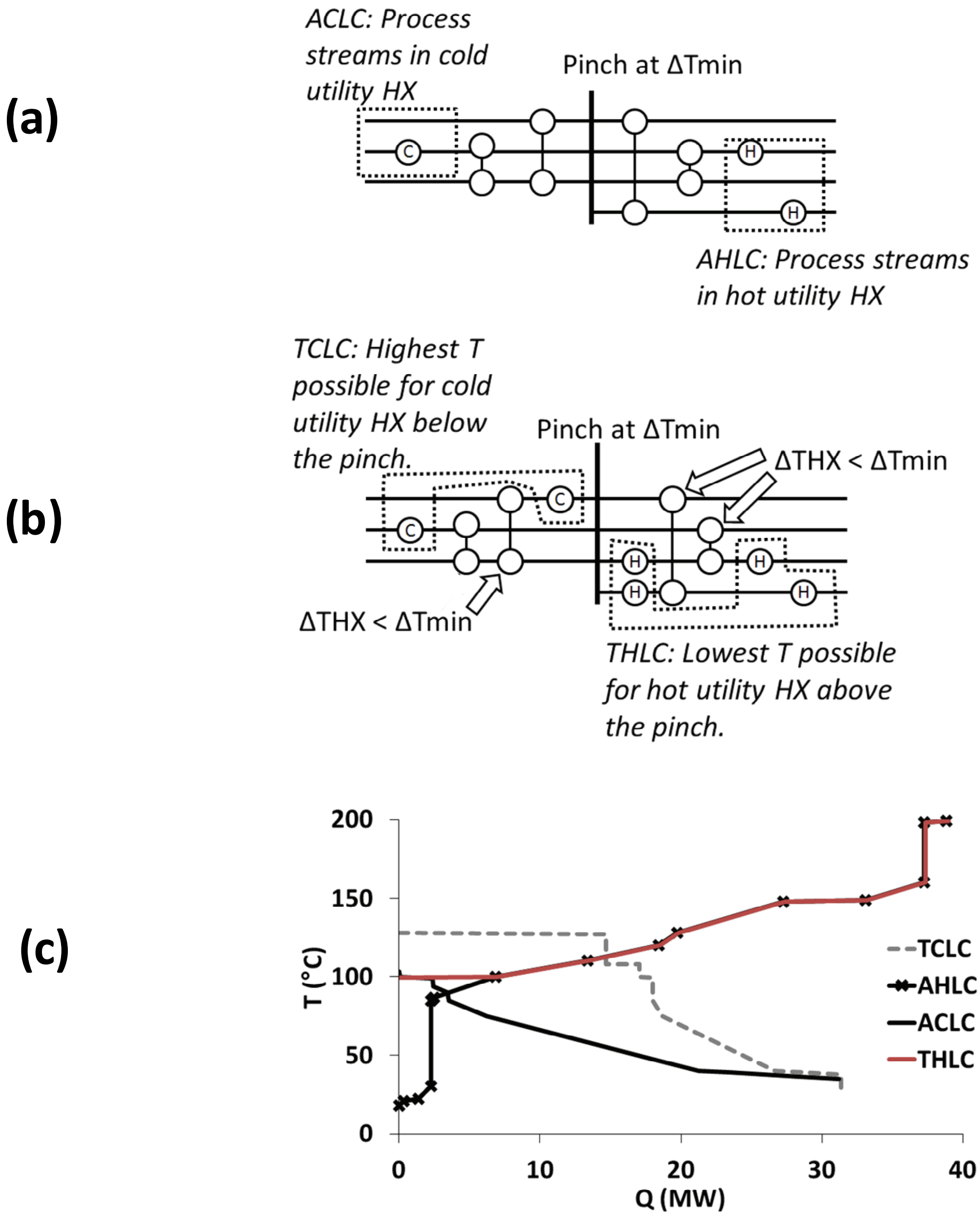

Figure 5.2. Actual heating and cooling loads (a), Theoretical heating and cooling loads (b), and advanced composite curves depicting these loads for the ethanol plant in Papers II and III (c).

In Papers II and III in this thesis the process has been divided into three different parts; the evaporation plant, the distillation sequence, and finally the rest of the process (named the background process). In the background process only the heat exchanger network is changed, while the evaporation and distillation plants are studied in more detail in order to improve integration. The reason for this is that making changes in the background process requires in-depth studies of pre-treatment, hydrolysis and fermentation, which are beyond the scope of the work presented here.

Tank curves for assessing process integration opportunities

In Paper V opportunities for the heat integration of a lignocellulosic ethanol plant with a state-of-the-art Kraft pulp mill have been studied. Excess heat in the pulp mill could be used for the purpose of integrating, e.g., evaporation or distillation in the ethanol process. In Kraft pulp mills the secondary heating system often produces more hot and warm water than needed. Using tank curves, the potential for reducing hot and warm water production and increasing the amount of excess heat available for integration with other processes can be assessed [82]. The assumption made when designing the tank curves was that water is heated in one or several tanks at specific temperatures, and demands for hot or warm water at other temperatures were met by mixing fresh water and hot water. One tank level was thus always the highest temperature in the hot and warm water system. As Figure 5.3 shows, the more tank temperature levels used, the more excess heat could be made available at a given ΔT_{min} for the secondary heating system.

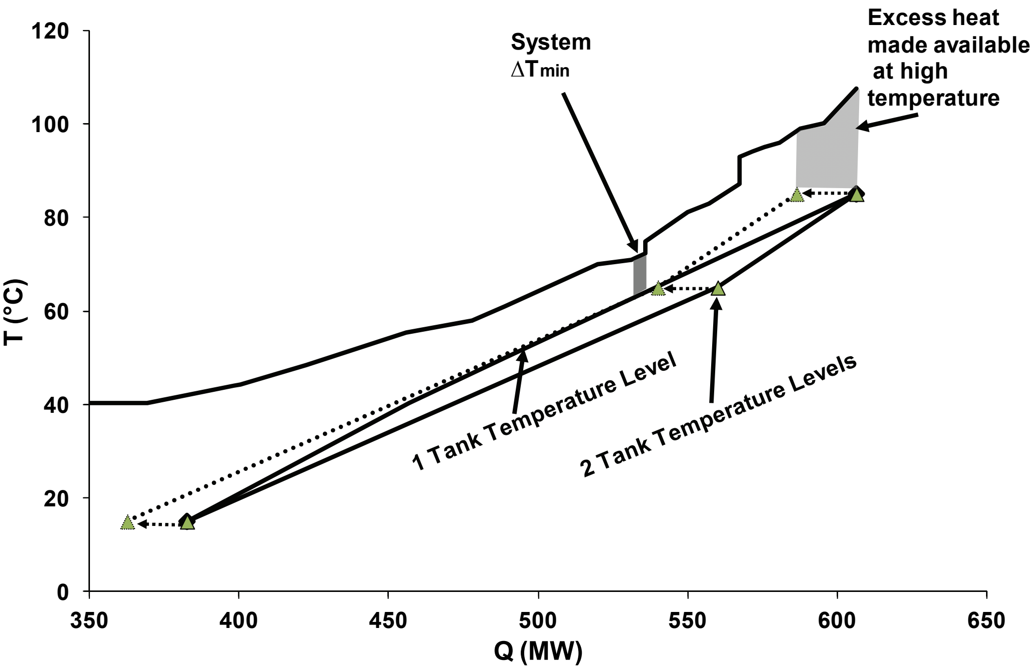

Figure 5.3. Tank curves with one and two tank temperature levels, indicating the excess heat made available for integration when increasing the number of tank temperature levels.

Total site analysis

In Paper IV the potential for heat integration between an ethanol process and a DME process is assessed. The integration of several processes through the utility system, as in Paper IV, can be studied by investigating the heat source-and sink profiles of the combined process (the site). This is done by starting from the GCC of each process, and then combining theses into a set of site composite curves, depicting the source and sink profile of the combined processes. The pockets in the GCC are normally omitted since it is assumed that this heat recovery will take place in the respective processes. In Figure 5.4 the site source and sink profiles are shown, as well as the potential for utility production (from the site source composite) and the utility demand (from the site sink composite). As can be seen in Figure 5.4 there is a utility pinch, which indicates that some of the utility steam cannot be used. The boxes in the figure indicate the potential for cogeneration in the utility system [70, 74, 76, 88].

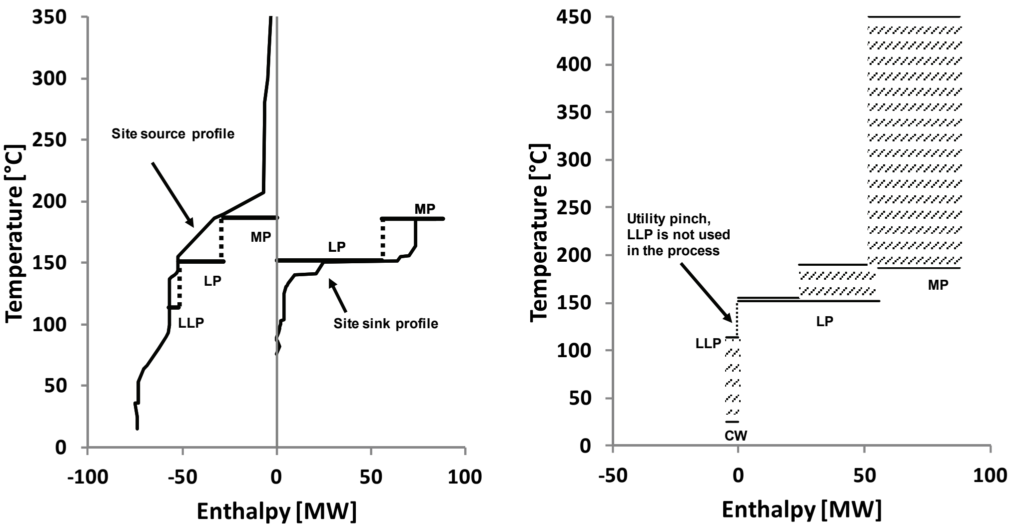

Figure 5.4. Composite curves depicting the site sink and source profiles (left) and the resulting site utility system (right).

Heat exchanger network design

In Papers III and V heat exchanger networks (HENs) have been designed and included in the economic analysis. There exist several different methods for designing HENs when retrofitting existing plants (cf. [79, 85, 89, 90]). For grassroots designs a network close to the Maximum Energy Recovery (MER) for a relevant ΔT_{min} of the system should be designed using a minimum number of units. In Paper III a network close to the MER was designed for each alternative with the help of the pinch analysis software Aspen Energy Analyzer [91]. In Paper V the existing network was retrofitted by using tank curves when necessary. This was done while changing the original design as little as possible, i.e., only removing the heat exchangers where excess heat could be released, and then adding the new heat exchange combinations. Detailed costs for piping and pressure drop have not been included in Papers III or V since the processes are only conceptual; the distance between units is not known.

Process simulations

The suggested heat integration options in this project have been studied in more detail using process simulations of the different unit operations, such as heat pump integration, evaporation of residues, and product purification. A short description of the methods used and the main processes that have been simulated is presented in this subchapter.

Evaporation plant simulations using OptiVap

A tool for simulating multi-effect evaporation plants in Kraft pulp mills, OptiVap, was developed by Algehed and Olsson [38, 81]. This tool has been used in this project to assess the evaporation plant in the ethanol process in more detail. Using OptiVap one can calculate material and energy balances while considering physical properties such as boiling point elevation, viscosity and heat transfer coefficients. In the current work the tool has been used to assess both lignin separation using the LignoBoost concept [61, 92], and for withdrawing and adding steam for heat integration at different stages of the evaporation train (Figure 5.5). In Papers III and V OptiVap has been used to assess the heat exchanger area needed for different plant designs. In Paper III an initial evaporation plant with defined size of the different units and heat transfer surfaces was included in OptiVap. This plant was then upgraded while reusing the existing units as much as possible and only investing in one or a few new effects. The tool is also capable of estimating viscosity changes when lignin is removed from the residue liquor, which is helpful when comparing lignin separation with electricity production in an ethanol process.

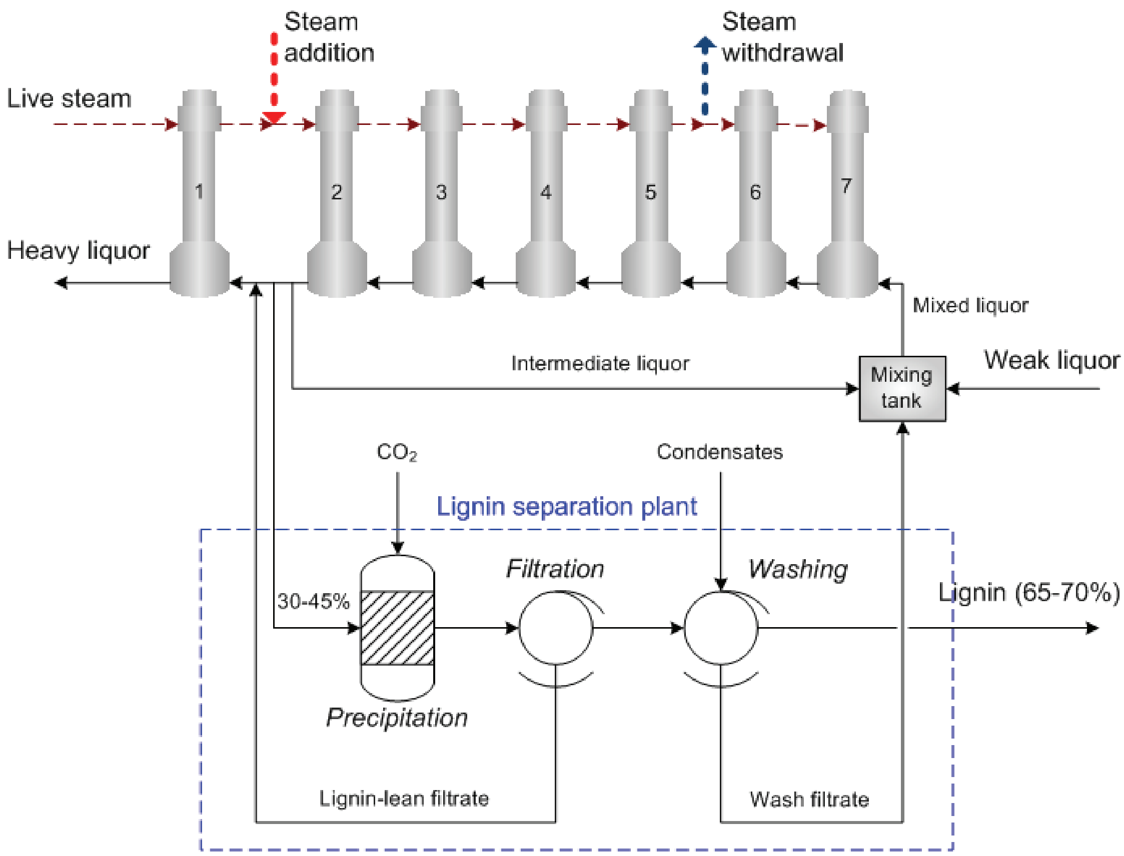

Figure 5.5. Evaporation plant with heat integration and lignin separation (which can be simulated in OptiVap).

For further information about the OptiVap-simulation software, please refer to Olsson (2009) [38].

Process simulations using Aspen Plus

Calculations connected to phase-changes in multicomponent mixtures are not easily done by hand. Flowsheeting software including predefined unit operations and databanks for physical properties for numerous compounds and mixtures of compounds are therefore often used. A multitude of different such software is available, e.g., Aspen HySys, Aspen Plus, ChemCad, Pro II. All these programmes use similar approaches for solving the problems set up by the user. Empirical methods using different types of equations of state and/or activity factor models are included in the programmes, including binary interaction parameters for a multitude of compounds. In this study Aspen Plus [91] has been used to analyse different relevant unit operations in more detail. The main issue to consider when using this type of process simulation software is the selection of property methods for estimating mass and energy balances. A simulation might give highly unrealistic results if an unsuitable property method has been used. It is therefore important to validate the calculations done by the programme in one way or another such as through experimental studies. In this project the property methods used for different simulations have been selected based on reference scientific literature, including experimental validation when possible (see appended papers for references).

The main constraints with regard to the design of distillation columns in this project have been the temperatures of the condensers and reboilers. A temperature that is too high might lead to severe fouling of the heat exchangers and thus problems with short maintenance intervals, which in turn affect the economics of the process. A very low temperature would mean large volumetric flowrates, and higher cost for cooling. In this project the upper and lower limits have been set to 150°C and 35°C. Within these constraints two different types of distillation sequences have been investigated; distillation column(s) that increase the concentration of ethanol from the feed to the product concentration directly (either one column, or two or three in parallel sequence), or using one or two strippers to remove the main part of the compounds in the feed, and then a rectifier to separate ethanol and water (Figure 5.6). The sizing of the columns has been done according to methods described in [93]. The number of stages and feed entering stage was set to reach a reboiler duty that was close to minimum, i.e., a reflux ratio close to minimum. When integrating columns the designs were also in some cases specified to match reboiler and condenser loads, i.e., with higher reflux ratios than minimum, which also leads to fewer equilibrium stages needed [76]. Further details of the distillation column designs and assumptions can be found in Paper II.

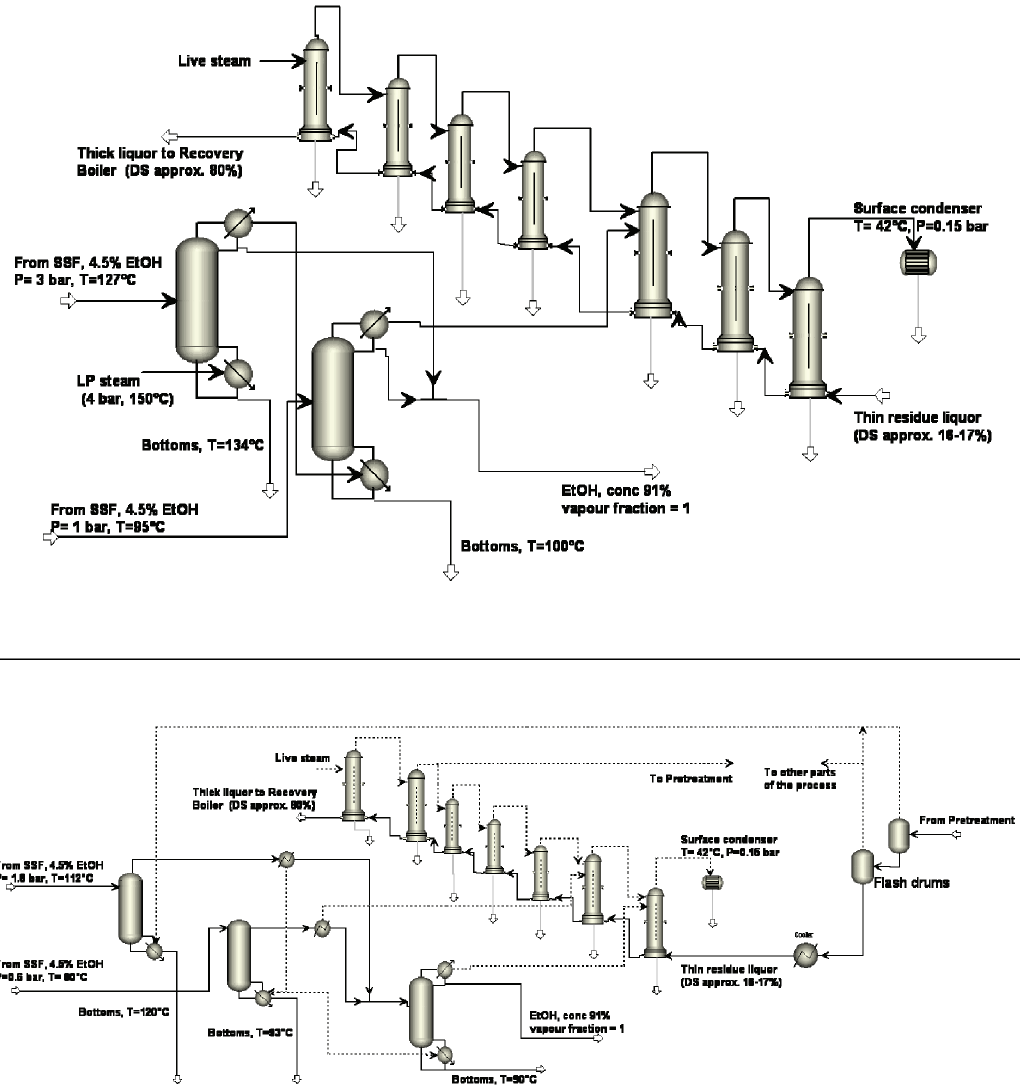

Figure 5.6. Distillation columns in parallel (upper), and stripper + rectifier (lower) sequence, integrated with other parts of the process (from Paper II).

In Papers II and III, distillation columns integrated with mechanical vapour recompression heat pumps (MVR) have been simulated. The heat pumps were all open cycles, i.e., ethanol-water was the working fluid. A flash drum was added after the heat pump and some of the ethanol-water from the stripper was recycled to the compressor in order to increase capacity (Figure 5.7). An open cycle gives both a lower investment cost and a higher coefficient of performance (COP) for the heat pump. The coefficient of performance (COP) was defined as the product of the heat sent to the sink and the work input ($COP=W_{in}/Q_{sink}$). The Carnot efficiency ($\eta_C=COP/COP_{Carnot}$, where $COP_{Carnot}=T_h/(T_h-T_l)$) includes the COP and is a good measure of the effectiveness of a heat pump. The Carnot efficiency has been calculated from the Aspen Plus simulations and has been found to be around 70% for all the suggested heat pumps in Paper III. In the process studied in Papers II and III there was no opportunity to introduce heat pumps other than in the distillation columns. Paper V includes an MVR integrated evaporation plant, however. The concept is similar to Papers II and III, but without the flash recycle. Instead the heat pump was designed with two-stage compression and intercooling.

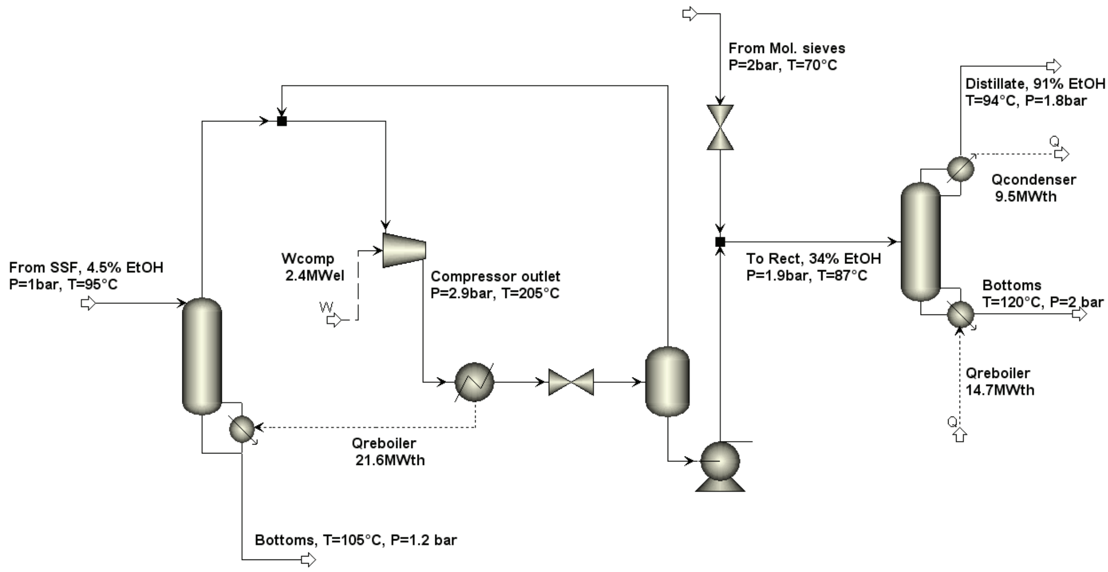

Figure 5.7. MVR-integrated distillation columns (from Paper III).

In Paper IV several different processes have been simulated using Aspen Plus. A cleaning process for removing CO_2 and H_2S was designed as well as a process for DME synthesis and purification. The suggested designs for both of these processes were then reviewed by industrial licensors.

Economic analysis

The different investments in this project have been evaluated using the annuity method and payback period estimations. These tools are standard tools for economic evaluations of investments in techno-economic studies (cf.[38, 40, 94]). They have been selected based on discussions with industrial representatives.

The payback period (PBP) calculation does not include interest rate or the economic lifetime of the investment, and is therefore a rough but simple calculation of profitability. The PBP gives the best indications for low values, but since the feasibility of an investment normally demands a low PBP (only a few years), this tool can be used.

$$Payback\ period\ (PBP) = \frac{Investment\ costs\ (I)}{\Delta\ annual\ (revenues - operating\ costs)}$$

The net annual profit, or net annual savings, has been estimated in order to annualize the economic results of the different investments discussed throughout the project. The revenues and operating costs were calculated for the year zero, and were assumed to be constant throughout the lifetime of the plant. The investment cost was annualized by using the annuity factor (also called the capital recovery factor), which was defined as the share of the loan for an investment that needs to be paid every year throughout the lifetime of the investment (n) in order to pay off investment and interest (i).

$$Capital\ recovery\ factor, or\ annuity\ factor\ (a) = \frac{i}{1-(1+i)^{-n}}$$

$$Net\ Annual\ Profit = \Delta\ annual\ (revenues - operating\ costs) - I \times a$$

Apart from the net annual profit, the economic analysis in Paper III has estimated the effect on ethanol production cost that the implementation of different investments have. The production cost was defined as the total operating costs and benefits (mainly from by-products) and the annualized investment cost for the plant.

$$EtOH\ prod.cost = operating\ costs + I \times a\ -\ revenues\ from\ byproduts$$

Capital cost estimations

The estimated costs for relevant equipment in the different studies have been retrieved in three different ways; for some equipment equations approximating correlations of costs dependent on a design variable have been used, in other cases estimations have been done using the economic process evaluation software Aspen Process Economic Analyzer [91], and finally reference investment cost data from other studies and industrial quotations have been used.

Operating cost estimations

Costs related to the operation of the different ethanol processes have mainly been obtained from studies made by Innventia (cf. [67, 68, 95]).

Estimation of the value of products

Paper I includes a sensitivity analysis with respect to lignin and electricity prices. In the following papers the economic analysis has included an assessment of the sensitivity of the different biorefinery concepts by using a scenario tool developed by Axelsson and Harvey [96]. The benefit of using the tool is that within each scenario different prices and CO_2 emissions are interconnected and related to the inputs in the tool, i.e., fossil fuel prices and different policy instruments. The results from the scenario analysis can thus give an indication of the potential and robustness of different biorefinery pathways under different assumptions regarding the future (Figure 5.8)

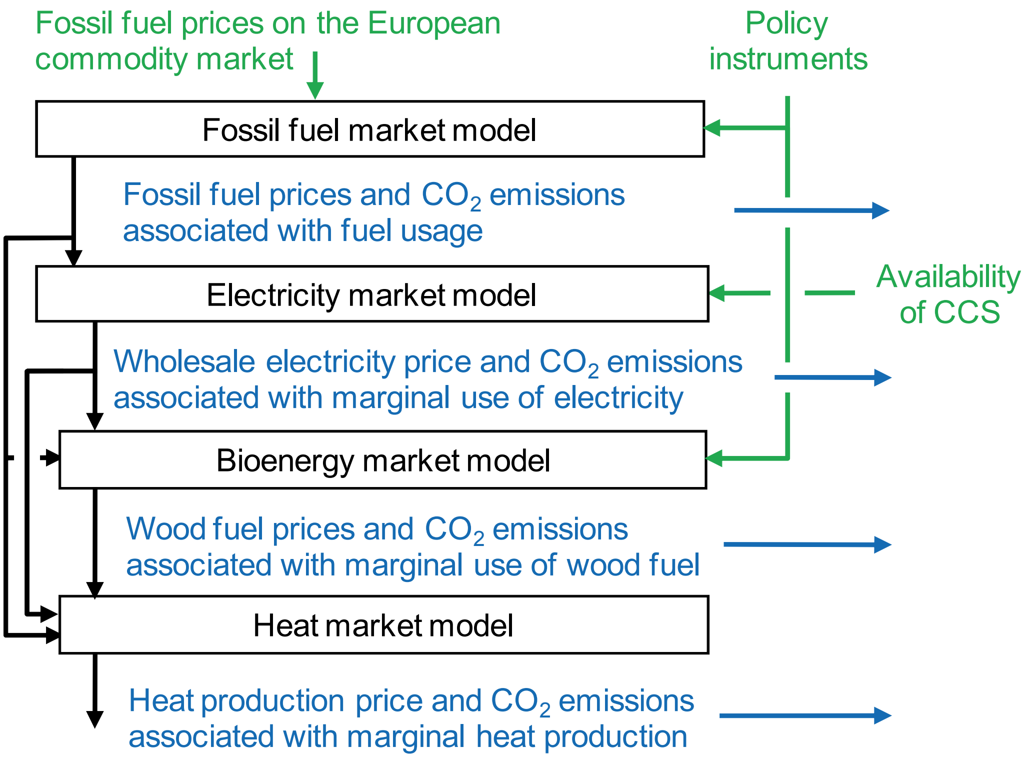

Figure 5.8. Overview of the calculation flow in the scenario model used in this project (courtesy of Axelsson and Harvey [96]). Green arrows represent required inputs, boxes represent calculation units, black arrows represent information flow within the model, and blue arrows indicate outputs from the tool.

In the papers in this thesis the scenario tool has been used for generating prices for electricity and lignin that are coherent. The model assumes that the price for electricity is based on the total generation cost for the power plant that is the build margin, i.e., has the lowest production cost, in the scenario used (in most cases coal condensing power plants). The price of lignin is assumed to be equal to the Willingness To Pay (WTP), defined as the price coal power plants are willing to pay for biomass for co-firing. The price is equal to the market coal price (including CO_2 emissions charge) with a small reduction due to the additional costs for the power plant related to the use and transport of wood fuel instead of coal. It should be mentioned that the value of lignin could be substantially higher in other applications, e.g., substituting fuel oil or being used for production of chemicals and materials. The prices used in here could therefore be seen as conservative.

In Paper III the repurposed pulp mill has been evaluated by using inputs to the model (fossil fuel prices) from a report by the European Commission [97]. The marginal producer of electricity is assumed to be a coal power plant in all scenarios (output from the scenario tool). Three different scenarios have been assessed, where the difference is the assumed level of the charge for CO_2 emissions. An assessment of the influence of financial support for green (renewable) electricity production has also been included in the paper (Table 5.1).

Table 5.1. Electricity and lignin prices (when lignin is assumed to be co-fired in a coal power plant) in Paper III.

Year 2020	**w/o support**			**with support**		
Scenario	**1**	**2**	**3**	**1**	**2**	**3**
Electricity [€/MWh]	59	95	65	85	121	91
Lignin [€/MWh]	19	41	23	34	57	41

In Paper IV the scenario tool has been used to estimate the effect of implementing CO_2 captured in a biorefinery producing ethanol and DME. The cost for electricity is related to the value of the captured CO_2, i.e., the CO_2 charge, according to the scenario tool. The inputs to the scenario tool come from the IEA technology roadmap on biofuels for transport [98]. Since there is a net deficit of electricity in the process in this paper, electricity needed for the compression of CO_2 to pipeline pressure is bought from an assumed marginal producer (Table 5.2).

Table 5.2. CO_2 charge and corresponding electricity price for the four scenarios used in Paper IV.

CO2 charge [€/ton]	*(corresponding el. price [€/MWh])* **2020**	**2030**	**2040**
level 1	15 *(58)*	15 *(62)*	15 *(62)*
level 2	20 *(63)*	27 *(72)*	37 *(79)*
level 3	30 *(72)*	45 *(87)*	68 *(93)*
level 4	52 *(92)*	85 *(94)*	117 *(100)*

6 Studied processes

The Kraft pulp mills

All the papers included in this thesis are based on computer models of Kraft pulp mills. In Papers I-IV a model of a typical Scandinavian Kraft pulp mill, developed in a Swedish research programme called FRAM (Future Resource Adapted Mill), was the basis [99, 100]. In FRAM several different models of Kraft pulp mills were defined, both typical mills and state-of-the-art mills with hardwood or softwood as feedstock. In Paper V an integration study was conducted on a modern state-of-the-art pulp mill based biorefinery. The model used in this paper was an updated version of one of the reference mills in the FRAM programme [101]. The feedstock to the mill was *Eucalyptus Urograndis* (hardwood) since this type of mill would most likely be built in a country with Eucalyptus feedstock, such as Brazil. Table 6.1 shows some key data and design information for the two model mills in this project [40, 101].

Table 6.1. Key data for the mills in this project (ADt = Air Dry tonne pulp).

	FRAM type mill	Updated reference mill	Units
Wood species	Spruce (softwood)	Eucalyptus (hardwood)	-
Pulp production	326 600	1 400 000	ADt/yr
Digester yield	46	55-56	%
Process steam consumption	17.4	7.7	GJ/ADt
Steam data:			
High pressure (HP)	60 bar (450°C)	101 bar (500°C)	
Medium pressure (MP)	11.5 bar	11.5 bar	
Low pressure (LP)	4.5 bar	4.5 bar	
Condensing turbine?	No	Yes	
Power generation	593	1438	kWh/ADt
Power consumption	791	640	kWh/ADt
Fossil fuel used?	Yes, in lime kiln	No	-
Evaporation plant	5.5 effects, 73 % DS	7 effects, 80% DS	-

In the pulp mill in Papers I-III the steam produced in the recovery boiler was at 60 bar(a) and 450°C, and there were two steam headers at 11.5 and 4.5 bar(a). Electricity was produced in a back-pressure turbine, but no condensing tail existed. Since upgrades to the steam network were assumed to have been made in the typical Scandinavian Kraft pulp mill, the turbine was too small to accommodate all the HP steam. Therefore some steam was let down through expansion valves and released to the atmosphere. A bark boiler existed in the plant, but was not used. Instead bark was assumed to be sold, and fuel oil was bought in order to fire the lime kiln in the chemical recovery cycle.

In Paper V the steam produced in the recovery boiler was at 101 bar(a) and 500°C. Electricity was produced in both a back-pressure and a condensing turbine. The power boiler was fired with bark and primary sludge from the waste water treatment plant, and the lime kiln was fuelled with bark. Process steam is supplied at two pressure levels, the same as in Papers I-III.

The ethanol process

In Papers I-IV the ethanol process was assumed to replace the pulping line in the typical Scandinavian Kraft pulp mill described in the preceding subchapter. The benefit of the design was that many of the unit operations in the ethanol plant already existed in the pulp mill to be converted. In Paper V the ethanol process was co-located with the state-of-the-art pulp mill. The benefit of this was that the pulp mill recovery boiler, chemical recovery cycle, and utility systems could be utilized.

Figure 6.1 shows a block diagram of the ethanol process studied in Papers I-III. The processes in Papers IV and V are conceptually the same as shown in Figure 6.1; the difference is that in Paper IV the recovery boiler was replaced with a gasifier, and in Paper V the chemical recovery cycle was integrated with the Kraft pulp mill.

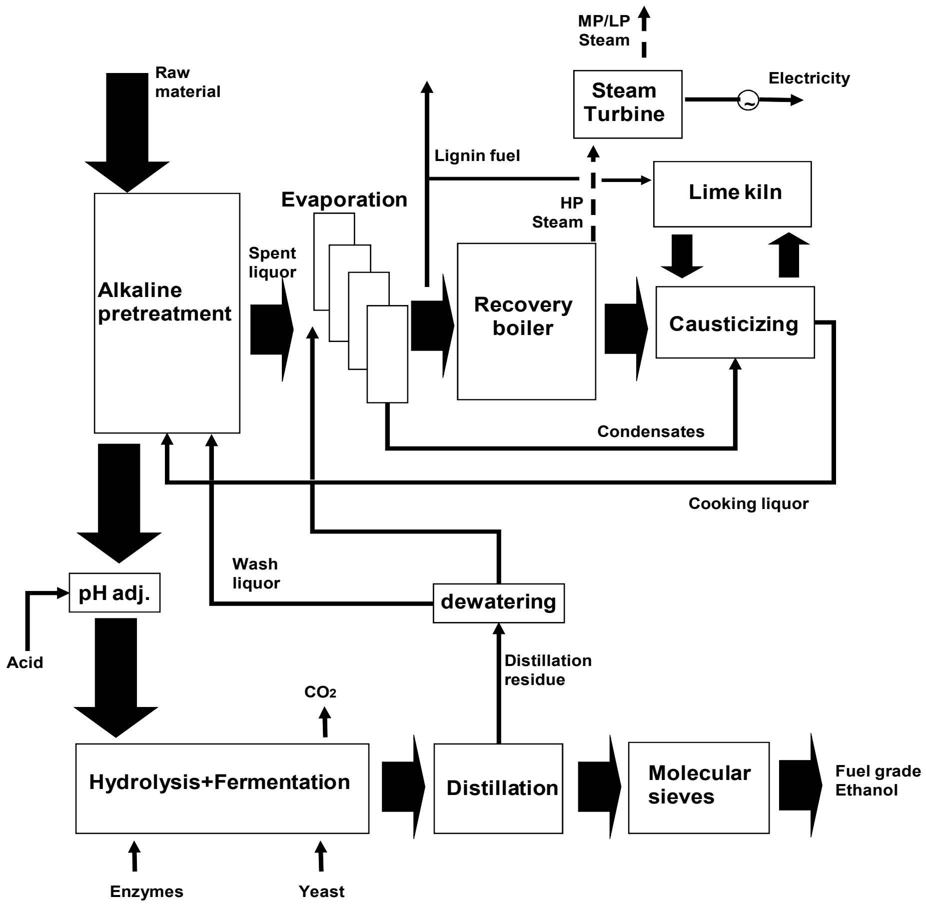

Figure 6.1. Block diagram of the conceptual ethanol production process.

The ethanol process is less sensitive to the quality of the raw material than the pulping process. Therefore it should be possible to switch to a lower quality (and cheaper) raw material, e.g., fines, forest residues or lignocellulosic waste fractions. One problem with lower quality fractions is the heterogeneity of the biomass. In Papers I-IV in this project no data for lower quality fractions had been put forth, instead existing data for softwood was used. The raw material composition in Paper V comes from studies made on lower quality feedstocks (Table 6.2).

Table 6.2. Chemical compositions of different biorefinery feedstocks (average values according to [19]) and the composition of the raw material in this project. The compositions of bark and forest residues vary substantially depending on wood species.

Component		Wood	Bark	Forest residue	Papers I-IV	Paper V
Cellulose		40-45	20-30	35-40	40	41
Hemicellulose		25-35	10-15	25-30	27	25
	- Hexoses				*14*	*15*
	- Pentoses				*8*	*10*
	- Other				*5*	
Lignin		20-30	10-25	20-25	26	31
Extractives		3-4	5-20	5	3	2
Other		1-2	5-25	4	4	1

The possible benefits of repurposing a Kraft pulp mill into an ethanol plant are that the pre-treatment can be done with the same chemicals as used in the pulping process, i.e., NaOH and Na_2S, and delignification can be done prior to the ethanol production line. Studies on pre-treatment in a Kraft digester using only OH^- as the cooking chemical were used in Papers I-III in this project [67, 68]. The benefit of this approach is the potential of extracting a sulphur-free lignin by-product.

The capacity of the ethanol production process in Papers I-III is approximately 1800 tonnes dry wood/day. In the Kraft pulp mill, with a capacity of 2065 tonnes dry wood/day, sodium hydroxide is also produced by sulphide hydrolysis ($S^{2-} + H_2O \rightarrow HS^- + OH^-$). The absence of sulphide ions will decrease the production rate of the digester at a given alkali charge [95]. Pre-treatment yields and conditions in the papers in this project are shown in Table 6.3.

In Paper IV it was assumed that both sodium hydroxide and sulphide are used as cooking chemicals. The yields were assumed to be the same as in the other papers, based on typical Kraft pulp mill pre-treatment yields, and references discussing hydrolysis and fermentation of Kraft pulp (cf. [48, 49]).

In Paper V only sodium hydroxide was used as the cooking chemical, but since the pre-treatment unit was integrated with the Kraft pulp mill the cooking liquor was a mixture of make-up NaOH from the pulp mill and oxidized white liquor. In the oxidized white liquor the sulphide was oxidized to SO_3^- and SO_4^{2-}. These sulphur ions were not active in the Kraft digester.

Table 6.3. Pre-treatment yields and conditions used in this project (cf. [67, 68, 95]).

NaOH charge	*% on wood*	*~20*
Kappa number		*~30*
Cellulose yield	*% on cellulose*	*80*
Hemicellulose yield	*% on Hemicellulose*	*40*
Total carbohydrate yield	*% on wood*	*43*
Temperature	*°C*	*160-180*

The DME process

In Paper IV it was assumed that the residue liquor in the ethanol plant was gasified and synthesised to DME (Di-Methyl-Ether) (Figure 6.2). Research projects on black liquor gasification from Chemrec in Sweden and Princeton University in the USA can be found in the scientific literature [47, 63]. A number of different process configurations and products were assessed in these projects. In Paper IV it was assumed that DME was produced according to the pathway presented by Chemrec, i.e., entrained flow gasification of the spent liquor, then removal of CO_2 and sulphur by absorption in chilled methanol, and finally a two-step synthesis from syngas (CO, H_2) via methanol to DME. The process is described in more detail in Paper IV.

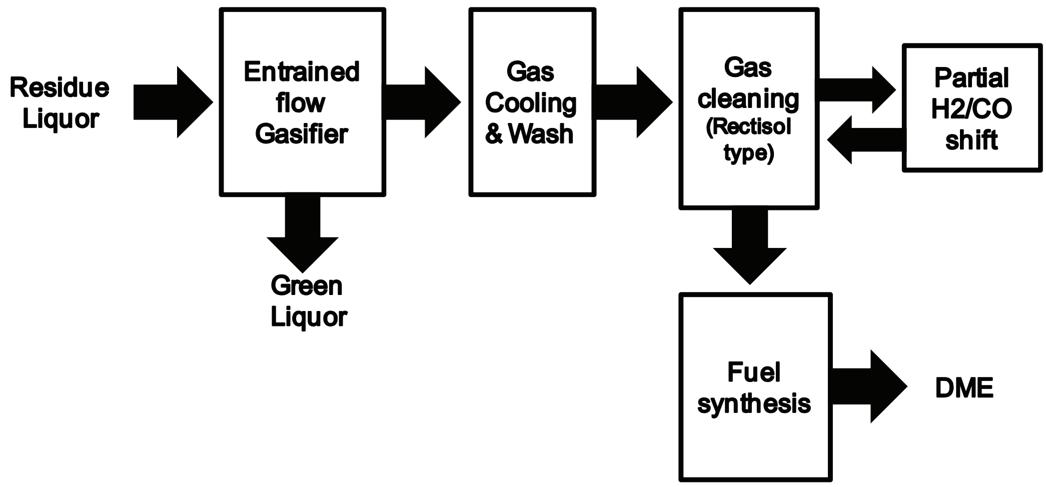

Figure 6.2. Block flow diagram of the black liquor gasification process for production of DME.

7 Results & Discussion

In this project three different Kraft pulp-mill-based biorefineries have been studied from a process integration point-of-view. In Papers I-III the ethanol plant was based on a repurposed average Scandinavian Kraft pulp mill, in Paper IV the biorefinery was designed to produce both ethanol through a biochemical pathway and DME through a thermochemical pathway, and finally in Paper V the ethanol process was co-located and combined (chemical recovery and residue processing) with a state-of-the-art reference mill. The results from the different studies have been expressed in terms of either opportunities for improving energy efficiency, or economics. In this chapter a brief description of the results from the studies of each of the processes is included followed by a short summary of the findings.

Energy efficiency

Energy efficiency in ethanol production is an important parameter since higher efficiency means greater potential for selling by-products if the decrease in energy usage is transformed into electricity or other biofuels. The different processes in this project have all been subjected to pinch analysis studies, and the results are presented in brief in this chapter.

Ethanol production in a repurposed Kraft pulp mill

The base case in these papers was a repurposed pulp mill where the only investment made was in the ethanol line. No improvements in the utilization of utility steam were implemented and no upgrading of the evaporation plant was done. Since this pulp mill had a large surplus of steam and since ethanol production has a lower steam demand than pulp production, the base case vented a lot of steam to the atmosphere.

Figure 7.1 shows the composite curves (CC) for a ΔT_{min} corresponding to the process steam demand of the background process, excluding evaporation and distillation, in the base case ethanol plant (ΔT_{min}=28.5 K). These curves indicate that there is potential for improving energy efficiency if the ΔT_{min} is decreased.

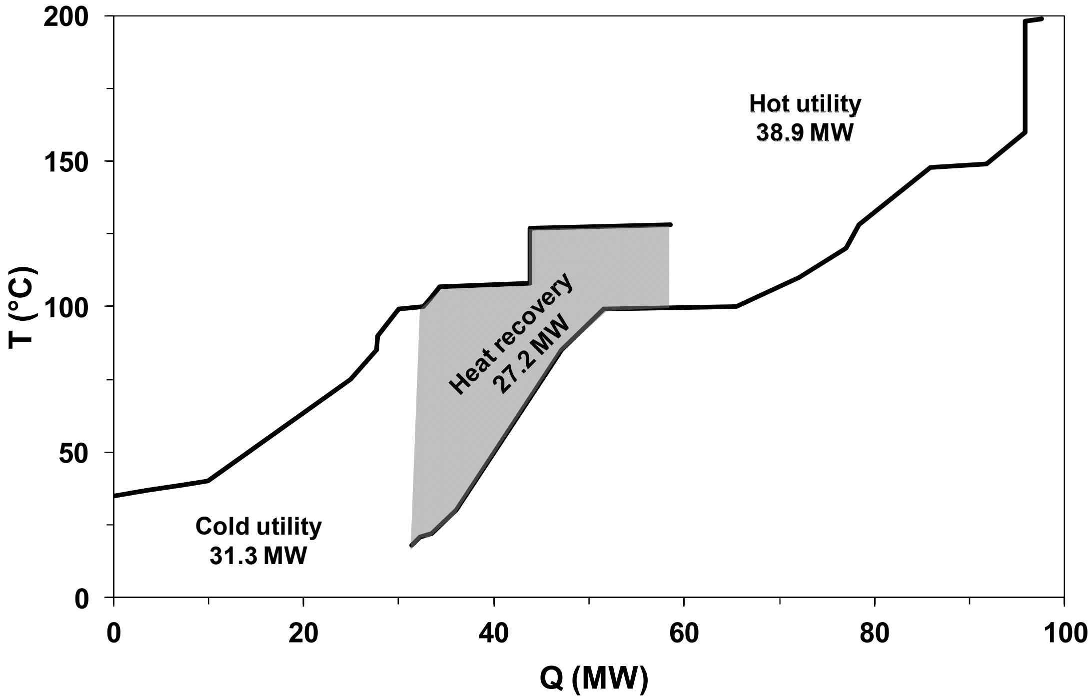

Figure 7.1. Composite Curves of the background process in the base case. The utility demand corresponds to a global ΔT_{min} of 28.5 K.

A number of different heat integration alternatives between the heat exchanger network of the background process and the distillation and evaporation plants were assessed for this process concept (Figure 7.2). Alternatives A-I were derived using conventional pinch methods, i.e., solving pinch violations in the heat exchanger network and then integrating distillation and evaporation. Alternatives J-M were derived using the advanced composite curves (TCLC, THLC) described in the method chapter and maximizing the integration of distillation and evaporation with the heat exchanger network of the background process in order to reduce utility demand. Alternatives N-Q show different suggestions for heat pump integration.

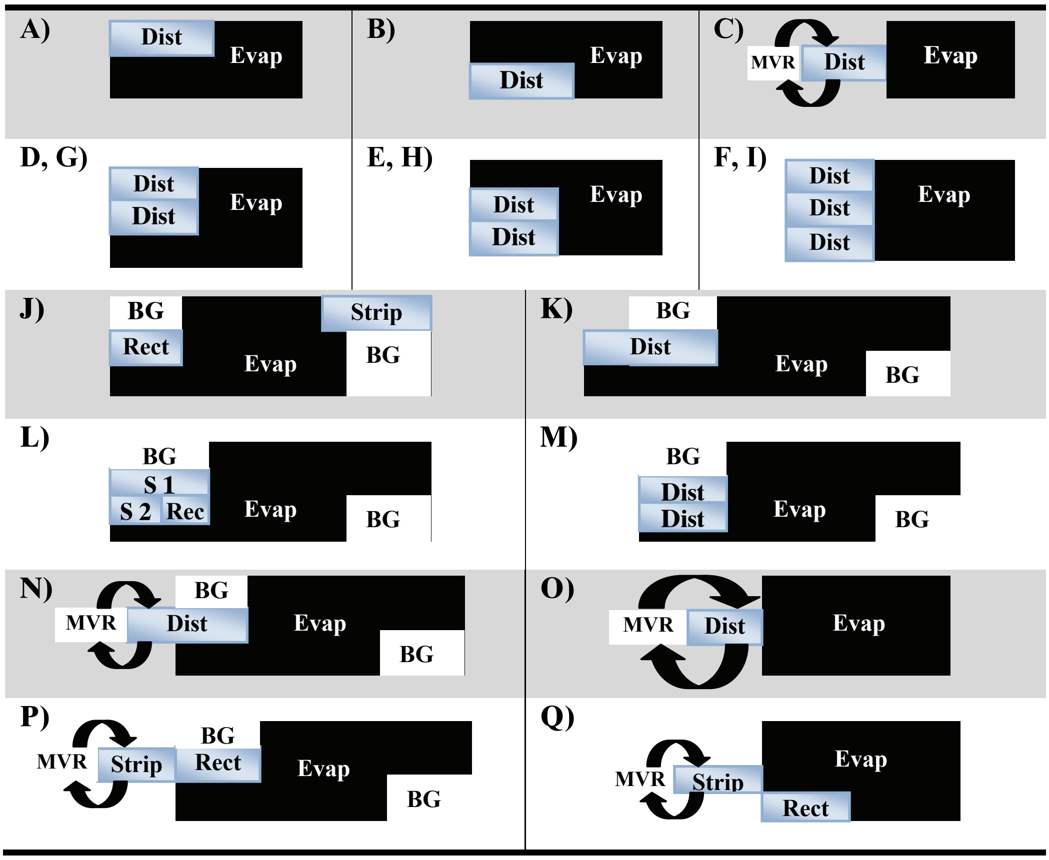

Figure 7.2. The different alternatives included in this work. BG stands for background process. Alternatives D-I are distillation columns (D-F) or stripper(s)/rectifier (G-I).

The demands for process steam in the different alternatives in Figure 7.2 are shown in Figure 7.3. As can be seen, the base case (orig) steam demand is approximately 105 MW, and the different suggested alternatives are about 25-40% lower. In the alternatives where heat is integrated with the advanced composite curves (TCLC/THLC), the resulting steam demand is marginally lower than in alternatives A to I. Figure 7.3 also shows that including a heat pump in distillation can result in an even lower steam demand, but since the distillation utility demand is already low in the base case the reduction is not that great. The utility reduction owing to heat pump integration also comes at the expense of increasing electricity demand in the process.

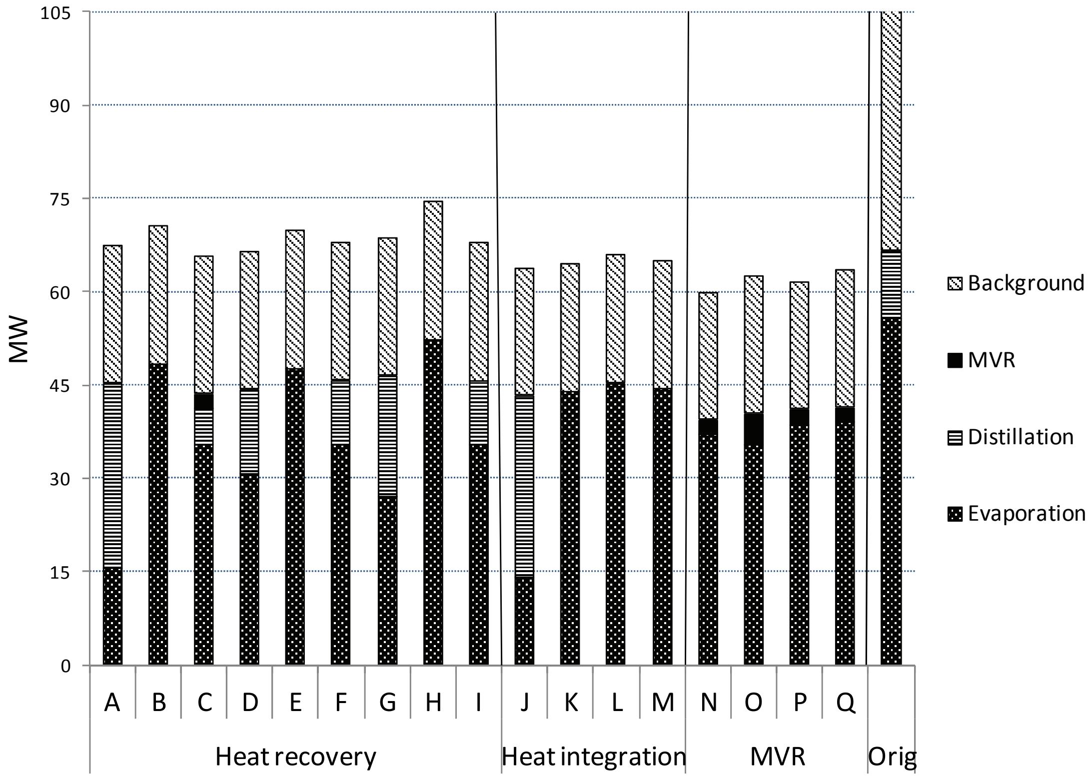

Figure 7.3. Steam demands in the studied process alternatives (based on data in Paper 2).

Ethanol-and DME production in a repurposed Kraft pulp mill

The conceptual design of a biorefinery, based on a repurposed typical Scandinavian Kraft pulp mill, producing both ethanol and DME, was assessed in this project. The ethanol process was designed previously, as described in the preceding subchapter. The thermochemical DME process was designed in this study by using process simulation software, however. In the study it was shown that in theory the two subprocesses could be thermally integrated enough to virtually remove the entire need for external fuel for hot utility production. If assuming a more realistic target, such as only heat integration through the utility system, the deficit of utility steam would be approximately 62 t/h, as indicated in Figure 7.4. Since the existing boiler at the plant only produces 50 t/h, there would be a need for external fuel in this case. One reason for this is that LLP steam is produced in the utility system, this steam cannot be utilized in the current design of the process.

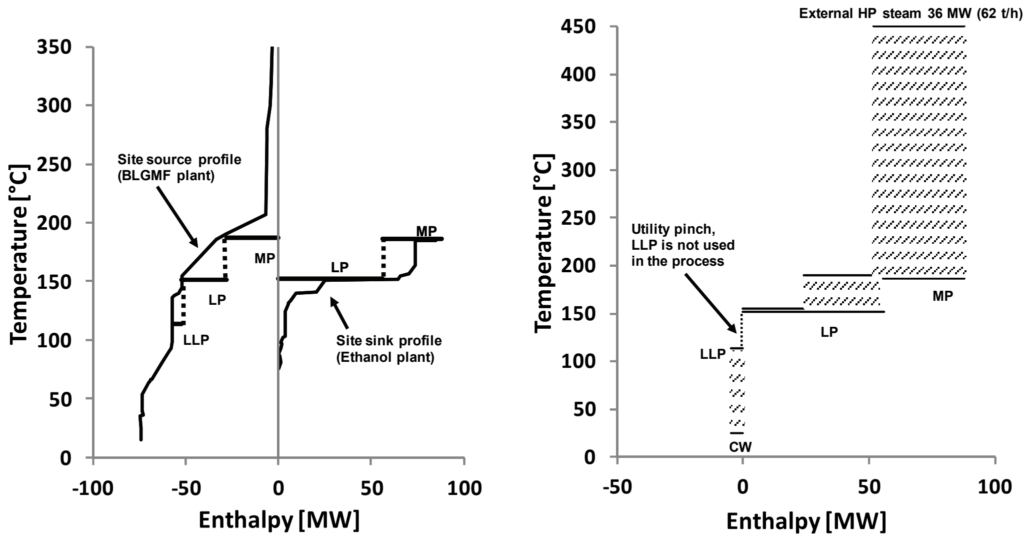

Figure 7.4. Site source and sink profiles and the resulting utility system for the combined ethanol and DME biorefinery.

The utility demand in Figure 7.4 can be reduced so that the internally produced hot utility will be enough to cover for the process, if the process is to some extent redesigned. This is shown in more detail in the appended paper.

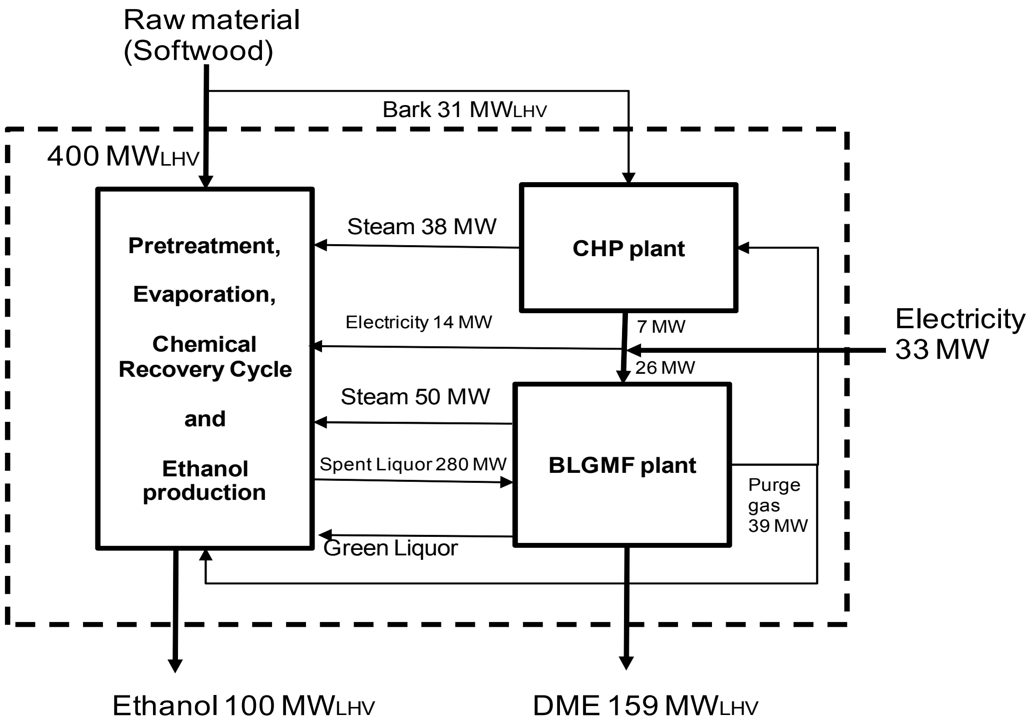

Figure 7.5. Energy flows in the ethanol + DME biorefinery.

One result of this study was the generation of the main energy flows for the total process, as shown in Figure 7.5. As can be seen in the figure there is no demand for external fuel in the CHP plant. This is valid ***if*** the ethanol and DME processes are well heat-integrated. When gasifying the residue liquor to produce DME, the only possibility to produce power is through the high pressure steam from the bark boiler. Therefore the electricity production in this biorefinery concept will be low, and external electricity must be bought (as shown in Figure 7.5).

Ethanol production co-located with a modern Kraft pulp mill

If a comparatively small ethanol production plant is designed in combination with a modern Kraft pulp mill several new heat integration opportunities emerge due to the combination of the two processes. Since lignin is extracted as a by-product in this ethanol process design, the residue liquor only needs to be evaporated to approximately 35% dry solids content (DS) in the ethanol plant. At this dry solids content the lignin can be extracted, and then the remaining residue liquor can be sent to the pulp mill evaporation plant. The difference in the evaporation target (35% DS instead of the 80% DS in the repurposed pulp mill) generates new possibilities for heat integration. There is also potential for heat integration between the ethanol process and the pulp mill that might result in an increase in the energy efficiency of the process.

The study was performed as a comparative analysis with a base case biorefinery process where no opportunities for heat integration were implemented. The evaporation plant was assumed to be designed with 4 steam effects, the distillation sequence was comprised of three heat-integrated columns (two parallel strippers followed by a rectifier column), and the pre-treatment unit utilized recycled flash steam for presteaming. The evaporation plant and distillation sequence were designed in various ways in this paper, in order to compare different alternatives in terms of energy efficiency.

The different heat integration alternatives investigated in this paper are shown in Figure 7.6.

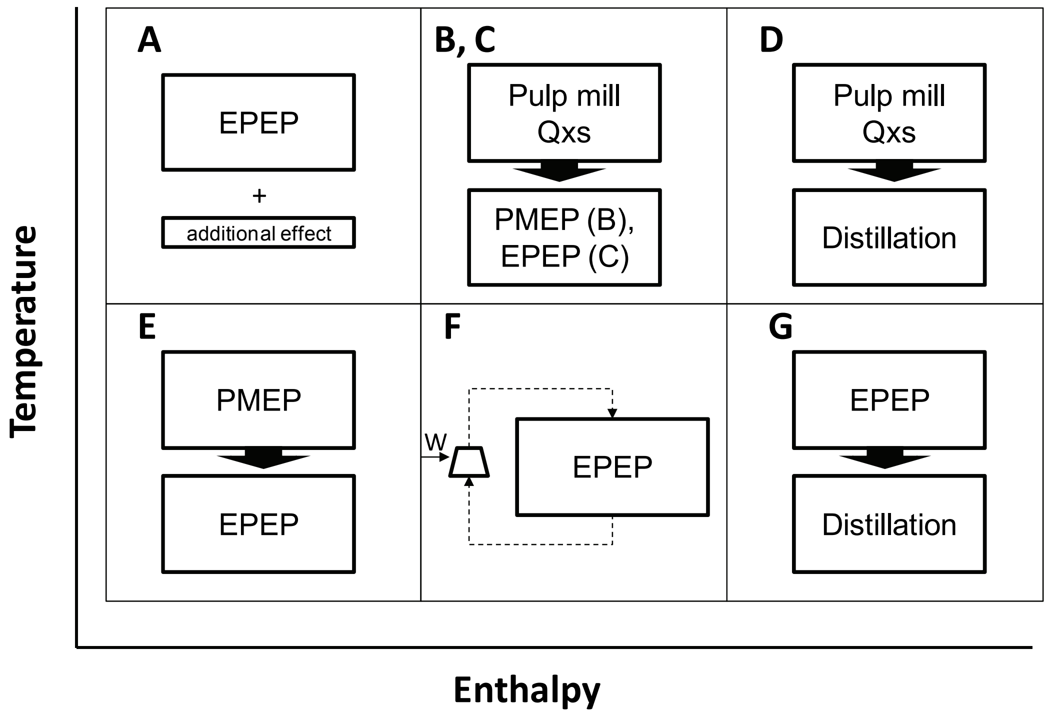

Figure 7.6. The different heat integration alternatives in the co-located ethanol plant and Kraft pulp mill. EPEP = Ethanol Process Evaporation Plant, PMEP = Pulp Mill Evaporation Plant.

One benefit of only evaporating the residue liquor to about 35% DS is that the elevation of the boiling point is low (approximately 4.5°C for one evaporation effect at atmospheric pressure). Due to the low temperature lift, an evaporation plant integrated with a mechanical vapour recompression heat pump (MVR) could be interesting (Figure 7.7, upper). Since the evaporation plant in this pulp mill is much larger than in the ethanol plant, and has a surface condenser operating at 54°C on the hot side, it is also possible to integrate the evaporation into the ethanol plant at temperatures below the surface condenser temperature of the pulp mill evaporation plant (Figure 7.7, lower). The benefit of this would be negligible live steam demand, and the downside would be that the size of the plant would have to be large due to large volumetric flowrates and low heat transfer coefficients.

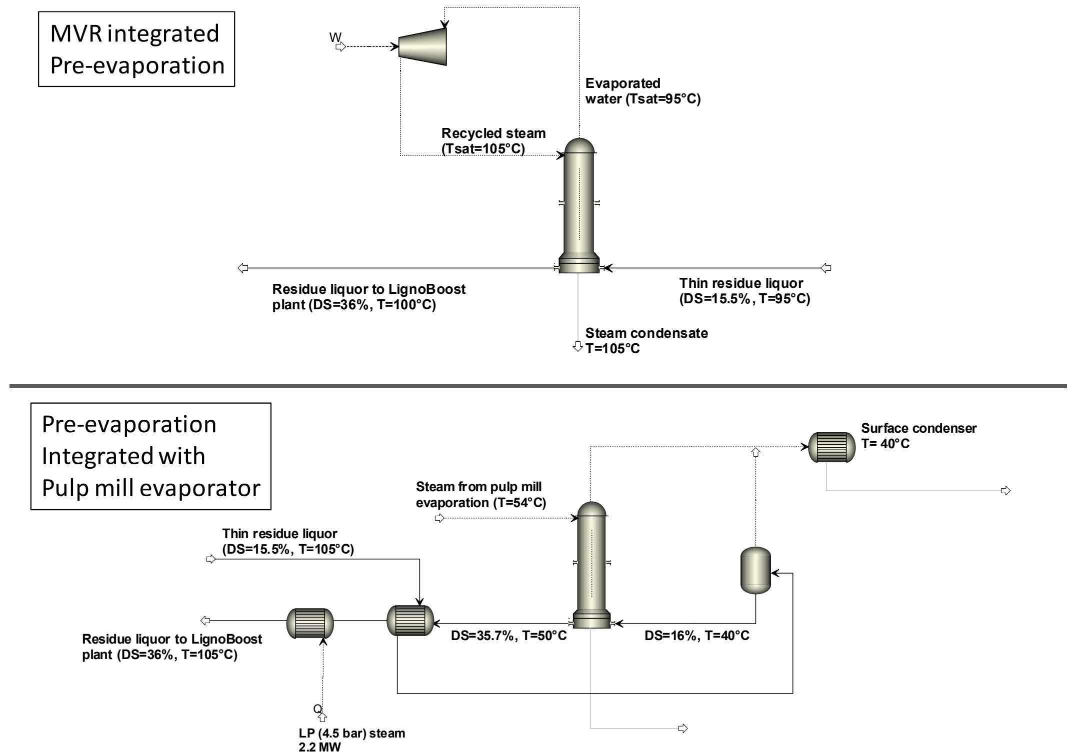

Figure 7.7. Ethanol process evaporation plant integrated with MVR-heat pump (upper) and pulp mill evaporation plant (lower).

The secondary heating system in the pulp mill could also be modified by using the tank curves, described in the methodology chapter, in order to improve the potential for heat integration between the two processes. Excess heat at high temperatures is available in the secondary heating system. This heat could be used for integration in several ways in this process concept. Both of the evaporation plants (in the ethanol process or in the pulp mill) and the distillation columns could be run with excess heat covering part or all of the hot utility. The distillation sequence in the ethanol process integrated with the excess heat from the secondary heating system is depicted in the split Grand Composite Curves (GCCs) in Figure 7.8.

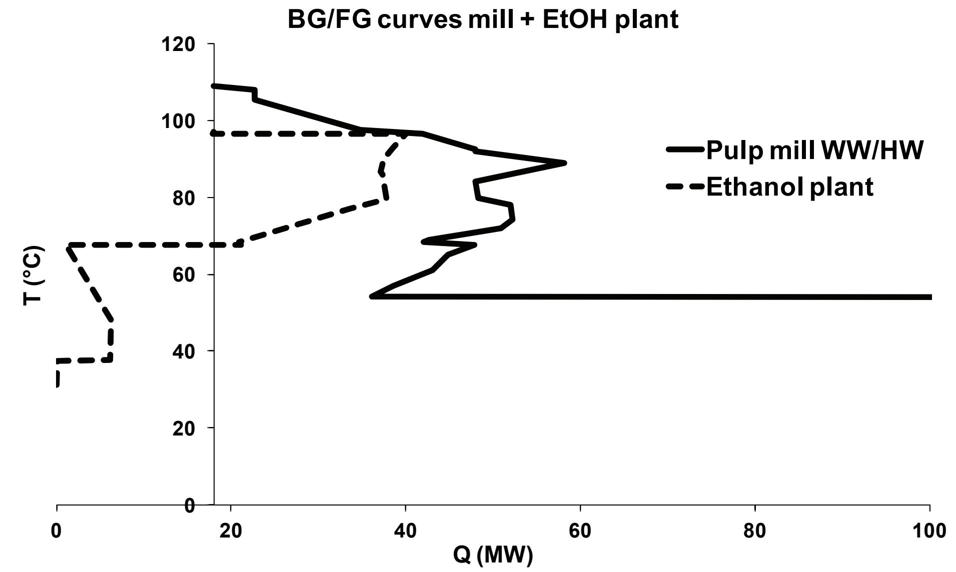

Figure 7.8. Split Grand Composite Curves indicating the potential for integration of the ethanol beer column and excess heat in the pulp mill secondary heating system.

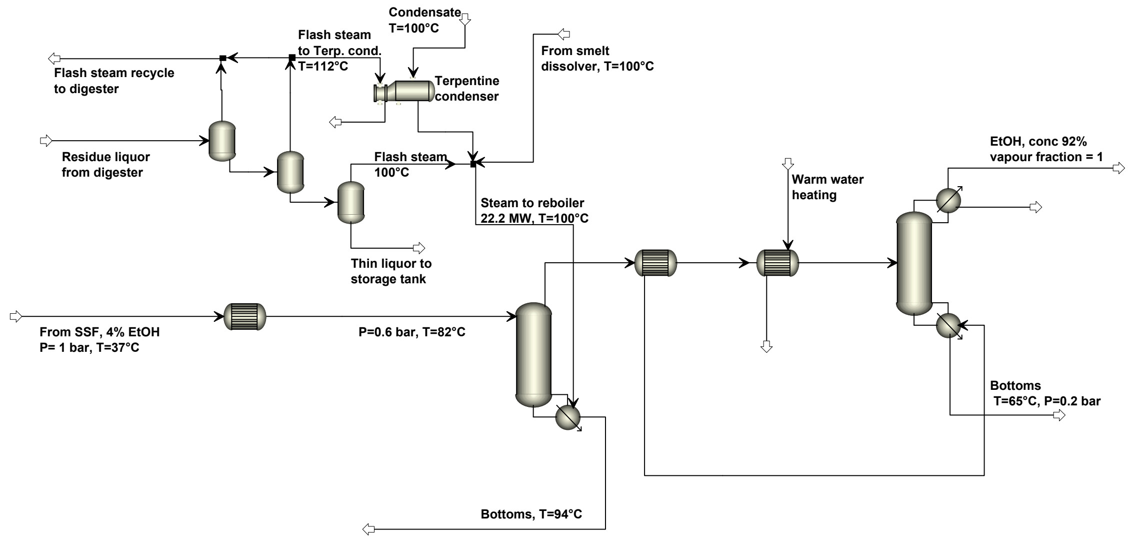

Figure 7.9. Process integration between excess heat from the pulp mill secondary heating system and the first column in the distillation sequence.

A more detailed description of the heat integration in Figure 7.8 is shown in Figure 7.9. The steam condensed in the turpentine condenser in the pulp mill is used to reform steam at atmospheric pressure. The atmospheric flash steam, the reformed steam, and the steam from the smelt dissolver, are used in the stripper reboiler in the distillation sequence. Some utility steam might be needed in the reboiler as well.

Another integration possibility included in the study was to upgrade the ethanol process evaporation plant to 5 effects, i.e., to reduce steam demand from the base case (30 MW) to 24 MW low pressure steam demand, and to have a high enough design pressure for this plant so as to be able to integrate it with the ethanol distillation section.

It is, in some cases, possible to integrate the pulp mill evaporation plant with the excess heat from the secondary heating system, and at the same time make improvements in the ethanol process. For example, the MVR-integrated evaporation in the ethanol process does not reduce the excess heat available in the secondary heating system in the pulp mill.

The resulting hot and cold utility demands for the different alternatives investigated are shown in Table 7.1. The table also includes a case where the evaporation plant is upgraded to 5 effects steam economy (alternative A) and a case where the pulp mill evaporation plant is integrated using the excess heat available in the hot and warm water system (alternative B).

Table 7.1. Hot and cold utility demands, and potential increase in electricity production, for the different alternatives.

Alternatives (A-G in Figure 6.7)	**Qh** [MW]	**Qc** [MW]	**ΔQh**	**ΔQc**	**ΔWoutput** [MW el]
Base case	400	410	-	-	
A - 5 eff EPEP	394	404	6	6	1.3
B - Pi PMEP	392	413	8	-3	1.7
C - Pi EPEP	375	398	25	12	5.3
D - Pi Dist	390	400	9	10	1.9
E - Int EPEP/PMEP	377	379	23	31	4.7
F - MVR EPEP	375	391	25	19	1.6
F with int PMEP	363	398	37	12	4.1
G - Int Dist/EPEP	386	401	14	9	2.9
G with int PMEP	371	410	29	0	6.1

The base case process has a hot utility demand of 400 MW and a cold utility demand of 410 MW. If the EPEP is designed with 5 heat integrated evaporation effects instead of the original 4 the savings would be 6 MW of LP steam (24 MW steam demand with 5 effects compared to 30 MW with 4 effects). If the distillation columns were integrated with the hot and warm water system the decrease in utility demand would be 9 and 10 MW, respectively (duties of reboiler and condenser connected to utility streams). The highest reduction of utility demand for one single measure is when the

EPEP is integrated with the PMEP. Combined measures (as in alternatives C, F and G) would reduce the hot and cold utility demands the most. Comparing the potential for reduction of utility demand when integrating the EPEP or PMEP with the excess heat from the hot and warm water system, it can be seen that integration of the EPEP shows much larger potentials.

Summary - energy efficiency

A comparison of the different ethanol process steam and electricity demands, and energy allocation possibilities, are shown in Figure 7.10. All of the processes are self-supplied in terms of hot utility, which means that the steam demand is supplied from a steam boiler at the process site. Electricity demands are also supplied internally in all cases except for the combined ethanol-and DME process.

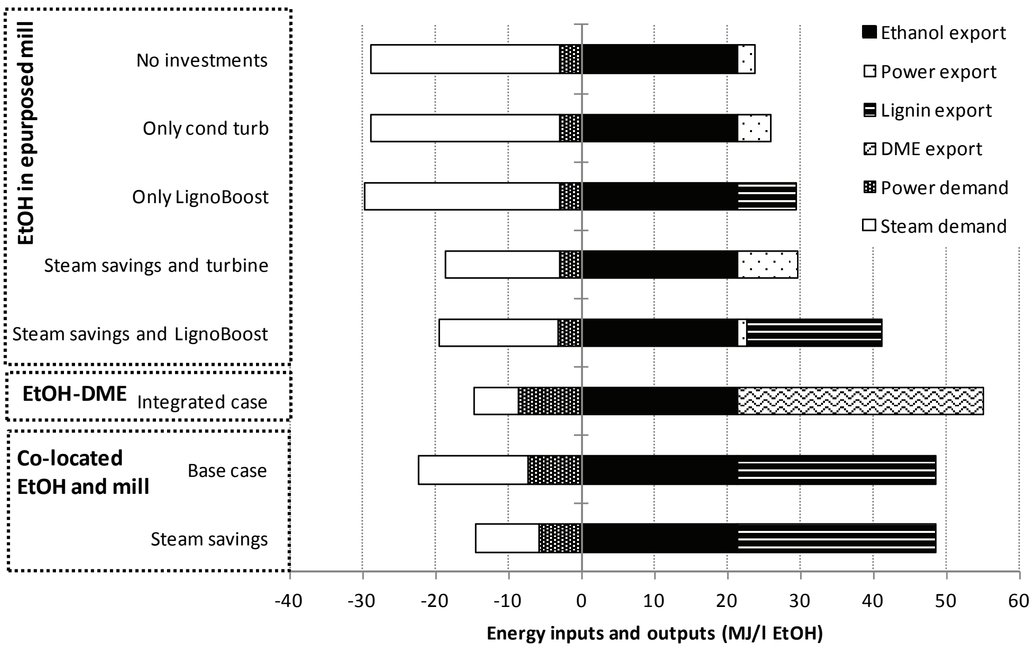

Figure 7.10. Utility demands (negative values) and energy allocation possibilities (positive values) in the different processes studied.

The results indicate that the repurposed Kraft pulp mill, in this case, almost doubles the output of by-products (electricity or lignin), if steam-saving measures are implemented. The output of lignin would almost be of the same order as ethanol. Adding a gasification plant to the ethanol process would substantially change the energy balance of the process. The steam demand would become lower due to the potential for the heat integration of the two processes, but the production of steam would also become lower since there is no recovery boiler. Power would need to be imported to the process, and DME would be the main product instead of ethanol. Finally, co-locating and combining an ethanol plant with a much larger Kraft pulp mill would not change the utility demands of the process in the base case. The new opportunities for heat integration in this process combination would, however, reduce the utility demand substantially, if implemented.

Economic analyses

An increase in energy efficiency can be transferred to an increase in by-products sales since less energy is needed internally in the process. Since an increase in by-products sales normally also demands an increase in investment costs owing to the larger production capacity needed, it is not always clear that the economics of the process will improve from a decrease in internal energy usage. In this chapter the results from the economic analyses made in this project are described in brief.

Ethanol production in a repurposed Kraft pulp mill

In the studies conducted on the ethanol process based on a repurposed Kraft pulp mill the energy efficiency analysis indicates that the process could be designed in a way that would enable the energy input to be transferred to the output of different products in a better way than is suggested in the base case design. But is this beneficial from an economic point-of-view? In Figure 7.11 the costs coupled to the different alternative investment possibilities analysed are shown, i.e., costs for evaporation, distillation and HX network redesign. ***Original*** means the base case process with minimum investment costs, i.e., only the investment in a new distillation unit is included in Figure 7.11. ***Only HX*** means that additional investments are necessary in order to improve the heat exchanger network, and ***only evap*** means that ***original*** + upgraded evaporation are invested in. ***Recovery*** includes the different alternatives where internal heat recovery in the background process is the objective (alternatives A-B and D-I in Figure 7.2), ***Integration*** means the alternatives for improving heat integration between the three parts of the process (alternatives J-M, N and P in Figure 7.2). ***MVR*** depicts the different alternatives including an MVR heat pump in the distillation (alternatives C and N-Q in Figure 7.2). As can be seen in

Figure 7.11 measures intended to decrease steam demand come at a cost, and the lower the steam demand the higher the cost. The lowest steam demand can be reached by investing in an MVR heat pump but the demand for electricity will consequently increase. It should also be noted that ***Integration*** alternatives in general have a lower steam demand than ***Recovery*** but that the cost is somewhat higher. The alternatives called ***only HX*** and ***only evap*** can be combined into alternative F or I, which are the best ***Recovery*** alternatives (with a steam demand similar to the ***Integration*** alternatives). The benefit of combining alternatives, as in alternatives F and I, are that the investment can be made in two steps, while all the ***Integration*** alternatives need to be dealt with in one major investment. Since high capital costs might be a barrier to implementing energy efficiency measures this might be an important parameter to consider [3].

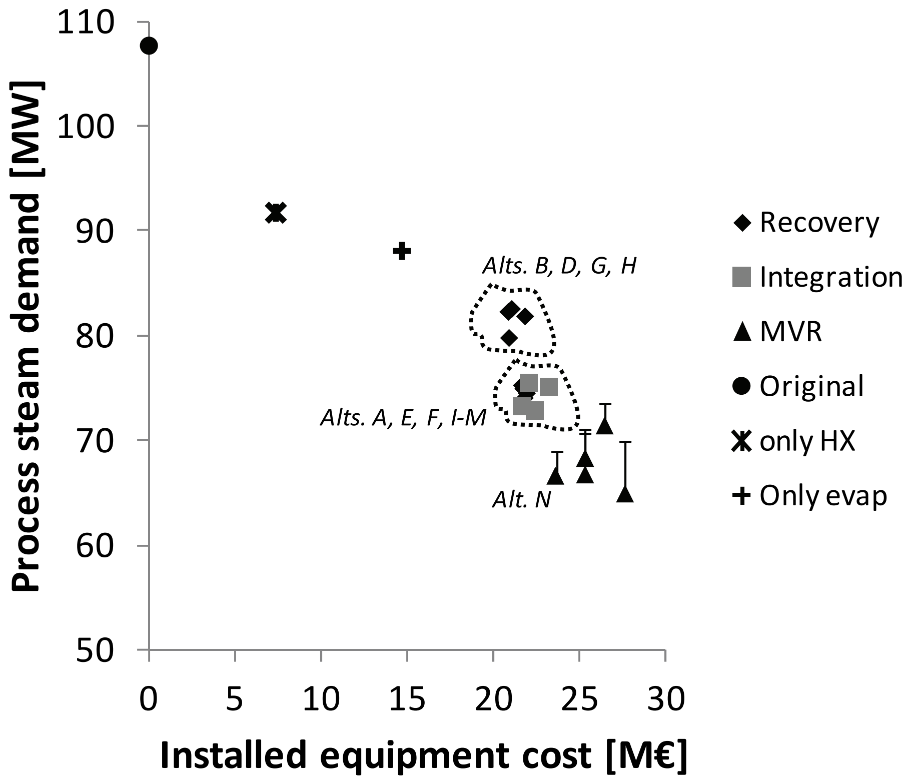

Figure 7.11. Installed equipment cost (distillation, evaporation and background process) vs. process steam demand for the studied alternatives in the repurposed pulp mill ethanol plant.

A comparison between extracting lignin and increasing electricity production was made for this biorefinery concept. As seen in Figure 7.12 the investment strategies employed (***Case 1*** is the base case, ***Case 2*** includes upgrading of evaporation and the HX network (no heat integration), ***Case 3*** includes heat integrated evaporation) showed similar correlations between electricity and lignin prices. If the electricity price was more than 2.9 -3.1 times higher than the lignin price, electricity would yield higher annual earnings than lignin.

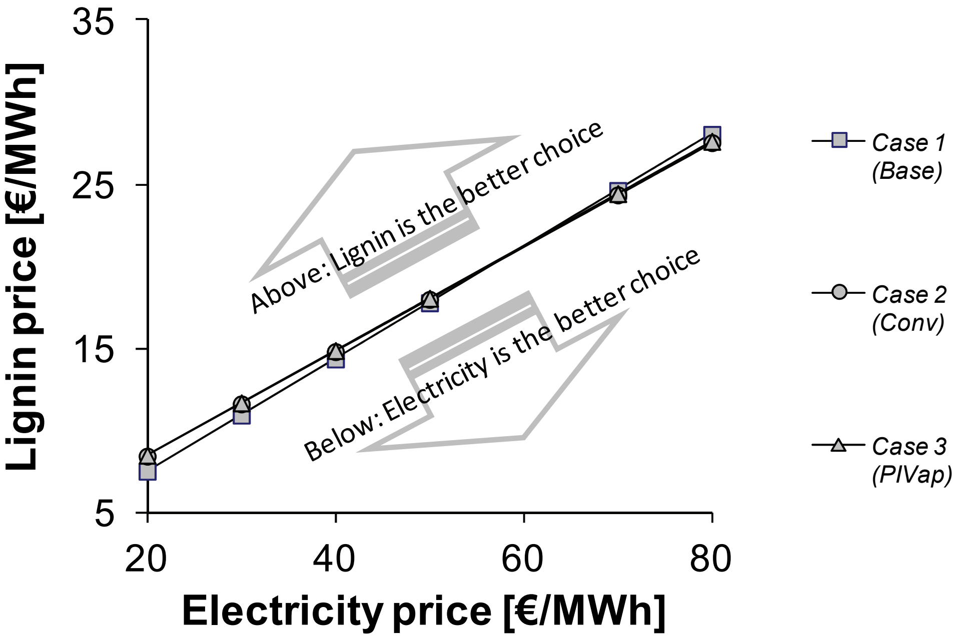

Figure 7.12. Lignin price where annual earnings for lignin extraction and increased power production are equal, at a given electricity price.

Figure 7.13 shows the ethanol production cost for 6 different alternatives. The ***alternatives F, L*** and ***N*** have been selected since they are the best alternatives in each category (heat recovery, heat integration and MVR) in terms of the incremental cost for steam-saving measures. Two other alternatives are included for comparison (***New*** is the base case with investment in turbines or lignin extraction, ***HX*** includes an improved HX network and investments in turbines/lignin extraction). With regard to the discussion above the electricity price / lignin price is 2.45, which implies that lignin in most cases would be the better choice in Figure 7.13. This is evidently not the case for the alternative with only a new HX network. The reason for this is that the relatively higher steam demand in the process limits the possibility of extracting lignin.

The ethanol production cost is largely dependent on the price of raw material and the investment cost. With the initial estimates of the investment cost for existing equipment, i.e., the pulp mill, and raw material, i.e., softwood, these two costs alone would add up to approximately 460 EUR/m^3 ETOH. This is set as the intersection between x/y-axes in Figure 7.13. In the original case the total ethanol production cost was 635 EUR/m^3 ETOH, indicating that raw material and investment costs comprise a very large part of the cost of ethanol. Nevertheless the decrease in ethanol production cost when implementing energy efficiency measures could be 84 €/m^3 EtOH (Alternative F with lignin as the by-product, compared with the base case), which in annual profits is a difference of almost 11 M€/yr. The difference between only using excess heat (New turb/lign) and far-reaching energy efficiency measures is 53 €/m^3 EtOH, i.e., almost 7 M€/yr in annual profits.

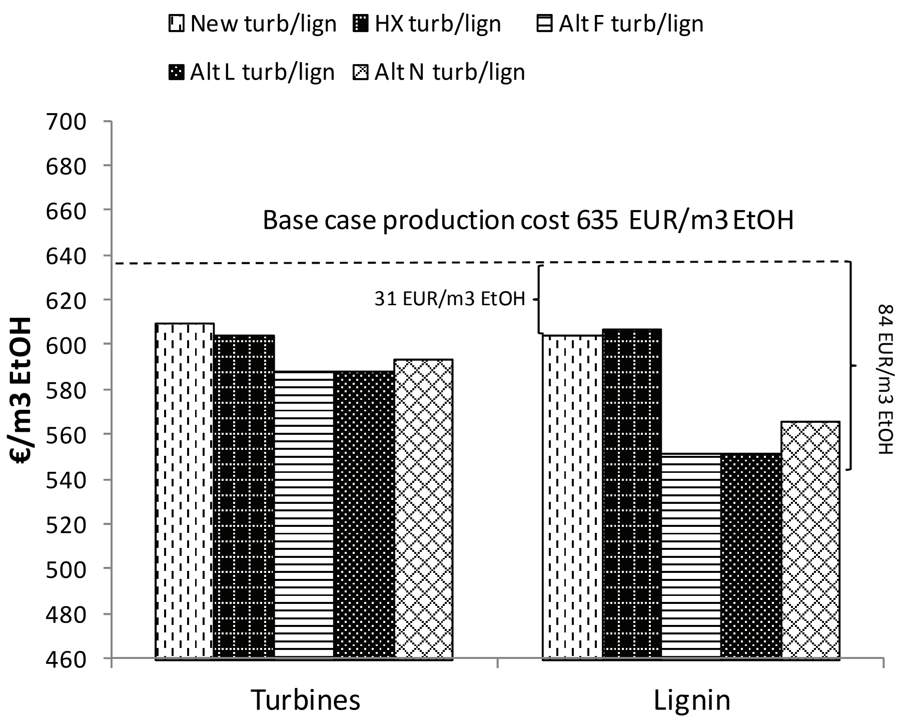

Figure 7.13. The ethanol production cost (Minimum selling price) for the evaluated design alternatives.

Figure 7.14 shows the effect of different measures in the short term, using the prices stated in Table 5.1. As seen in the figure all improvements done in the process will lead to a lower production cost for all three scenarios. It can also be seen that if the by-product in the process is electricity a more energy efficient process leads to a lower production cost. The only exception is alternative N where the MVR heat pump adds to the production cost.

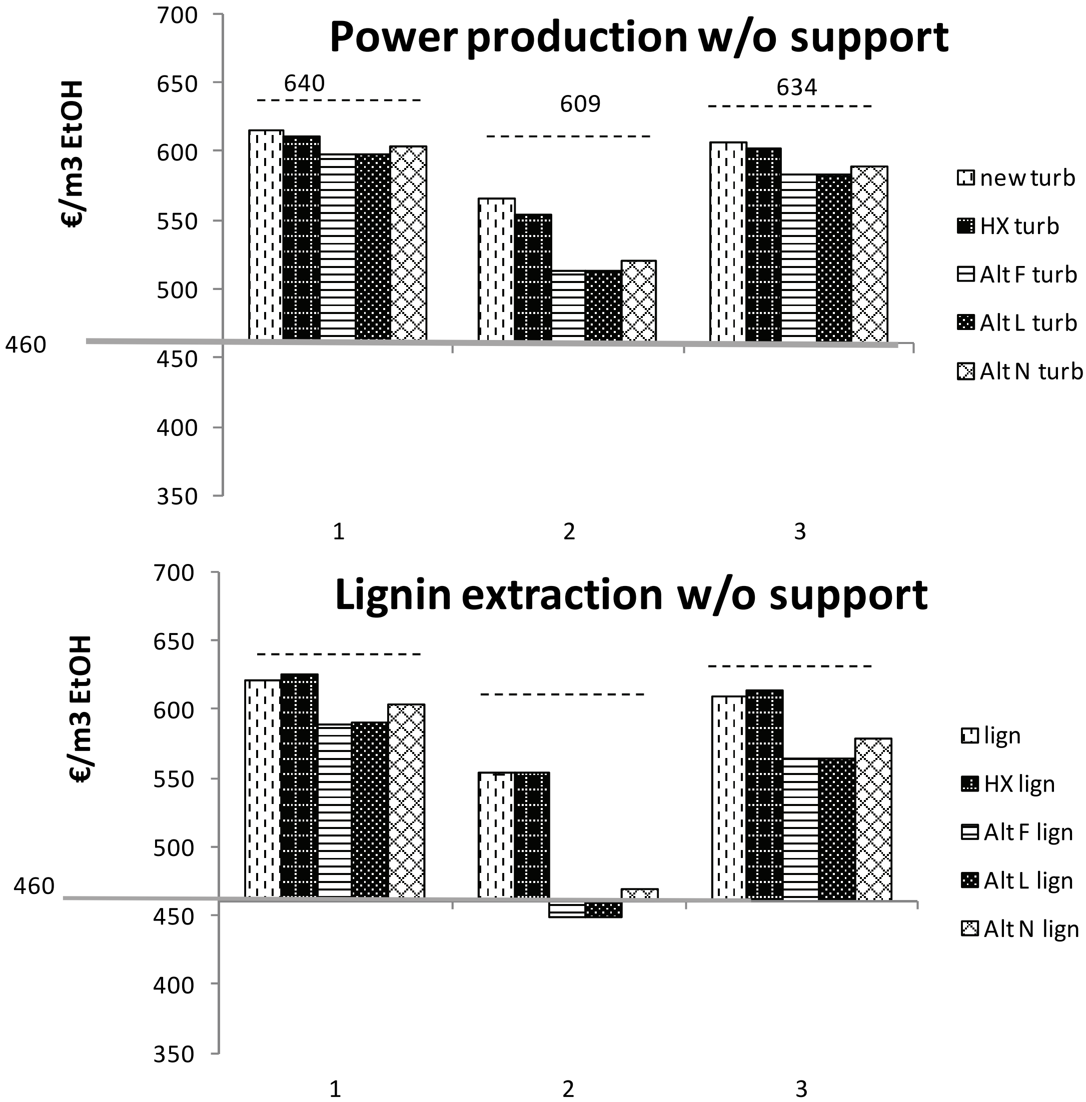

Figure 7.14. Short-term effects of by-product sales on the total ethanol production cost, given 3 different energy market scenarios. (The x-axis and y-axis intersect at 460 €/m^3 EtOH, corresponding to the cost for raw material and purchase of the existing pulp mill). The dotted line in the figure indicates the base case production cost.

The first scenario indicates that even if the prices for lignin and electricity are somewhat lower than today the increase in by-product sales will help decrease the production cost of ethanol. The second scenario shows that if the fossil fuel price is assumed to increase and the CO_2-charge for emissions from non-renewable sources is high, a process with high energy efficiency will be clearly better than the original process. In the third scenario, which is somewhere in between the two others, the results are slightly better than scenario 1.The PBP for making investments in energy efficiency improvements are between 8 years (alternative N with lignin in scenario 1) and 1 year (only extracting lignin in scenario 2), and the PBP for the total investment (assuming the same ethanol revenue as before, 0.6 €/l) is between 12 years (HX with lignin in scenario 1) and 6 years (alternatives F and L with lignin as by-product in scenario 2).

Figure 7.15 shows the effect of different measures when a support of 26 €/MWh_{el} for renewable electricity production is introduced (as shown in Table 5.1). It is obvious that all alternatives benefit from the higher value of the by-product, and also that the alternatives with a high degree of energy efficiency measures benefit the most.

The PBP for making investments in energy efficiency improvements are between 5 years (alternative N with turbines in scenario 2) and 1 year (only extracting lignin in scenario 3), and the PBP for the total investment (assuming the same ethanol revenue as before, 0.6 €/l) is between 9 years (new turbines in scenario 1) and 6 years (alternative F with lignin and L with lignin in scenario 2).

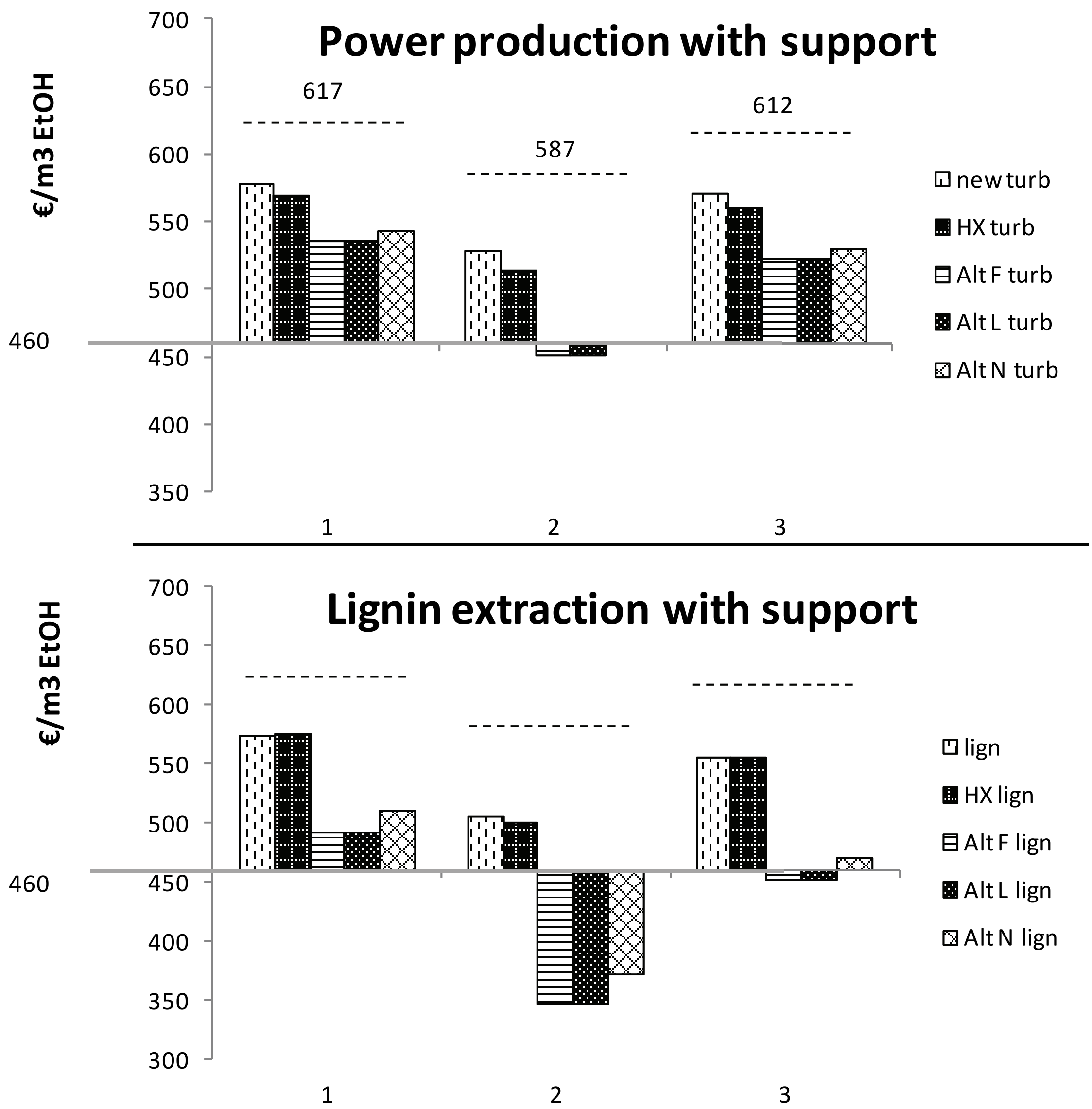

Figure 7.15. Long-term effects of by-product sales on the total ethanol production cost, given 3 different energy market scenarios. (The x-axis and y-axis intersect at 460 €/m^3 EtOH, corresponding to the cost for raw material and purchase of the existing pulp mill). The dotted line in the figure indicates the base case production cost.

Ethanol-and DME production in a repurposed Kraft pulp mill

The feasibility of the biorefinery that produces both ethanol and DME is sensitive to several different variables. In the base case, with an annuity factor of 0.1, an electricity price of 60 €/MWh, and estimated selling prices of ethanol and DME at 490 and 440 €/m^3, respectively, the net annual earnings would be approximately 25 M€/yr. Since the investment cost is high, the annuity factor will have a substantial effect on the profitability of the process concept (Figure 7.16).

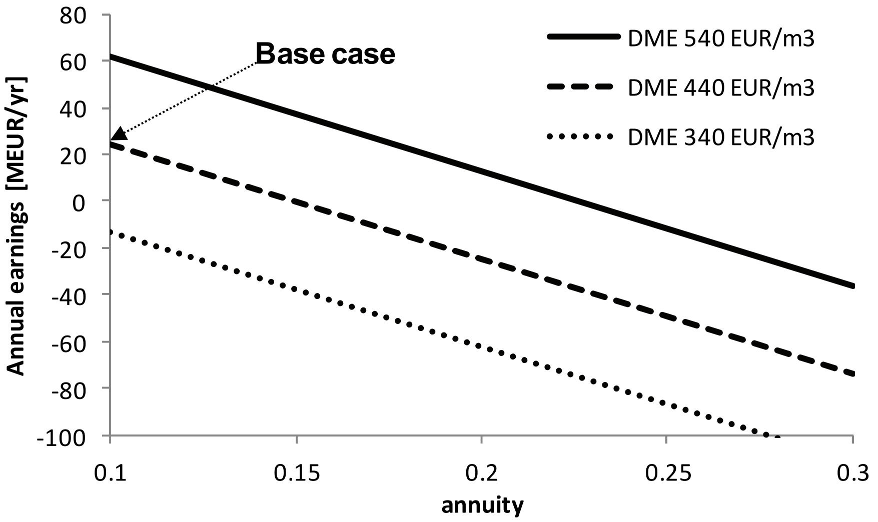

Figure 7.16. Sensitivity analysis of net annual earnings vs. annuity.

Other important parameters are shown in Figure 7.17. In the figure, different variables have been increased/decreased up to 30% in order to study the effects on annual earnings.

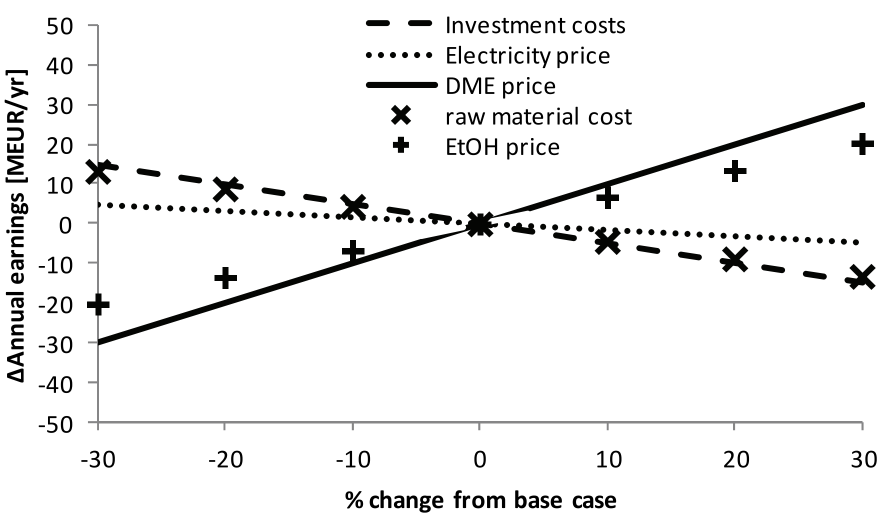

Figure 7.17. Sensitivity analysis of net annual earnings vs. different important parameters.

As can be expected, the prices of the products (DME and ethanol) have the greatest effect on plant profitability. An increase in ethanol or DME price by 30% would give an increase in annual earnings of 20 to 30 M€/year. The

costs of investment and raw material are the two other major influences on the feasibility of this process; a 30% change in these parameters would imply a change in annual earnings of 15-20 M€/year.
The net annual earnings allocated to CCS in this conceptual biorefinery are shown in Figure 7.18, for four different CO_2 charge levels (Table 5.2). Since the lowest charge level is constant and below the calculated cost for CCS, the net annual earnings will be negative. For the other three cases the CCS will give positive annual earnings, although for level 2 the increase is low.

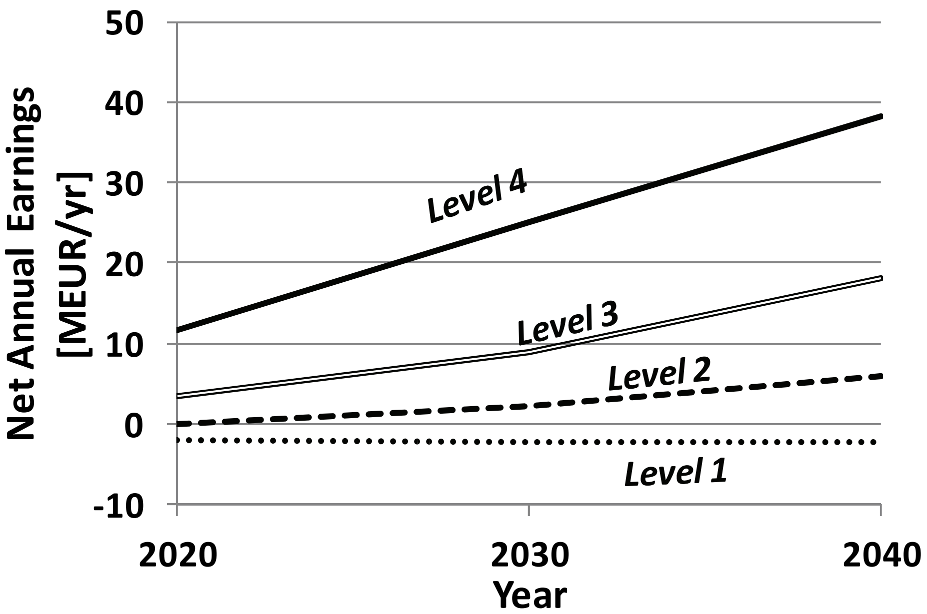

Figure 7.18. Net annual earnings when investing in a CCS plant for four different CO_2 charge levels.

Ethanol production co-located with a modern Kraft pulp mill

The different suggested designs for the ethanol process co-located with a state-of-the-art Kraft pulp mill, shown in Figure 7.5, have been subjected to a comparative profitability analysis. If the annuity factor is 0.1 and the electricity price 60 €/MWh, the increase in revenue from greater electricity production versus the increase in investment cost compared to the base case can be estimated according to Figure 7.19.

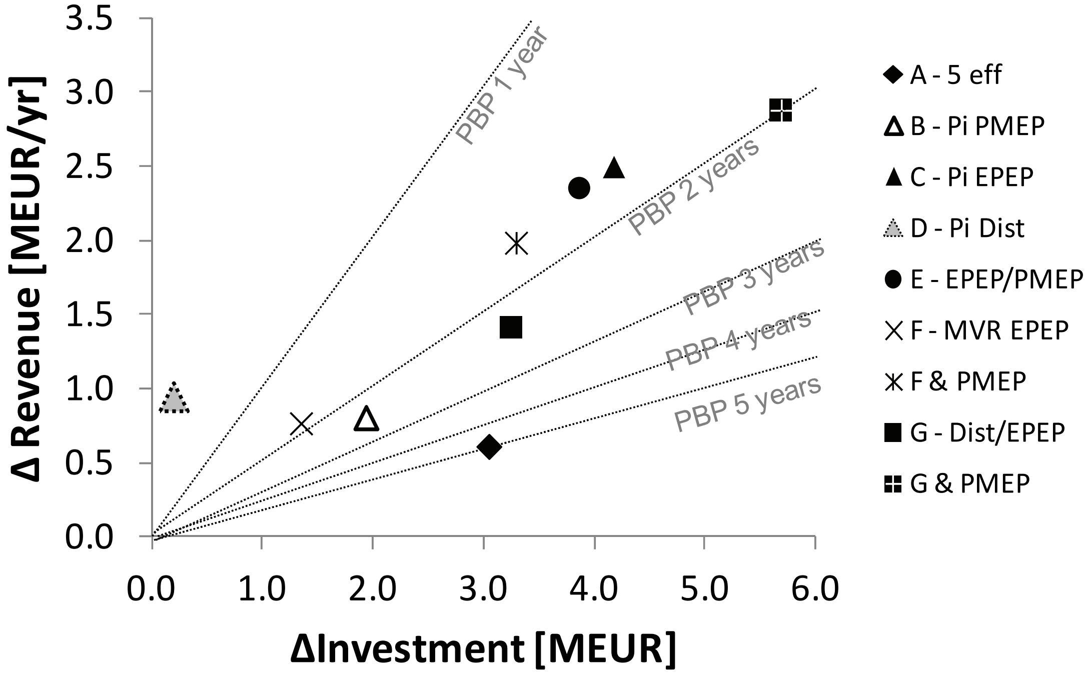

Figure 7.19. Results from the economic analysis at an annuity factor of 0.1 and an electricity price of 60 €/MWh. Pi = integration with pulp mill hw/ww system, EPEP = Ethanol Process Evaporation Plant, PMEP=Pulp Mill Evaporation Plant.

Several of the alternatives in Figure 7.19 have similar economic potential. Alternatives B, C, D, and E differ in terms of investment needed and in the expected revenue from electricity, but have similar payback periods. Alternatives A, F and G have less potential (are located low and to the right), but since these alternatives can be combined with the heat integration of the pulp mill evaporation plant and the secondary heating system, they can still be of interest. The complexity of the process would increase due to the need for several measures, however.

In Figure 7.20 the payback periods for the different heat-integration alternatives are shown at different electricity prices. Since the cost for integrating ethanol distillation is low the payback period for this alternative will be close to 0. The payback period for the 5-effect evaporation plant is long, while all the other alternatives show approximately similar results, between 1 and 3.5 years depending on the electricity price.

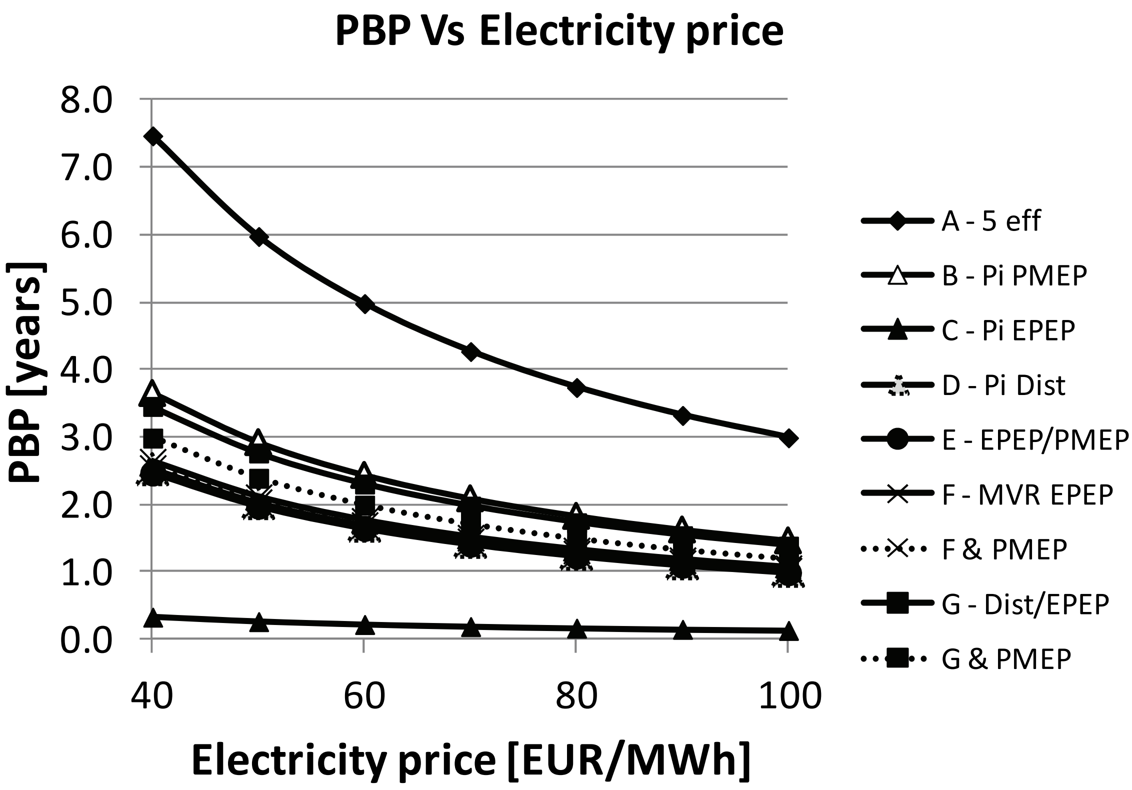

Figure 7.20. Sensitivity analysis of the payback period versus the electricity price for the alternatives in Table 2. EPEP = Ethanol Process Evaporation Plant, PMEP=Pulp Mill Evaporation Plant.

Summary - economic analyses

The studies show that there are large potentials for improving the profitability in the ethanol process when repurposing a typical Scandinavian Kraft pulp mill, in part due to the fact that the mill is old and inefficient. The economic analysis indicates that energy efficiency measures are beneficial even if only existing excess steam is utilised in the process. It was found that the process will be substantially improved, i.e., the production cost will decrease, in all the scenarios, whether electricity or lignin is the by-product, if far-reaching energy efficiency measures are implemented, however.

The by-products are shown to play an important part in the economic feasibility of the conceptual biorefinery. As shown in Figure 7.21, the combined ethanol and DME process shows a similar ethanol production cost as the best alternatives for production of ethanol in a repurposed mill with a recovery boiler, i.e., when the lignin price is high, if the revenue from

DME sales are allocated to the ethanol production cost. As can be seen in the figure, the ethanol and DME process is sensitive to the selling price of the products. A change in the annuity factor will also affect this process substantially due to the high investment cost, as shown in Figure 7.16.

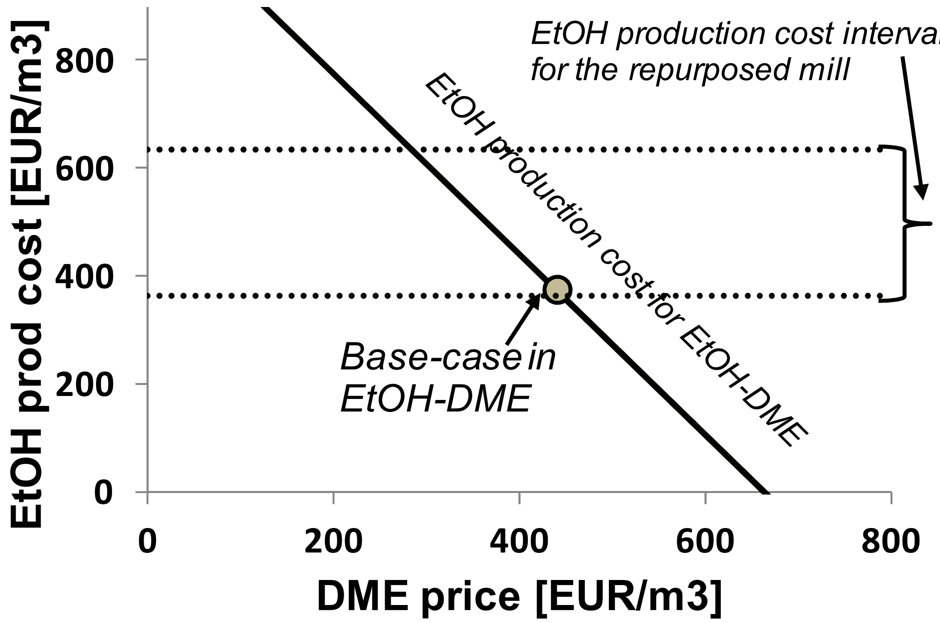

Figure 7.21. Comparison between the repurposed mill producing ethanol, and the ethanol and DME process. Both the ethanol and DME selling prices are varied.

The ethanol plant co-located with a modern Kraft pulp mill cannot be compared with the other two concepts since the information given is not enough to assess the production cost in this case. Only the opportunities for heat integration have been studied, but the results indicate that there is great potential for decreasing the utility demand in this conceptual ethanol process as well. As Figure 7.17 indicates there are different levels of measures that can be implemented that show similar economic results, and for most of the alternatives the payback period is less than 3.5 years even for low values of the product which the steam savings are transformed into (electricity).

8 Conclusions

In this project different biorefinery concepts in connection to a Kraft pulp mill have been explored. Process integration studies have been produced and the economics and energy efficiencies of the processes have been assessed. Some overall conclusions can be drawn from the different studies included in this thesis.

When repurposing a typical Scandinavian Kraft pulp mill to an ethanol plant, process integration studies can play an important part in making the investment feasible. It was shown that instead of only making investments to utilise excess steam, the aim should also be to improve energy efficiency by means of improved heat integration.

There are several different process designs that lead to a similar improvement of energy efficiency and economics in the repurposed Kraft pulp mill, therefore the practical potential for implementation should be based on issues of operability.

Lignin extraction, by means of the LignoBoost process, shows higher potential (if compared with electricity production) in an ethanol plant than in a Kraft pulp mill. This is due to the possibility of using internally produced CO_2 (a by-product in fermentation) for precipitating lignin.

Lignin extraction, by means of the LignoBoost process, in a typical Scandinavian Kraft pulp mill repurposed to an ethanol process can be increased substantially by implementing measures found in process integration studies. The output of lignin, if well-integrated, is limited by the capacity of the LignoBoost process and not the utility demand of the ethanol plant. In fact lignin can be deemed as the main product, in terms of energy output from the plant, in a well-integrated process.

Repurposing a typical Scandinavian Kraft pulp mill to a combined ethanol and DME biorefinery can be an interesting option since the conversion efficiency from raw material to biofuel product is high, but the process has a high investment cost compared to producing ethanol and power and/or lignin.

CO_2 Capture and Storage could play a vital role in process feasibility for the ethanol and DME biorefinery if implemented, since the cost for capturing CO_2 in this process is low.

Integration studies show that improvements in both energy efficiency and economic profitability are possible when an ethanol plant is integrated with a state-of-the-art Kraft pulp mill to utilise the chemical recovery cycle and recovery boiler process. Compared to the repurposed Kraft pulp mill biorefinery, this concept shows new heat integration opportunities that have short payback periods.

The process integration studies in this project indicate potential design alternatives that give improvements in both the energy efficiency and the economic feasibility of the suggested concepts. This shows the importance of including these types of studies in the preliminary assessment of 2nd generation biorefinery investments in the early phases of deployment. As the different studies have shown there are often several different design alternatives that can generate high energy efficiency and low cost process. These alternatives can be valuable for more practical discussions related to matters of, e.g., operability before deciding which design to include in the more detailed design studies.

9 Further work

This project shows the importance of process integration studies in the early stages of the deployment of the biorefinery concepts included. It has also indicated the importance of residual fractions in ethanol processes. Some ideas for future work on the concepts described, and using the methods included, are proposed in this chapter.

The studies in this project have all been based on conceptual computer models of typical or reference pulp mills. In future work the biorefinery concepts, as well as the heat integration opportunities, would benefit from assessments in cooperation with industry, and in case studies conducted at real mills. This would give information on the practical feasibility of the alternative designs, as well as possibilities for more detailed process integration studies. The potential benefits of supply chain issues in this type of process could also be addressed more readily in a case study.

The studies in this project have not included assessments of the potential for refining the residual fraction of carbohydrates to value-added products other than electricity or DME. There are numerous alternative pathways for these compounds that could be assessed and compared with the products in this project, e.g. pre-extraction of hemi-cellulose in the pre-treatment unit, fermentation to other products than ethanol, such as lactic acid or butanol, anaerobic digestion of residual fractions from ethanol purification, gasification, and the production of compounds other than DME.

Another factor that could have a great effect on the feasibility of process integration and feasibility in the different biorefinery concepts studied in this project is the composition of the raw material. Therefore, it should be interesting to assess different types of feedstocks in future studies.

There are a number of different concepts for the production of lignocellulosic ethanol in the scientific literature. There can be differences in pre-treatment conditions, process design and the structure of residual fractions. A comparative analysis of the process integration opportunities in these different alternatives could therefore be interesting in order to assess when and why one concept is preferable over another.

Finally, assumptions are made in the studies included in this project based on the residual components in the process. Further experimental analyses of the formation of by-products in the ethanol line, and the physical properties of the residue liquor (in comparison with black liquor in a Kraft pulp mill) could be of benefit for generating a more detailed understanding of the process.

10 References

1. IPCC, *Climate Change 2007: Synthesis report.* 2007.
2. IPCC, *Contribution of Working Group III to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change*, ed. B. Metz, et al. 2007: Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA.
3. IEA/OECD, *25 Energy Efficiency Policy recommendations - 2011 update*. 2011.
4. Geiss, J., A.-D. Müller, R. Schüle, C. Arens, V. Höfele, D. Becker, T. Boermans, K. Bettgenhäuser, J. Harnisch, and P. Jaworski, *Promoting energy efficiency in Europe*. 2009, EEWP (Energy Efficiency Watch Project), European Forum for Renewable Energy Sources.
5. IEA/OECD, *Implementing Energy Efficiency Policies - Are IEA Member Countries on Track?* 2009.
6. Jokinen, J., *Development of Pulp Capacities 2003-2008 (presentation material)*, in *Andritz Capital Market Days*. 2009.
7. Solomon, B.D., J.R. Barnes, and K.E. Halvorsen, *Grain and cellulosic ethanol: History, economics, and energy policy.* Biomass and Bioenergy, 2007(31): p. 416-425.
8. *BNDES (the Brasilian development bank) and CGEE (Center for Strategic Studies and Management in Science Technology and Innovation in Brazil), Sugarcane-based bioethanol; Energy for sustainable development*. 2008, Rio de Janeiro, Brazil.
9. Thorbjörnson, B., *Tillverkning av råbrännvin.* Teknisk Tidskrift Kemi, 1931. **häfte 3**.
10. www.sekab.se, *last visited: 2012-02-21.*
11. www.agroetanol.se, *last visited: 2012-02-21.*
12. Sapp, M., *Europe´s ethanol affair.* Biofuels, Bioproducts & Biorefining, 2007. **1**(2): p. 88-91.
13. Sims, R., M. Taylor, J. Saddler, and W. Mabee, *From 1st to 2nd generation biofuel technologies - An overview of current industry and R&D activities*, IEA Bioenergy, Editor. 2008, OECD/IEA.
14. Galbe, M., P. Sassner, A. Wingren, and G. Zacchi, *Process engineering economics of bioethanol production*, in *Advances in Biochemical Engineering/Biotechnology*. 2007. p. 303-327.
15. Hamelinck, C.N., G. Van Hooijdonk, and A.P.C. Faaij, *Ethanol from lignocellulosic biomass: techno-economic performance in short-, middle- and long-term.* Biomass and Bioenergy, 2005. **28**: p. 384 - 410.
16. Sassner, P., *Lignocellulosic ethanol production based on steam pretreatment and SSF*, in *Department of Chemical Engineering*. 2007, Lund University: Lund.
17. http://www1.eere.energy.gov/biomass/integrated_biorefineries.html, *last visited: 2012-02-21.*

18. http://www.biofuelstp.eu/cell_ethanol.html, *Last visited: 2012-02-21.*
19. Alén, R., *Biorefining of Forest Resources*. Papermaking Science and Technology. Vol. 20. 2011: Paper Engineers' Association/ Paperi ja Puu Oy.
20. Bogren, J., H. Brelid, and H. Theliander, *Reaction kinetics of softwood kraft delignification - General considerations and experimental data.* Nordic Pulp and Paper Research Journal, 2007. **22**(2).
21. Wigell, A., H. Brelid, and H. Theliander, *Kinetic modelling of (galacto)glucomannan degradation during alkaline cooking of softwood.* Nordic Pulp and Paper Research Journal, 2007. **22**(4).
22. Gullichsen, J. and C.-J. Fogelholm, *Chemical Pulping*. Papermaking Science and Technology. Vol. 6A. 1999: Paper Engineers' Association/ Paperi ja Puu Oy and TAPPI.
23. Aden, A., M. Ruth, K. Ibsen, J.Jechura, K. Neeves, J. Sheehan, B. Wallace, L. Montague, A. Slayton, and J. Lukas, *Lignocellulosic Biomass to Ethanol Process Design and Economics Utilizing Co-Current Dilute Acid Prehydrolysis and Enzymatic Hydrolysis for Corn Stover*. 2002, National Energy Renewable Laboratory, NREL/TP-510-32438: Technical Report.
24. Galbe, M. and G. Zacchi, *A review of the production of ethanol from softwood.* Applied Microbiology and Biotechnology, 2002. **59**(6): p. 618-628.
25. Garcia, A., M.G. Alriols, R. Llano-Ponte, and J. Labidi, *Energy and economic assessment of soda and organosolv biorefinery processes.* Biomass and Bioenergy, 2010. **35**(1): p. 516-525.
26. Haelssig, J.B., A.Y. Tremblay, and J. Thibault, *Technical and economic considerations for various recovery schemes in ethanol production by fermentation.* Industrial and Engineering Chemistry Research, 2008. **47**(16): p. 6185-6191.
27. Stephen, J.D., W.E. Mabee, and J.N. Saddler, *Will second-generation ethanol be able to compete with first-generation ethanol? Opportunities for cost reduction.* Biofuels, Bioproducts & Biorefining, 2012. **6**: p. 159-176.
28. Wilkins, M.R., R.L. Belyea, V. Singh, P. Buriak, M.A. Wallig, M.E. Tumbleson, and K.D. Rausch, *Analysis of heat transfer fouling by dry-grind maize thin stillage using an annular fouling apparatus.* Cereal Chemistry, 2006. **83**(2): p. 121-126.
29. Collura, M.A. and W.L. Luyben, *Energy-saving distillation designs in ethanol production.* IND. & ENGNG. CHEM.:RES., 1988. **27**(9): p. 1686-1696.
30. Ficarella, A. and D. Laforgia, *Energy conservation in alcohol distillery with the application of pinch technology.* Energy Conversion and Management, 1999. **40**(14): p. 1495-1514.
31. Grisales, R., C.A. Cardona, O.J. Sanchez, and L.F. Gutierrez, *Heat integration of fermentation and recovery steps for fuel ethanol production from lignocellulosic biomass.* 2nd Mercosur Cong.

Chemical Engineering and 4th Mercosur Cong. Process Systems Engineering, 2005.

32. Summers, D.R., *Rectifier Design for Fuel Ethanol Plants*, in *AIChe Annual Meeting: Advances in Distillation Equipment and Applications, Paper 264b*. 2006: San Francisco, USA.
33. Wingren, A., M. Galbe, and G. Zacchi, *Energy considerations for a SSF-based softwood ethanol plant.* Bioresource Technology, 2008. **99**(7): p. 2121-2131.
34. Bruce, D.M., *Benchmarking energy consumption and identifying opportunities for conservation.* Pulp and Paper Canada, 2000. **101**(11): p. 35-38.
35. Martin, N., N. Anglani, D. Einstein, M. Khrushch, E. Worrell, and L.K. Price, *Opportunities to Improve Energy Efficiency and Reduce Greenhouse Gas Emissions in the U.S. Pulp and Paper Industry*. 2000, Ernest Orlando Lawrence Berkeley National Laboratory.
36. Lutz, E., *Identification and analysis of energy saving projects in a kraft mill.* Pulp and Paper Canada, 2008. **109**(5): p. 13-17.
37. Wising, U., *Process Integration in Model Kraft Pulp Mills - Technical, Economic and Environmentail Implications*, in *Department of Chemical Engineering and Environmental Science*. 2003, Chalmers University of Technology: Gothenburg.
38. Olsson, M.R., *Simulations of Evaporation Plants in Kraft Pulp Mills*, in *Div. Heat and Power Technology, Dept. Energy and Environment*. 2009, Chalmers University of Technology: Gothenburg.
39. Nordman, R., *New process integration methods for heat-saving retrofit projects in industrial systems*, in *Div. Heat and Power Technology, Dept. Energy and Environment*. 2005, Chalmers University of Technology: Gothenburg.
40. Axelsson, E., *Energy Export Opportunities from Kraft Pulp and Paper Mills and Resulting Reductions in Global CO2 Emissions*, in *Div. Heat and Power Technology, Dept. Energy and Environment*. 2008, Chalmers University of Technology: Gothenburg.
41. Olsson, M.R., E. Axelsson, and T. Berntsson, *Exporting lignin or power from heat-integrated kraft pulp mills: A techno-economic comparison using model mills.* Nordic Pulp and Paper Research Journal, 2006. **21**(4): p. 476-484.
42. Van Heiningen, A., *Converting a kraft pulp mill into an integrated forest biorefinery.* Pulp and Paper Canada, 2006. **107**(6): p. 38-43.
43. Werpy, T., Petersen, G., *Top Value Added Chemicals from Biomass Volume I—Results of Screening for Potential Candidates from Sugars and Synthesis Gas*. 2004, U.S. Department of Energy.
44. Holladay, J., Bozell, JJ., White, JF., Johnson, D., *Top Value-Added Chemicals from Biomass Volume II—Results of Screening for Potential Candidates from Biorefinery Lignin*. 2007, U.S. Department of Energy.
45. Frederick Jr, W.J., S.J. Lien, C.E. Courchene, N.A. DeMartini, A.J. Ragauskas, and K. Iisa, *Co-production of ethanol and cellulose fiber*

from Southern Pine: A technical and economic assessment. Biomass and Bioenergy, 2008. **32**(12): p. 1293-1302.

46. Mao, H., J.M. Genco, S.H. Yoon, A. van Heiningen, and H. Pendse, *Technical economic evaluation of a hardwood biorefinery using the "near-neutral" hemicellulose pre-extraction process.* Journal of Biobased Materials and Bioenergy, 2008. **2**(2): p. 177-185.
47. Larson, E.D., S. Consonni, R.E. Katofsky, K. Iisa, and J.W. Frederick, *A cost-benefit assessment of gasification-based biorefining in the kraft pulp and paper industry, final report (in four volumes).* Available at: www.princeton.edu/~energy 2006.
48. Phillips, R.B., H. Jameel, and E.C. Clark Jr. *Technical and Economic Analysis of Repurposing a Kraft Pulp and Paper Mill to the Production of Ethanol*. in *TAPPI Press - Engineering, Pulping and Environmental Conference*. 2008.
49. Gonzalez, R., T. Treasure, R. Phillips, H. Jameel, and D. Saloni, *Economics of cellulosic ethanol production: Green liquor pretreatment for softwood and hardwood, greenfield and repurpose scenarios.* BioResources, 2011. **6**(3): p. 2551-2567.
50. Xue, Y., H. Jameel, R. Phillips, and H.M. Chang, *Split addition of enzymes in enzymatic hydrolysis at high solids concentration to increase sugar concentration for bioethanol production.* Journal of Industrial and Engineering Chemistry, 2012. **18**(2): p. 707-714.
51. Xue, Y., J. Rusli, H.m. Chang, R. Phillips, and H. Jameel, *Process Evaluation of Enzymatic Hydrolysis with Filtrate Recycle for the Production of High Concentration Sugars.* Applied Biochemistry and Biotechnology, 2012: p. 1-17.
52. Koo, B.W., T.H. Treasure, H. Jameel, R.B. Phillips, H.M. Chang, and S. Park, *Reduction of enzyme dosage by oxygen delignification and mechanical refining for enzymatic hydrolysis of green liquor-pretreated hardwood.* Applied Biochemistry and Biotechnology, 2011. **165**(3-4): p. 832-844.
53. Jin, Y., H. Jameel, H.M. Chang, and R. Phillips, *Green liquor pretreatment of mixed hardwood for ethanol production in a repurposed kraft pulp mill.* Journal of Wood Chemistry and Technology, 2010. **30**(1): p. 86-104.
54. Huang, H.J., Ramaswamy, S., Al-Dajani, W. W., Tschirner, U., *Process modeling and analysis of pulp mill-based integrated biorefinery with hemicellulose pre-extraction for ethanol production: A comparative study.* Bioresource Technology, 2009. **101**(2): p. 624-631.
55. Holmbom, B. *Specialty high-value chemical products -from wood and bark at pulp and paper mills*. in *PulPaper 2007 Conference: Innovative and Sustainable use of Forest Resources*. 2007.
56. Axegard, P., B. Backlund, and P. Tomani. *The pulp mill based biorefinery*. in *PulPaper 2007 Conference: Innovative and Sustainable use of Forest Resources*. 2007.

57. Axegard, P. *Overview of Pulp Mill Biorefinery Concepts at Innventia*. in *Nordic Wood Biorefinery Conference*. 2009. Helsinki, Finland.
58. Lundberg, V., E. Axelsson, M. Mahmoudkhani, and T. Berntsson, *Process integration of near-neutral hemicellulose extraction in a Scandinavian kraft pulp mill - Consequences fro the steam and Na/S balances.* Applied Thermal Engineering, 2012, doi:10.1016/j.applthermeng.2012.03.037.
59. Helmerius, J., J.V.v. Walter, U. Rova, K.A. Berglund, and D.B. Hodge, *Impact of hemicellulose pre-extraction for bioconversion on birch Kraft pulp properties.* Bioresource Technology, 2010. **101**: p. 5996-6005.
60. Jönsson, A.-S. and O. Wallberg, *Cost estimates of kraft lignin recovery by ultrafiltration.* Desalination, 2009. **237**: p. 254-267.
61. Öhman, F., *Precipitation and separation of lignin from kraft black liquor.*, in *Dept. of Chemical and Biological Engineering*. 2006, Chalmers University of Technology: Gothenburg.
62. Tomani, P., *The LignoBoost process.* Cellulose Chemistry and Technology, 2010. **44**: p. 53-58.
63. Ekbom, T., N. Berglin, and S. Lögdberg, *Black Liquor Gasification with Motor Fuel Production - BLGMF II*, in *Swedish Energy Agency, P21384-1*. 2005: Stockholm, Sweden.
64. Ekbom, T., M. Lindbom, N. Berglin, and P. Ahlvik, *Technical and Commercial Feasibility Study of Black Liquor Gasification with Methanol/DME Production as Motor Fuels for Automotive Uses - BLGMF*, in *Altener II report*. 2003.
65. Pettersson, K., *Black Liquor Gasification-Based Biorefineries - Determining Factors for Economic Performance and CO_2 Emission Balances*, in *Div. Heat and Power Technology, Dept. of Energy and Environment*. 2011, Chalmers University of Technology: Gothenburg.
66. KAM, *Final report from the Ecocyclic pulp mill programme, 1996-2002*, in *KAM Report A100*. 2003: Stockholm, Sweden.
67. Jansson, M., N. Berglin, and L. Olm, *Second generation ethanol through alkaline fractionation of pine and aspen wood.* Cellulose Chemistry and Technology, 2010. **44**(1-3): p. 47-52.
68. von Schenck, A., N. Berglin, and J. Uusitalo. *Ethanol from Nordic wood raw material by alkaline simplified sodacooking pretreatment*. in *proceedings of the International Symposium of Alcohol Fuels (ISAF) conference*. 2011. Verona, Italy.
69. SEA, *Swedish Pulp Mill Biorefineries - a vision of future possibilities* in *The Swedish Energy Agency, Report no. ER 2008:26*. 2008: Eskilstuna, Sweden.
70. Klemes, J., F. Friedler, I. Bulatov, and P. Varbanov, *Sustainability in the Process Industry: Integration and Optimization*. 2011, New York, USA: McGraw-Hill.

71. Kemp, I.C., *Pinch analysis and Process Integration: A User Guide on Process Integration for the Efficient Use of Energy*. 2007, Oxford: Butterworth-Heinemann, Elsevier Ltd.
72. Bandyopadhyay, S., J. Varghese, and V. Bansal, *Targeting for cogeneration potential through total site integration.* Applied Thermal Engineering, 2010. **30**(1): p. 6-14.
73. Hackl, R., E. Andersson, and S. Harvey, *Targeting for energy efficiency and improved energy collaboration between different companies using total site analysis (TSA).* Energy, 2011.
74. Klemes, J., V.R. Dhole, K. Raissi, S.J. Perry, and L. Puigjaner, *Targeting and design methodology for reduction of fuel, power and CO2 on total sites.* Applied Thermal Engineering, 1997. **17**(8-10): p. 993-1003.
75. Varbanov, P. and J. Klemes, *Integration and management of renewables into Total Sites with variable supply and demand.* Computers and Chemical Engineering, 2011. **35**(9): p. 1815-1826.
76. Smith, R., *Chemical Process Design and Integration*. 2005: John Wiley & Sons Ltd, West Sussex, England.
77. Anantharaman, R., O.S. Abbas, and T. Gundersen, *Energy Level Composite Curves - A new graphical methodology for the integration of energy intensive processes.* Applied Thermal Engineering, 2006. **26**(13): p. 1378-1384.
78. Linnhoff, B. and V.R. Dhole, *Shaftwork targets for low-temperature process design.* Chemical engineering Science, 1992. **47**(8): p. 2081-2091.
79. Morandin, M., A. Toffolo, A. Lazzaretto, F. Marechal, A.V. Ensinas, and S.A. Nebra, *Synthesis and parameter optimization of a combined sugar and ethanol production process integrated with a CHP system.* Energy, 2011. **36**(6): p. 3675-3690.
80. Linnhoff, B., D.W. Townsend, D. Boland, G.F. Hewitt, B.E.A. Thomas, A.R. Guy, and R.H. Marsland, *User guide on process integration for the efficient use of energy*. 1st ed. 1982 (revised edition 1994): IChemE, Rugby, UK.
81. Algehed, J., *Energy Efficient Evaporation in Future Kraft Pulp Mills*, in *Dept. Heat and Power Technology*. 2002, Chalmers University of Technology: Gothenburg.
82. Nordman, R. and T. Berntsson, *Design of kraft pulp mill hot and warm water systems - A new method that maximizes excess heat.* Applied Thermal Engineering, 2006. **26**(4): p. 363-373.
83. Carlsson, A., P.-A. Franck, and T. Berntsson, *Design better heat exchanger network retrofits.* Chemical Engineering Progress, 1993. **89**(3): p. 87-96.
84. Nordman, R. and T. Berntsson, *Use of advanced composite curves for assessing cost-effective HEN retrofit I: Theory and concepts.* Applied Thermal Engineering, 2009. **29**(2-3): p. 275-281.

85. Nordman, R. and T. Berntsson, *Use of advanced composite curves for assessing cost-effective HEN retrofit II. Case studies.* Applied Thermal Engineering, 2009. **29**(2-3): p. 282-289.
86. Nordman, R. and T. Berntsson. *Advanced pinch technology based composite curves for evaluating the usable excess heat potential*. in *The International Conference on Efficiency, Cost, Optimization, Simulation and Environmental Impact of Energy Systems, ECOS*. 2005. Trondheim, Norway.
87. IEA, *Industrial Heat Pumps - Experiences, Potential and Global Environmental Benefits*. 1995, IEA Heat Pump Centre, Sittard, the Netherlands.
88. Dhole, V.R. and B. Linnhoff, *Total site targets for fuel co-generation, emissions, and cooling.* Computers and Chemical Engineering, 1993. **17**(Suppl): p. 101-109.
89. Smith, R., M. Jobson, and L. Chen, *Recent development in the retrofit of heat exchanger networks.* Applied Thermal Engineering, 2010. **30**(16): p. 2281-2289.
90. Wang, Y., M. Pan, I. Bulatov, R. Smith, and J.K. Kim, *Application of intensified heat transfer for the retrofit of heat exchanger network.* Applied Energy, 2012. **89**(1): p. 45-59.
91. AspenTech, *AspenOne Engineering v7.2*. 2010.
92. Tomani, P., N. Berglin, and P. Axegård. *The LignoBoost process and use of lignin as a new biofuel*. in *proceedings of the TAPPI Engineering, Pulping and Environmental Conference*. 2009. Memphis, TN, USA.
93. Luyben, W.L., *Distillation Design and Control Using Aspen Simulation*. 2006, Hoboken, New Jersey: American Institute of Chemical Engineers (AICHE) and John Wiley & Sons, Inc. .
94. Jönsson, J., *Analysing different technology pathways for the pulp and paper industry in a European energy systems perspective*, in *Div. Heat and Power Technology, Dept. Energy and Environment*. 2011, Chalmers University of Technology: Gothenburg.
95. von Schenck, A., E. Axelsson, and N. Berglin, *System study of ethanol production in a pulp mill converted to a biorefinery*, in *STFI-Packforsk report no. 266*. 2007.
96. Axelsson, E. and S. Harvey, *Scenarios assessing profitability and carbon balances of energy investments in industry*, in *AGS Pathways report 2010:EU1*. 2010: Goteborg, Sweden.
97. Capros, P., L. Mantzos, V. Papandreou, and N. Tasios, *Energy and transport: Trends to 2030 - update 2007*, in *European Commission: Directorate-General for Energy and Transport*. 2008.
98. IEA, *Technology Roadmap - Biofuels for Transport*. 2011, Paris, France: International Energy Agency.
99. Axelsson, E., M.R. Olsson, and T. Berntsson, *Heat integration opportunities in average Scandinavian kraft pulp mills: Pinch analyses of model mills.* Nordic Pulp and Paper Research Journal, 2006. **21**(4).

100. Delin, L., N. Berglin, A. Lundström, Å. Samuelsson, B. Backlund, and Å. Sivard, *Bleached market kraft pulp mill - Reference and type mill*, in *Report FRAM 9*. 2004.
101. Berglin, N., A. Lovell, L. Delin, and J. Törmälä. *The 2010 Reference Mill for Kraft Market Pulp*. in *proceedings of the TAPPI Peers conference* 2011. Portland, Oregon, USA.

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