THESIS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

Chemical and Biochemical Biorefineries in Kraft Pulp Mills – Process Integration and Economics for Three Concepts

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Industrial Energy Systems and Technologies
Department of Energy and Environment
CHALMERS UNIVERSITY OF TECHNOLOGY
Göteborg, Sweden 2014

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ISBN 978-91-7597-169-8

Doktorsavhandlingar vid Chalmers tekniska högskola
Ny serie nr 3850
ISSN 0346-718X

Publication 2015:2
Industrial Energy Systems and Technologies
Department of Energy and Environment
CHALMERS UNIVERSITY OF TECHNOLOGY, GÖTEBORG
ISSN 1404-7098

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Printed by Chalmers Reproservice
CHALMERS UNIVERSITY OF TECHNOLOGY
Göteborg, Sweden 2015

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ABSTRACT

Some of the advantages of integrating biorefinery concepts with kraft pulp mills are that the utility system can be shared and that mass and energy streams can be exported from the pulp mill to the biorefinery or vice versa. These measures may result in lower investments and operating costs for the biorefinery compared with stand-alone operations. However, the implementation of biorefinery concepts can interact and occasionally interfere with pulp production.

In this thesis, assessment results for the integration of three chemical and biochemical biorefinery concepts are presented. The studied concepts include (1) "near-neutral" hemicellulose extraction and upgrading of the hemicellulose-containing stream to ethanol, (2) conversion of a kraft pulp mill to a dissolving pulp mill, and (3) high-solids ethanol production next to a kraft pulp mill. The results of this work show that efficient heat integration within and between the pulp mill and the biorefinery can result in a substantial decrease in utility demand and thereby energy costs. However, changes in composition/flowrates of some material streams at the pulp mill that arise from implementing the biorefinery concept appear to play a crucial role in the technical and economic feasibility of these concepts.

For the first biorefinery concept, efficient heat integration can make the processes self-sufficient in terms of steam; however, exporting chemicals from the pulp mill to the biorefinery can destabilize the sodium and sulfur balance in the pulp mill. In the second biorefinery concept, the modified cooking conditions at the pulp mill result in a lower pulp yield. Although the wood input could, in principle, be increased to compensate for the lower yield, the limited capacity of the equipment may result in a pulp production reduction by up to 40% in the worst-case scenario. For the third biorefinery concept, the potential advantages of operating at high-gravity conditions in terms of energy use are almost negligible in practice because very efficient heat integration is possible for both high-solids loading and a more conventional solids loading. Therefore, these advantages cannot compensate for the likely lower ethanol yield in the high-gravity process.

The results of this work demonstrate the importance of extending the focus from only the biorefinery reactor to include the entire biorefinery and pulp mill (including the energy system and the available equipment capacity) when evaluating the feasibility of biorefineries. The results are also a reminder of the importance of conducting system studies during the initial development of new processes and in parallel with experimental work.

Keywords: biorefinery, process integration, energy efficiency, bottleneck, ethanol, high gravity, pulp mill.

Appended papers

This thesis is based on the work contained in the following papers:

I. Process integration of “near-neutral” hemicellulose extraction in a Scandinavian kraft pulp mill- Consequences for the steam and Na/S balances
Lundberg V, Axelsson E, Mahmoudkhani M, Berntsson T (2012)
Applied Thermal Engineering, 43: 42-50.

II. Converting a kraft pulp mill into a multi-product biorefinery – Part 1: Energy aspects
Lundberg V, Axelsson E, Mahmoudkhani M, Berntsson T (2013)
Nordic Pulp and Paper Research Journal, 28(4): 480-488.

III. Converting a kraft pulp mill into a multi-product biorefinery – Part 2: Economic aspects
Lundberg V, Svensson E, Axelsson E, Mahmoudkhani M (2013)
Nordic Pulp and Paper Research Journal, 28(4): 489-497.

IV. Converting a kraft pulp mill into a multi-product biorefinery – techno-economic analysis of a case mill
Lundberg V, Bood J, Nilsson L, Axelsson E, Berntsson T, Svensson E (2014)
Clean Technologies and Environmental Policy, 16(7): 1411-1422 .

V. The effect of high solids loading in ethanol production integrated with a pulp mill – Part 1: Technical aspects
Lundberg V, Jansson M, Xiros C, Svensson E, Berntsson T
Submitted to *Chemical Engineering Research and Design*.

VI. The effect of high solids loading in ethanol production integrated with a pulp mill – Part 2: Economic aspects
Lundberg V, Svensson E
Submitted to *Chemical Engineering Research and Design*.

Co-authorship statement

Lundberg is the main author of papers I-V. Paper VI is a joint effort of Lundberg and Svensson. Lundberg contributed input data, investment cost calculations and was active in analyzing the results and writing portions of the paper. Berntsson was the main supervisor of the work in all papers. Mahmoudkhani co-supervised the work in papers I-III, Axelsson co-supervised the work in papers I-IV and Svensson co-supervised the work in papers III-V. The heat integration study and the input to the economic assessment conducted in Paper IV were originally part of an MSc thesis[1] by Bood and Nilsson, which was supervised by Lundberg.

[1] Bood, J. & Nilsson, L., 2013. Energy Analysis of Hemicellulose Extraction at a Softwood Kraft Pulp Mill - Case Study of Södra Cell Värö. Master’s Thesis. Göteborg: Chalmers University of Technology. Available at: publications.lib.chalmers.se/records/fulltext/182305/182305.pdf

Related work not included in this thesis

- Scandinavian hardwood biorefinery using "near-neutral" hemicelluloses pre-extraction - Energy efficiency measures
  Mora V, Mahmoudkhani M, Berntsson T (2011)
  Chemical Engineering Transactions, 25: 411-416.
  (This paper is an earlier conference version of **Paper I**.)

- Energy analysis for conversion of a kraft pulp mill into a dissolving pulp mill
  Lundberg V, Axelsson E, Mahmoudkhani M, Berntsson T (2011)
  Chemical Engineering Transactions, 29: 13-18.
  (This paper is an earlier conference version of **Paper II**.)

- Enlarging the product portfolio of a kraft pulp mill via hemicellulose and lignin separation - Process integration studies in a case mill
  Lundberg V, Bood J, Nilsson L, Mahmoudkhani M, Axelsson E, Berntsson T (2013)
  Chemical Engineering Transactions, 35: 127-132.
  (This paper is an earlier conference version of **Paper IV**.)

- High Solids Loading in Ethanol Production – Effects on Heat Integration Opportunities and Economics
  Lundberg V, Svensson E
  Manuscript submitted to the *18th Conference on Process Integration, Modelling and Optimisation for Energy Saving and Pollution Reduction PRES, 23-27 August 2015. Kuching, Malaysia*.

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1 Introduction

This thesis presents the results of an assessment of three biorefinery concepts regarding their process integration potential and economic performance. The selected biorefinery concepts are based on chemical or biochemical processing of lignocellulosic biomass and are integrated with a pulp mill. Most of the studied biorefineries are still in a conceptual stage, and more technological development is necessary before they can be implemented at an industrial stage. Conducting system studies during the earlier stages of technological development is challenging because many parameters are unknown (e.g., technological development, process configuration and markets of products and by-products), yet the results of system studies are crucial for identifying the most important areas for further improvement and process development. This thesis is a contribution to the development of a biorefinery-based economy.

1.1 Background

The Swedish forest industry is a cornerstone in the country's economy and is the second largest exporter of pulp and paper and sawn goods worldwide (SkogsIndustrierna, 2014). In particular the pulp and paper industry is highly energy intensive and is consequentially the largest industrial energy user in Sweden (Energimyndigheten, 2013) (see Figure 1). However, unlike other industrial sectors, the pulp and paper industry is a large bioenergy producer and can largely satisfy its own energy needs by combusting internal biomass residues (e.g., black liquor and bark).

Due to the high energy intensity of the pulp and paper industry, initiatives to improve energy efficiency at pulp mills can result in large energy savings and potentially large decreases in CO_2 emissions. Although burning biomass is considered to be CO_2-neutral, reducing the biomass demand at a pulp mill via energy savings would make biomass available for other purposes and could replace fossil fuel in other parts of the energy system if biomass is a limited resource. Thus, energy savings at pulp mills could lead to large off-site CO_2 reductions (E. Axelsson, 2008).

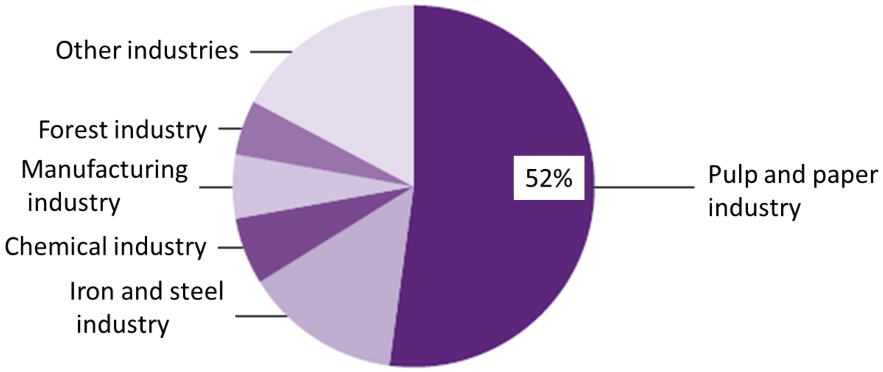

Figure 1 Energy use by industry type in Sweden (year 2001; %). Figure adapted from Energimyndigheten, 2013.

Moreover, energy savings are likely to bring economic benefits for pulp mills. Many strategies are possible for improving their energy efficiency, e.g., improving internal heat exchange, waste heat recovery, purchasing more energy-efficient equipment and improving maintenance and monitoring (Kramer et al., 2009). Research has shown that significant benefits can be obtained through increased heat integration at pulp mills (e.g., Algehed, 2002; E. Axelsson, 2008; Bengtsson, 2004; Fornell, 2012). By increasing heat integration, the demand for fuel, heat or power decreases and/or the potential to export those energy products increases.

1.2 Kraft pulping

Kraft pulping is currently the dominant process for the production of pulp for most types of paper products. For a detailed description of the kraft pulping process, the reader is referred to the numerous resources on this topic (e.g., Biermann, 1996; Gullichsen & Fogelholm, 1999).

Wood is essentially composed of cellulose fibers encased in a matrix of hemicellulose and lignin. The kraft pulping process (see Figure 2) converts wood into wood pulp by cooking the wood chips in a water solution of sodium sulfide and hydroxide that is called white liquor and breaks, in this way, the bonds that link lignin to the cellulose. During cooking, lignin and some hemicellulose degrade in the strong alkaline solution. Thereafter, the pulp is separated from the cooking liquor and proceeds through washing, bleaching and drying processes.

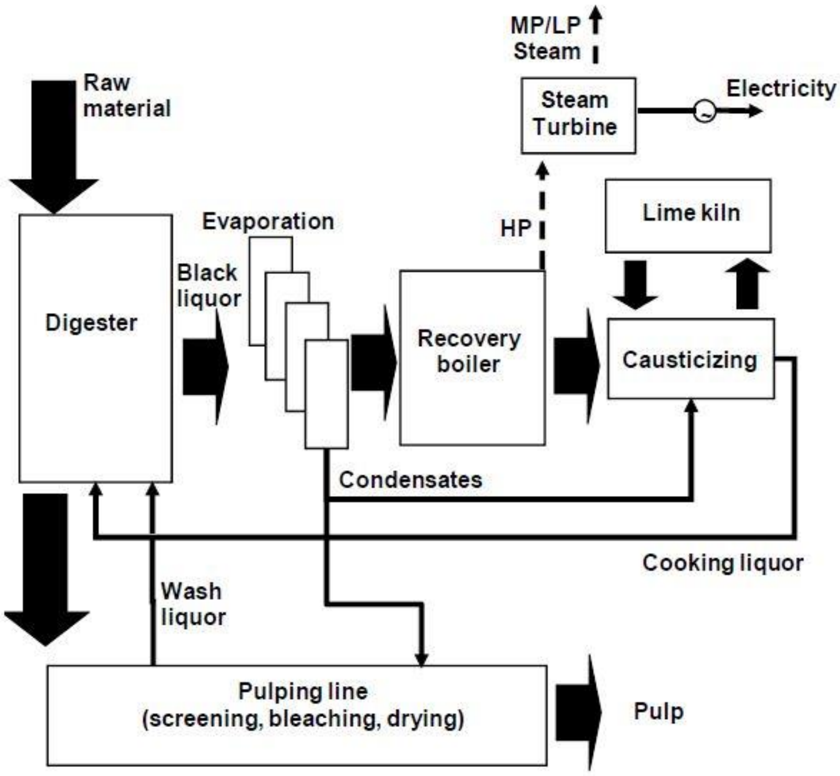

Figure 2 Block flow diagram of the kraft pulping process. Image reproduced from Fornell, 2012.

The spent cooking liquor consists mainly of degraded hemicellulose and lignin fragments; spent cooking chemicals are also included. This liquor, known as weak black liquor, is concentrated in a multiple-effect evaporator before being fired in the recovery boiler. Combustion of the organics dissolved in the strong black liquor provides heat for steam generation, whereas the inorganic chemicals are collected as a molten smelt at the bottom of the recovery boiler.

The smelt is dissolved in water to form green liquor, which is mixed with calcium hydroxide to regenerate the white liquor used for digesting the wood chips. Lime mud precipitates from the white liquor, after which it is calcined in the lime kiln and converted to calcium oxide (lime). This lime reacts with water to regenerate the calcium hydroxide.

The steam generated in the recovery boiler is passed through back-pressure turbines for power generation and delivered to the process at the required pressure. The delivered steam is usually sufficient to satisfy the steam demand of modern and efficient pulp mills.

The host pulp mill for the integration of the biorefinery concepts studied in this project is always a kraft pulp mill. Hence, unless specified otherwise, the terms *mill* and *pulp mill* refer to a market kraft pulp mill throughout this thesis. A short description of the studied pulp mills is presented in *Section 3.1*.

1.3 Biorefineries

One often used definition of biorefinery is the following: "*A biorefinery is a facility that integrates biomass conversion processes and equipment to produce fuels, power, and chemicals from biomass*" (NREL, 2009).

A recent attempt has been made to develop a unified and homogeneous system to classify biorefineries (Cherubini et al., 2009). This classification approach relies on four main features: (1) platforms; (2) products; (3) feedstock; and (4) processes. A simpler and more common way to classify biorefineries is based on two main platforms or pathways: (1) the sugar platform (i.e., biochemical platform) and the (2) syngas platform (i.e., thermochemical platform) (NREL, 2009). For the purpose of studying the biorefinery concepts presented in this thesis, a more appropriate classification system is the one proposed by Chambost et al. (2008):

- Biochemical processes: e.g. fermentation, anaerobic digestion and trans-esterification;
- Thermochemical processes: e.g. combustion, pyrolysis and gasification; and
- Chemical processes: e.g. extraction, separation and fractionation.

In Table 1, the types of biomass treatment methods included in this thesis are presented.

Table 1 Types of biomass treatment methods included in this thesis

Biochemical processes	**Chemical processes**
· Fermentation of C5/C6 sugars (from hemicellulose) to ethanol · Fermentation of C6 sugars (from cellulose) to ethanol	· Chemical pretreatment of wood with either green liquor, water or oxidized white liquor (alkaline pretreatment) · Acid hydrolysis of hemicellulose to monomeric sugars · Enzymatic hydrolysis of cellulose to monomeric sugars · Lignin extraction with carbon dioxide

The products of a biorefinery can be broadly grouped into energy products and material products. Some products, e.g., lignin, might be used as an energy product or a material product depending on its purity. In this PhD project, the products studied are as follows:

- Material products: dissolving pulp, kraft pulp and high quality lignin; and
- Energy products: bioethanol, electricity, low quality lignin and hydrolysate[2].

The products and by-products studied in this project are presented in Figure 3. The expected value of a particular product increases from bottom to top.

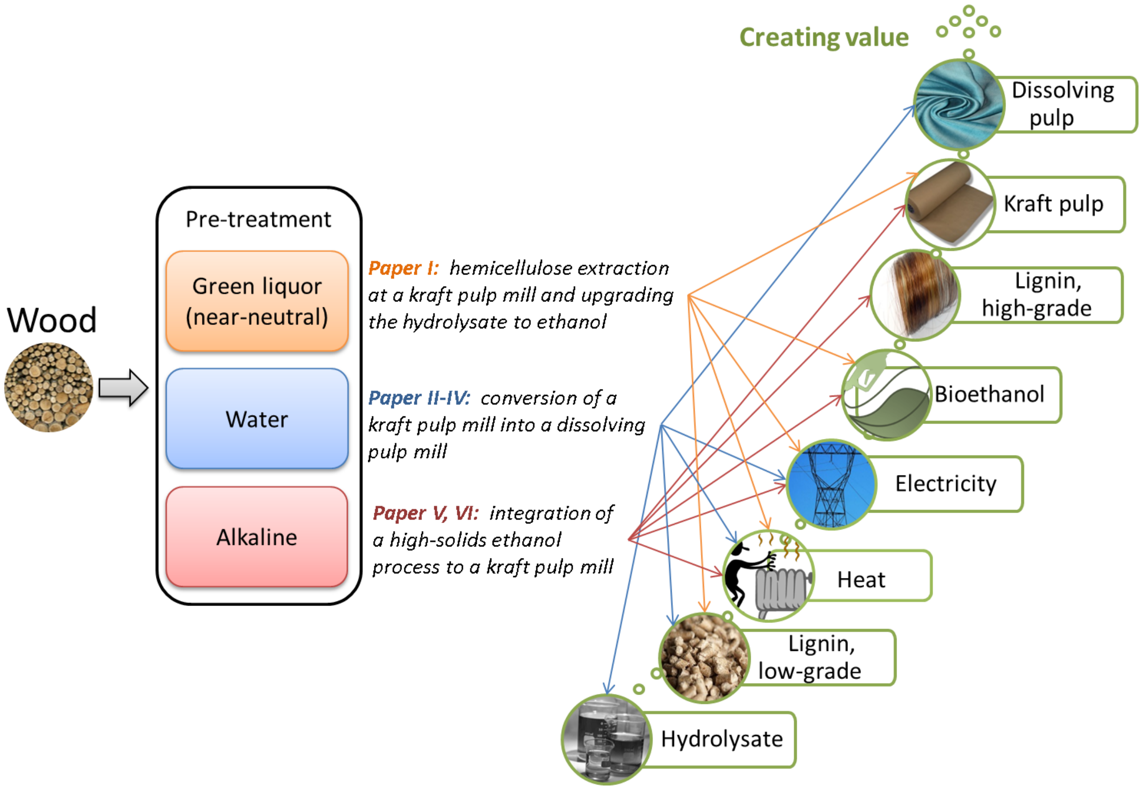

Figure 3 Types of pretreatment methods used and products and by-products produced in the studied biorefineries.

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1.4 Integration of biorefinery concepts to kraft pulp mills

Biorefinery concepts can be integrated with existing industrial processes to achieve a more attractive economic performance compared with stand-alone operations. Different types and levels of integration are possible, e.g., process integration, infrastructure integration, feedstock and product integration, supply-chain integration and policy an environmental integration (Stuart & El-Halwagi, 2013).

Integration of biorefinery concepts to kraft pulp mills enables the possibility to reduce capital costs by potentially utilizing redundant equipment or capacity and to reduce variable costs by reducing energy, chemical and raw material costs and by sharing utilities. Moreover, pulp mills generally have existing infrastructure, logistics and know-

[2] The hydrolysate is a by-product of the production of dissolving pulp. It is a diluted steam containing hemicellulose that could potentially be upgraded to value-added products.

how for processing large amounts of lignocellulosic materials. Moreover, some by-product streams, e.g., black liquor, are already partly processed in pulp production and can be more suitable for further refining than other biomass feedstock (Sanden, 2014).

The integration of three biorefinery concepts to kraft pulp mills is discussed in this thesis: (1) “near-neutral” hemicellulose extraction and upgrading the hemicellulose-containing stream to ethanol, (2) conversion of a kraft pulp mill to a dissolving pulp mill, and (3) high-solids ethanol production next to a kraft pulp mill

All of the biorefinery concepts studied are heat integrated to the pulp mill to some extent (in the form of utilities integration or heat exchange from process streams). The concepts also involve some level of material integration. The first and third biorefineries import chemicals from the pulp mill to pretreat the biomass. All three biorefineries export residual streams back to the pulp mill.

1.5 Appended papers

This thesis is based on six papers. A general overview of the papers and how they are related to one another is illustrated in Figure 4. The arrows between articles represent knowledge or results from one article that was useful for another article. Although a strict clear-cut classification of the topics addressed in each article is not possible, the articles can be roughly grouped into two main categories: those addressing technical aspects and those addressing economic aspects. In general, the technical aspect papers are focused on the heat integration potential between the pulp mill and the biorefinery processes, whereas the other articles explore the (economic) consequences of material integration (e.g., debottlenecking costs and pulp yield losses).

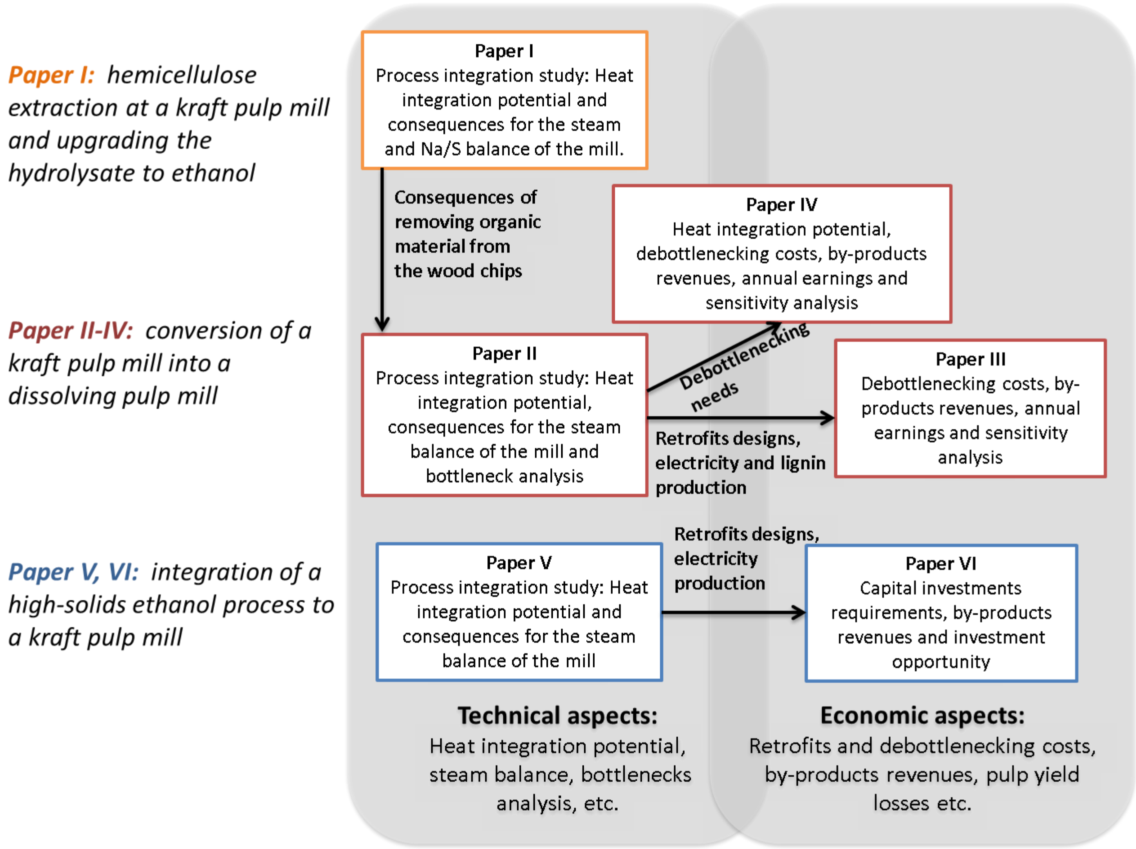

Figure 4 Overview of the appended papers and their relationships.

In **Paper I,** the most important consequences of integrating a bioethanol production plant with a pulp mill are evaluated. The bioethanol plant is based on the "near-neutral" hemicellulose pre-extraction method, in which green liquor is exported from the pulp mill to the biorefinery for use as extracting liquor. The consequences of exporting chemicals from the pulp mill to the biorefinery on the pulp mill Na/S balance are quantified, and the consequences of removing organic material from the wood chips on the steam balance of the mill are also discussed.

Paper II is the first part of a trilogy of papers addressing the conversion of a kraft pulp mill into dissolving pulp production by extracting nearly all of the hemicellulose from the wood chips. The consequences of removing organic material from the wood chips on the steam balance of the mill are evaluated (similar to **Paper I**), and the consequences of different choices for process configuration on the pulp production capacity of the mill are discussed.

In **Paper III**, the results of **Paper II** are used as the basis for investigating the importance of debottlenecking equipment with limited capacity at the pulp mill. The most cost effective ways to debottleneck the equipment are investigated, and the focus is widened to include aspects related to the uncertainty in the prices of raw material, dissolving pulp and by-products.

Paper IV is the last paper in the trilogy regarding the conversion into dissolving pulp production. In this paper, the results of the bottleneck analysis conducted in **Paper II** are adapted to the hypothetical conversion of an existing Swedish kraft pulp mill. In this case study, the economic performance of the conversion is assessed, and a comparison is made with the results presented in **Paper III**.

Paper V is the first of two papers concerning the integration of a high-solids ethanol process to a pulp mill. In these papers two ethanol processes with different high-solids loading are compared with respect to their process integration potential with a pulp mill and their economic performance. In **Paper V**, the potential for heat integration within the ethanol plant itself is examined, and the benefits of pursuing heat integration between the pulp mill and the ethanol plant are discussed.

In **Paper VI**, the advantages of the high-solids ethanol process in terms of investment costs for distillation are compared against the disadvantages related to a lower overall process yield. Moreover, the effect of exporting stillage from the ethanol plant to the pulp mill is evaluated for both the conventional and high-solids loading process.

2 Literature review and research needs

The literature review presented in this chapter provides a background regarding the main drivers for producing lignocellulosic ethanol and dissolving pulp and on the processes available for this purpose. This chapter focuses on the system studies that have been conducted to address the main technical and economic challenges of these processes and on the identified research gaps. Technical descriptions of the biorefinery concepts are presented in *Chapter 3.* In *Chapter* 5, relevant literature regarding the methods applied in the project is presented in conjunction with the input data sources.

2.1 Lignocellulosic ethanol production

Bioethanol is the most widely used biofuel for transportation worldwide (Balat, 2011). Second-generation bioethanol can be produced from lignocellulosic materials via hydrolysis of cellulose and/or hemicellulose to fermentable sugars and the fermentation of sugars to ethanol. However, a high production cost remains as one of the main barriers for large-scale commercial production of lignocellulosic ethanol (Balat, 2011). Methods for making the process more cost efficient are thus very important.

Feedstock costs are normally the largest components of the total production cost of ethanol, followed by investment costs and the costs of steam and enzymes (Gnansounou & Dauriat, 2010; Wingren, 2005). Accordingly, using cheaper raw material could have a large impact on the profitability of the process, which can be achieved using forestry residues or rejects from pulp mills (Fornell et al., 2012). Alternatively, improving ethanol yields and decreasing raw material inputs for a given ethanol output can also have profound effects. Other strategies to reduce investment and/or operating costs are to integrate the ethanol plant with another process and to perform enzymatic hydrolysis at high-solids loadings. These strategies are discussed in the following sections.

2.1.1 Process integration aspects

Investment costs can be reduced by integrating the ethanol plant with a power plant or with a pulp and paper mill. According to one study (Ångpanneföreningen-IPK, 1994), the production costs can be reduced by up to 20% by integrating the processes (due to the possibility of utilizing redundant equipment or capacity or sharing utilities).

Another possibility for reducing production costs is to reduce energy costs by increasing the energy efficiency of the process. Various studies have focused on determining energy-efficient designs for distillation and evaporation plants. Wingren et al. (2008) studied various designs, including a base case with 3 distillation columns and a 5-effect evaporation train and four other designs (integration of a stripper with the evaporation step, increasing the number of evaporation effects, using a heat pump and replacing the evaporation plant with anaerobic digestion). The authors concluded that using a heat pump and anaerobic digestion were the most promising alternatives.

Haelssig et al. (2008) simulated 6 different fermentation and distillation schemes and evaluated their energy demands and economic performances. The distillation sequence was based on either one or two columns; heat pumps were included in two of the alternatives. The authors concluded that either two heat-integrated columns or one column using a heat pump would be the most feasible options.

In his PhD project, Fornell (2012) studied various pulp-mill-based biorefinery concepts for producing ethanol. He conducted process simulations of various designs for ethanol distillation plants and broaden the perspective for studying the process integration potential with the rest of the ethanol plant and with the pulp mill. In particular in the last article included in his thesis (Fornell et al., 2012), he presented a techno-economic assessment for an ethanol plant co-located with a kraft pulp mill. In this study, different design alternatives were evaluated and compared, including designs with heat integration within the ethanol plat only (by integrating the distillation plant with the evaporation plant, using heat pumps or increasing the number of evaporation effects) and designs with heat integration between the pulp mill and ethanol plant. The results showed that several designs have low payback times (<2 years), although the capital investment required and the revenues obtained were found to vary.

2.1.2 Hemicellulose extraction at a kraft pulp mill and upgrading of the hydrolysate into ethanol

In this biorefinery concept, hemicellulose is extracted from wood chips before kraft pulping and sent to an ethanol plant. Hemicellulose can be extracted by different methods, such as acid extraction (Frederick et al., 2008), water extraction (Kautto et al., 2010), alkaline extraction (Ramaswamy et al., 2010) and green liquor extraction - the so-called “near-neutral” pre-extraction method (van Heiningen et al., 2008). Hemicellulose extraction will affect the pulp mill in various ways, e.g., by affecting the pulp properties, the pulp yield, the amounts of by-products produced (e.g., tall oil) and the steam production in the recovery boiler.

Frederick Jr et al. (2008) assessed the technical and economic feasibility of co-producing ethanol and cellulose fiber and compared it against stand-alone ethanol production. The concept studied was based on hemicellulose extraction by dilute acid hydrolysis and sub-sequent conditioning and fermentation to ethanol. The results showed that hemicellulose extraction resulted in significant pulp yield losses, which had a substantial impact on the production cost of ethanol. The authors concluded that for the conditions studied, the cost of producing ethanol when co-produced with cellulose fiber exceeded the cost of only producing ethanol.

Kautto et al. (2010) modeled a biorefinery consisting of a kraft pulp mill with water extraction based on results of laboratory experiments. A significant pulp yield loss was also observed for this biorefinery concept. Accordingly, the wood input needed to be increased by 16% to maintain constant pulp production. However, such an increase in wood input would have large effects on the operation of the pulp mill, in particular on the evaporation plant, which would have to be expanded from a 7-effect plant to a 9-effect plant, the heat transfer areas would have to be increased by approximately 65%, and the steam consumption would increase by 27%.

The same simulation model was used by Hamaguchi et al. (2013) to study the consequences of implementing water extraction on a kraft pulp mill in more detail. In this study, the final end product manufactured from the extracted hemicellulose was not specified; therefore, the analysis was limited to only the hemicellulose extraction. The results showed again that an increase in wood input is required to maintain the same pulp production level (due to pulp yield losses) and that large impacts are to be expected on the capacity utilization of different pieces of equipment in the recovery cycle (evaporators, recovery boiler, recausticizing and lime kiln). The authors demonstrated that the removal of approximately 17% of lignin from the black liquor would debottleneck the recovery boiler enough to maintain the original pulp production level.

Contrary to acid and water hemicellulose extraction, the pulp yield can be maintained if extraction is performed at alkaline conditions. Huang et al. (2010) simulated a biorefinery manufacturing ethanol and pulp based on alkali extraction with sodium hydroxide. Because the same pulp production could be maintained and organic material was removed from the studied pulp mill, the pulping capacity increased by approximately 22%. However, the organic material available for combustion decreased; thus, the steam production in the recovery boiler and the power generation also decreased.

van Heiningen et al. (2008) studied the “near-neutral” extraction process, where hemicellulose is extracted with green liquor prior to kraft pulping. According to the authors, hemicellulose can be extracted from hardwood while maintaining the quantity (i.e., pulp yield) and quality (e.g., tear index) of the pulp. Although several studies have been conducted to fine-tune the conditions for hemicellulose extraction to minimize the impacts on the pulp properties (e.g., van Heiningen, 2010; Yoon et al., 2011), only limited research has been conducted by focusing on the energy aspects of the process and on the integration with a host kraft pulp mill (Marinova et al., 2009).

Marinova et al. (2009) evaluated the impact of implementing “near-neutral” hemicellulose extraction on the energy supply and demand of a kraft pulp mill and identified energy-efficient measures to face the energy shortage of the process. After implementing the proposed measures, the steam production of the studied pulp mill was able to satisfy the biorefinery needs and even generate an excess amount of steam. The authors emphasized the importance of energy optimization for the successful implementation of biorefinery concepts.

Genco et al. (2010) conducted an economic assessment of a variant of the “near-neutral” biorefinery concept that uses a minimal amount of green liquor to maximize sugar production while maintaining the strength and quality of the final kraft pulp. The results showed that the discounted cash flowrate of return was unacceptably low except for very large mills that had an existing extraction vessel, sufficient utilities and waste treatment facilities.

According to the literature review, the need to evaluate the “near-neutral” extraction process by including both heat integration aspects, such as the changes in steam demand of different parts of the mill, and the consequences on the operability of the pulp mill was identified. In particular, the need to evaluate the consequences of material integration on the Na/S balance of the pulp mill was identified, i.e., the consequences of exporting green liquor from the pulp mill to the ethanol plant and exporting stillage from the ethanol plant to the pulp mill.

2.1.3 Integration of a high-solids ethanol process with a kraft pulp mill

Another way to potentially reduce the production costs of ethanol is by performing enzymatic hydrolysis at high-solids loadings, resulting in high sugar and ethanol concentrations (Modenbach & Nokes, 2013; Phillips et al., 2013). One of the main effects is that the ethanol concentration in the distillation feed is higher; therefore, less water must be preheated between (or inside) the distillation towers, which could reduce the steam demand and the capital costs of distillation (Modenbach & Nokes, 2013). Furthermore, the lower water volumes in the bioreactors could allow for smaller equipment and/or fewer reactors, thus reducing capital costs. Smaller or fewer reactors would also result in reduced energy demand for heating and cooling (Kristensen, Felby & Jørgensen, 2009).

However, running the process at higher solids loadings is generally associated with various challenges. At high-solids loadings, the concentrated solution has a high viscosity, which may reduce the productivity of the reactors. To compensate for this, longer residence times or reactors with advanced mixing arrangements may be needed (Jørgensen et al., 2007), which would counteract the reduction in equipment size and cost. Most importantly, running the process at higher solids loadings is generally associated with yield reductions (Hoyer et al., 2013; Kristensen, Felby & Jorgensen, 2009), which increases feedstock costs for a given output level.

Much experimental work has been conducted to develop the high-gravity concept, which has been summarized in recent review articles (e.g., Koppram et al., 2014; Modenbach & Nokes, 2012), reflecting the increasing interest in this concept and possibly the optimism for achieving an economically feasible process that can be implemented on a commercial scale. However, very few articles have been published addressing this concept from a system perspective.

Janssen et al. (2014) conducted a life cycle assessment for the production of bioethanol under high-gravity conditions from second-generation feedstock (wheat straw). The results showed that the yield is the main determinant of the environmental impact for any given process configuration and that higher dry matter contents led to a higher environmental impact of the ethanol production. Yield enhancing strategies (addition of enzymes or polyethylene glycol) were associated with negative environmental impact. Accordingly, the authors concluded that future development work should focus on finding an optimal dry matter content for hydrolysis and fermentation that decreases enzyme use while maintaining a high yield.

According to the literature review, the need to study potential reductions in ethanol production costs by integrating high-gravity ethanol production with other processes was identified. In **Papers V** and **VI**, the focus was to evaluate process integration opportunities between a pulp mill and a high-solids ethanol plant, particularly the impact of solids loadings on the energy balances of the ethanol plant and the pulp mill, the heat integration opportunities between the pulp mill and ethanol plant, and process economics. Moreover, critical parameters that affect the profitability of the studied process were identified.

2.2 Conversion of a kraft pulp mill into a dissolving pulp mill

Dissolving pulp consists of cellulose fibers of very high purity that can be used as feedstock for textile fibers or other cellulose derivatives. Currently, dissolving pulp is produced via the acid sulfite and vapor-phase prehydrolysis kraft processes, which were both developed in the 1950s (Sixta et al., 2013). Dissolving pulp can also be produced in a modified kraft pulp mill in which hemicellulose is extracted prior to kraft cooking either via steam or water pre-hydrolysis (Mateos-Espejel et al., 2013).

The market for dissolving pulp is dependent on the markets of other textile fibers. By the end of 2010, cotton reached a record high price that had not been seen in several decades due to bad harvests. This increase boosted the interest in dissolving pulp production such that a potential long-term price of approximately 1200-1800 USD per ton of dissolving pulp (Macdonald, 2011) was expected in 2011. Immediately after the price of dissolving pulp had peaked, several kraft pulp mills announced their conversion to dissolving pulp production (Macdonald, 2011). However, the price fluctuated widely thereafter. In 2013 the price was as low as 875 USD per ton (McCormick, 2013), which was comparable to the kraft pulp price of ~840 USD per ton (Södra, 2012). This uncertainty made some mills cancel their conversion plans (McCormick, 2013). By the time this thesis was written (November 2014), an American pulp mill had recently announced their plans to swing back to kraft pulp production despite the 170 million USD investment for conversion (Pulp_&_Paper_Week, 2014). At the same time, the annual per capita consumption of cellulosic fibers is expected to increase, while cotton production is expected to stagnate, which may result in an expansion of man-made cellulosic fibers from the current annual global production from 4.2 to 19.0 million t in 2030 (Sixta et al., 2013).

Due to the large uncertainty regarding the profitability of converting a kraft pulp mill into dissolving pulp production, techno-economic studies are particularly important. These system studies can be used as grounds for discussing the feasibility of such an endeavor and must be a vital and early component of any conversion strategy.

One of the most important challenges for achieving profitability is the pulp yield losses associated with the production of very pure cellulose fibers. The total pulp yield decreases from approximately 43% in an average kraft pulp mill to approximately 33% (Lundberg et al., 2013). This decrease means that larger quantities of wood and a greater capacity for the process equipment are required to handle the increased throughput. However, existing mills seldom have sufficient spare capacity to maintain the same level of pulp production. Consequently, conversion to dissolving pulp production may result in an overall decrease in pulp production (McCormick, 2013) or the need to debottleneck existing equipment.

Several journal articles regarding the production of kraft-based dissolving pulp have been published. However, most of these works were either experimental studies with the purpose of optimizing the conditions for hemicellulose extraction (Li et al., 2010) or attempted to find ways to upgrade the extracted hemicellulose (Liu et al., 2013; Shen et al., 2011).

Only a few system studies have been conducted by focusing on the conversion of a kraft pulp mill to dissolving pulp production. For example, Marinova et al. (2010a) conducted a techno-economic assessment and showed that the revenues of the products and by-products produced in a kraft-based dissolving pulp mill could be larger than those of an unconverted pulp mill. However, the capital and operating costs of the conversion were not estimated, which makes it impossible to draw conclusions regarding the economic attractiveness of this concept.

A more detailed assessment was made by Mateos-Espejel et al. (2013), who studied the conversion of a Canadian pulp mill. Two scenarios with different production levels were investigated: the same dissolving pulp production as that of kraft pulp production before the conversion (via an increase in the wood input to the mill) or the same wood input to the mill (and a resulting decrease in pulp production). For both cases, the pulp production capacity of the converted mill was mainly limited by the capacity of the digester plant. For the same production of dissolving pulp as that of kraft pulp, the recovery boiler and lime kiln also needed to be upgraded.

Based on the literature review, the need to investigate the technical and economic aspects of kraft-based dissolving pulp production in more detail was identified. The aim of the studies presented in **Papers II-IV** was to investigate the importance of several critical design choices on the profitability of the conversion and the potential for steam savings and by-product production (lignin and power). Different methods to debottleneck the recovery boiler of the pulp mill were also investigated; the influence of the prices of pulp, wood, by-products and specific upgrading requirements on the overall profitability of a converted mill were also discussed.

3 Studied systems and case definitions

In this chapter, the three studied biorefinery concepts and the host pulp mills are described. The studied kraft pulp mills are as follows:

i. model of an average Scandinavian hardwood kraft pulp mill (2005);
ii. model of a state-of-the-art Scandinavian softwood kraft pulp mill (2005);
iii. model of a state-of-the-art Scandinavian softwood kraft pulp mill (2010); and
iv. existing softwood kraft pulp mill (2013)

The year in brackets denotes the year in which the model was developed for mills i-iii and the year for which data were collected for mill iv. The mills are further described in *Section 3.1*.

The studied biorefinery concepts are as follows:

1. Hemicellulose extraction at a kraft pulp mill and upgrading the hydrolysate to ethanol;
2. Conversion of a kraft pulp mill into a dissolving pulp mill; and
3. Integration of a high-solids ethanol process to a kraft pulp mill.

These biorefinery concepts are presented in more detail in *Section 3.2*.

The studied kraft pulp mills and biorefinery concepts were combined as described in Figure 5.

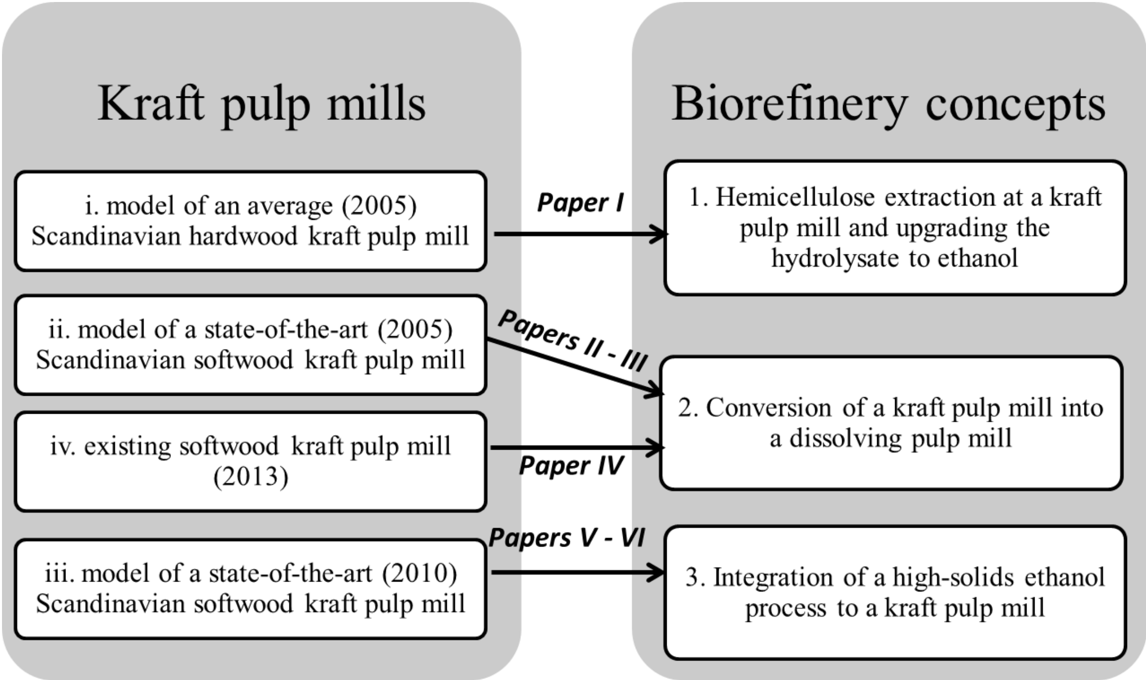

Figure 5 Overview of the studied kraft pulp mills and biorefinery concepts.

3.1 The studied kraft pulp mills

Three computer models and one existing mill were studied. Two of the three computer models were developed within the Swedish research program called FRAM (Future Resource Adapted Mill) (Delin et al., 2005b) during the period 2003-2005. The purpose of this program was to investigate ways to reduce the resource demand of pulp and paper mills and to study new or emerging technologies, such as lignin separation and black liquor gasification, and energy management issues, such as energy savings and maximized electricity production. The other computer model was developed by Innventia Research Institute and is an update (year 2010) to a state-of-the-art (2005) kraft pulp mill. All three model mills were modeled in WinGEMS (Metso, 2014), which is a process simulation tool designed specifically for the pulp and paper industry. In addition to the model mills, an existing kraft pulp mill located in western Sweden was studied. In this case, data were gathered from extensive flowsheet documentation at the plant and from their local information and control program. Table 2 shows a comparison of important data for the mills studied in this project. A more detailed description of each mill is provided in the following subsections.

Table 2 Important data for the studied pulp mills

	Average mill 2005	**State-of-the-art 2005**	**State-of-the-art 2010**	**Existing mill 2013**
General				
Raw material	Hardwood (90% birch, 10% other)	Softwood (50% pine, 50% spruce)	Softwood (100% spruce)	Softwood (70% spruce, 30% pine)
Pulp production [ADt/d]	1250	2000	3270	1250
Water consumption [t/ADt]	35	19	17	17
Steam [GJ/ADt]				
High-pressure steam (HP)	61 bar, 450 °C	81 bar, 490 °C	101 bar, 505 °C	86 bar, 482 °C
Production in recovery boiler	14.9	19.0	17.8	19.3
Production in bark boiler	0.4	0.0	1.5	0.0
Steam use (process and turbines)	14.9	19.0	19.4	18.6
Steam export (district heating)	0.0	0.0	0.0	0.7
Electricity [GJ/ADt]				
Production in back-pressure turbine	1.6	2.8	3.0	3.5
Production in condensing turbine	0.0	2.0	2.7	0.0
Electricity use	2.5	2.6	2.6	2.8
Electricity export	-0.9	2.3	3.2	0.8

3.1.1 Model of an average (2005) Scandinavian hardwood kraft pulp mill

The average mill was designed as a typical Nordic mill with nearly the same resource utilization as an average Scandinavian mill. The feedstock to the mill is hardwood, and the daily pulp production is 1250 ADt/d (annual production: 408 250 ADt/y).

Incoming chips are steamed and subsequently cooked in a conventional two-flash digester. The pulp is then oxygen delignified, washed, bleached and dried. In the recovery cycle, the black liquor is flashed in two steps and subsequently evaporated to 72% dry solid content in a 5.5-effect evaporation plant. Strong black liquor is burned in the recovery boiler to produce steam and recover the inorganic compounds as a smelt. High-pressure steam is produced in the recovery boiler at 60 bar(g) and 450 °C. The steam production in the recovery boiler is not sufficient to satisfy all of the steam demand for the mill; consequently, supplementary steam needs to be produced in a bark boiler. The back-pressure steam turbine is not sufficient to accommodate all of the high-pressure steam; thus approximately 25% of the steam is passed through let-down valves.

3.1.2 Model of a state-of-the-art (2005) Scandinavian softwood kraft pulp mill

The model for this mill includes resource utilization similar to a modern Scandinavian mill with state-of-the-art equipment available in 2005. The feedstock to the mill is softwood, and the daily pulp production is 2000 ADt/d (annual production: 653 200 ADt/y).

In this mill, wood chips are cooked according to the compact cooking concept (Metso, 2013). The pulp is then oxygen delignified, washed, bleached and dried. Black liquor is extracted via a single-stage flash and sent to the evaporation plant. Once there, the liquor is concentrated to 80% dry content via a 6-effect evaporation plant. The recovery boiler is designed to produce high-pressure steam at 80 bar(g) and 490°C. The produced steam is sufficient to satisfy all of the steam demand for the mill; therefore, there is no need for a bark boiler. The back-pressure turbine is sufficiently large to reduce the produced high-pressure steam to the required pressure for the process, which eliminates the need for let-down valves and maximizes back-pressure electricity production. In addition, there is a considerable amount of excess low-pressure steam that is not required in the process; this steam is utilized in a condensing turbine for further power generation.

3.1.3 Model of a state-of-the-art (2010) Scandinavian softwood kraft pulp mill

This mill is an update to the state-of-the-art mill discussed in the previous subsection, with equipment and practices available in 2010. The feedstock to the mill is softwood, and the daily pulp production is 3270 ADt/d (annual production: 1 068 000 ADt/y).

The incoming chips are cooked according to the compact cooking concept. The pulp is then oxygen delignified, washed, bleached and dried. Black liquor is extracted via a single-stage flash and sent to a 7-effect evaporation plant where it is concentrated to 80% dry content. High-pressure steam is produced in both the recovery boiler and the power boiler at 100 bar(g) and 505 °C. The power production in the back-pressure turbine is more than sufficient to satisfy the power demand of the process. The excess back-pressure power and significant amounts of condensing power are exported.

3.1.4 Existing (2013) softwood kraft pulp mill

This existing mill was built in 1972, although it can be considered to be a modern mill because it has undergone several recent upgrades to its recovery boiler, causticization plant, turbines and evaporation plant. The feedstock to the mill is softwood, and the daily pulp production is ~1250 ADt/d (annual production: ~425 000 ADt/y).

The incoming wood chips are cooked in a batch digesting plant with two digester lines and five digesters in each line. Thereafter, the pulp is washed, oxygen delignified, bleached and dried. Black liquor is extracted from the digester in one step during the cooking sequence and is sent to a 7-effect evaporation plant to be concentrated to approximately 75% dry content. The black liquor is burned in the recovery boiler, and high-pressure steam is produced at 86 bar and 482 °C. The mill has a bark boiler that is only used during start-ups, process disturbances and seasonal variations. Otherwise, during normal operation, the steam produced in the recovery boiler is more than sufficient to satisfy the process steam demand; excess low-pressure steam is used to produce district heating to a nearby community.

3.2 The studied biorefinery processes

Three biorefinery concepts were studied. The concepts have a common characteristic: second generation ethanol is produced or a by-product stream suitable for upgrading ethanol or other chemicals is produced. The concepts differ according to their primary produced products (kraft pulp or dissolving pulp) and the way ethanol is produced (from a hemicellulose-containing stream or from wood).

3.2.1 Hemicellulose extraction at a kraft pulp mill and upgrading the hydrolysate to ethanol

In the “near-neutral” method, (Mao, 2007; van Heiningen et al., 2008) wood chips are steamed and exposed to a solution of green liquor (imported from the pulp mill) and anthraquinone (Figure 6). The level of wood mass (mainly hemicellulose, but also some lignin) extracted in this biorefinery concept was set to ~10% because the quantity and quality of kraft pulp produced at this rate is expected to remain unchanged (Mao et al., 2008). To do this, hemicellulose extraction is performed in a pre-hydrolysis vessel at approximately 160 °C and a liquid-to-wood ratio of 4:1.

The extracted wood chips are washed and sent to the kraft process. According to Mao and co-workers (Mao et al., 2008), hemicellulose can be extracted while maintaining the quantity (i.e., pulp yield) and quality (e.g., tear index) of the pulp. The diluted extract (so-called hydrolysate) is concentrated by flashing before further processing. Hydrolysis is performed under strongly acidic conditions (pH=1) in which all of the lignin is precipitated and separated by filtration. The delignified hydrolysate is subsequently cooled before further purification and separation stages. In the first step, acetic acid and furfural are removed by liquid-liquid (L-L) extraction, which is followed by distillation. Then, lime is imported from the pulp mill to raise the pH of the substrate to that required for fermentation and to detoxify the solution by precipitating sulfate ions as gypsum. Thereafter, the detoxified sugar solution is fermented and upgraded by distillation.

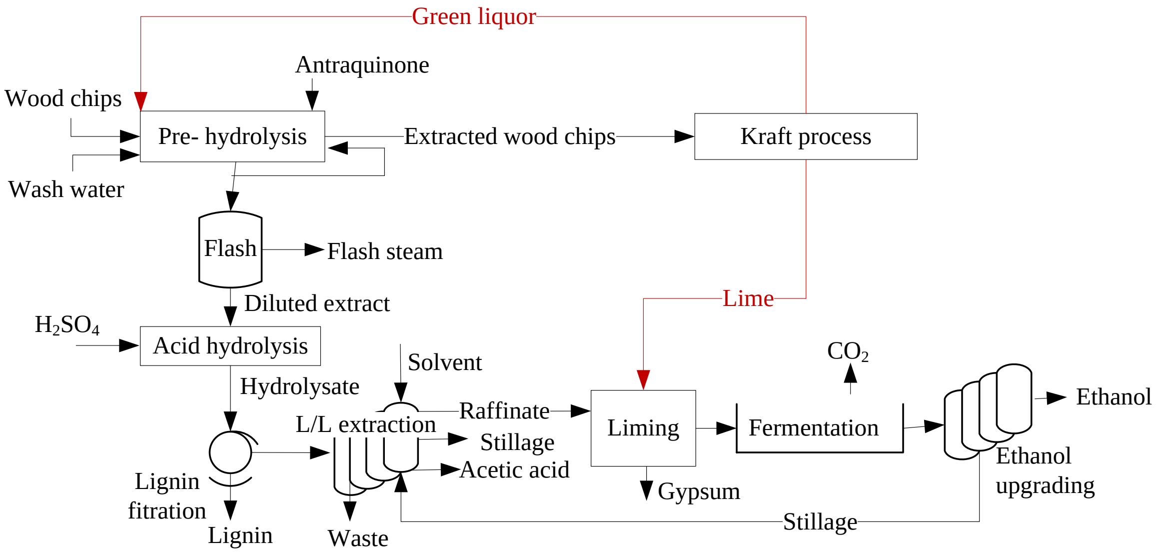

Figure 6 Near-neutral hemicellulose extraction process.

To investigate the advantages of increasing the level of heat integration, three cases were studied. The base case represents a mill in which changes in process streams that result from implementing hemicellulose pre-extraction (i.e., changes in composition, mass or enthalpy flowrate) were considered, although no attempt was made to improve the system by process integration. Thereafter, two cases with different levels of process integration were studied. In the simplest case, the possibility of saving steam and releasing excess heat on a stand-alone basis (i.e., separately within each of the processes) was investigated. In the second case, the benefits of total integration were studied, i.e., heat/steam could also be transferred between the mill and the bioethanol plant.

3.2.2 Conversion of a kraft pulp mill into a dissolving pulp mill

Dissolving pulp can be produced by extracting hemicellulose prior to kraft pulping (Sixta et al., 2013). While hemicellulose can be extracted either via steam or water pre-hydrolysis, in steam hydrolysis, most of the extracted hemicellulose remains in the voids of the extracted wood chips and is degraded during the subsequent treatments (Mateos-Espejel et al., 2013). However, in water pre-hydrolysis, the hemicellulose is found in the extraction liquor, i.e., the so-called hydrolysate, which could potentially be upgraded to value-added products, e.g., furfurals, xyloses and xylitol (Marinova et al., 2010b).

The biorefinery concept studied in this project is based on the water pre-hydrolysis process. In this process, steamed wood chips are exposed to extraction water. The mixture is heated up to approximately 175 °C (Figure 7). After extraction, the wood chips are cooked under modified conditions, e.g., higher temperatures and chemical loadings than during kraft cooking, and then washed, bleached and dried. Due to the extraction of hemicellulose and more intense degradation of cellulose, the pulp yield is decreased from approximately 43% in an average kraft pulp mill to approximately 33%, which means that more wood is required to produce the same amount of pulp. In the pulp mill model, a constant pulp production was set (1986 ADt/d). As a result, an increase in wood input was obtained (from 2.1 to 2.7 t/ADt upon conversion from kraft to dissolving pulp production). Thus, conversion into a dissolving pulp mill may result in excess organic material that could be burned to produce steam and/or power or could be extracted as lignin in a lignin separation plant.

The hydrolysate that contains the extracted hemicellulose could be evaporated and combusted in the recovery boiler for heat recovery or sent to a hemicellulose upgrading plant. Upgrading the hydrolysate to value-added products could potentially become a source of extra revenue to the mill. Because many different alternatives for upgrading hemicellulose are possible and the most profitable option is mill-specific, the hemicellulose upgrading process has not been defined and is consequently considered to be beyond the system boundaries. However, the effect on the energy balance of the mill due to exporting the hydrolysate and the potential for producing excess steam have been investigated. Even if the hydrolysate is not upgraded, it can be considered as a source of revenue for the mill because combustion of the hydrolysate would result in additional excess steam available for by-product (power or lignin) production.

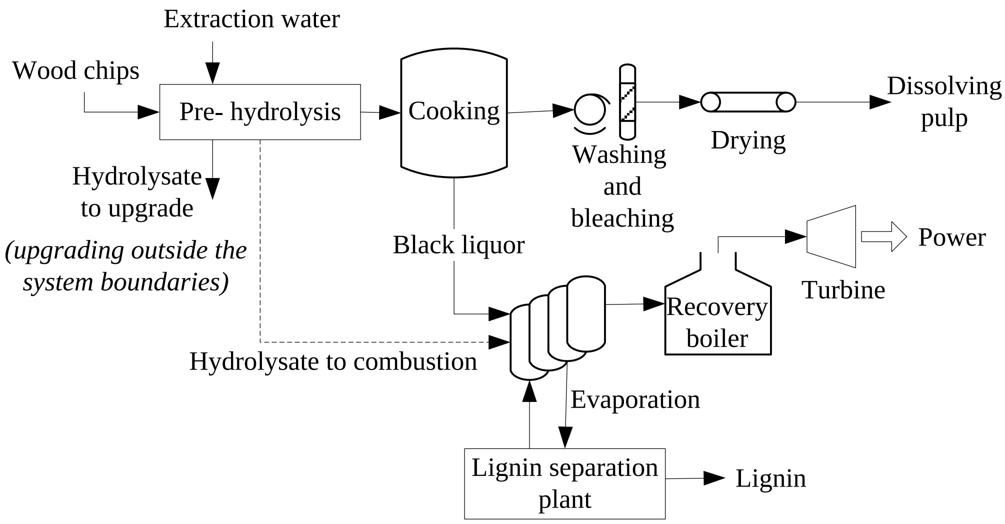

Figure 7 Kraft-based dissolving pulp process.

This biorefinery concept was studied in the most detail in this PhD project. In total, 15 cases were studied, i.e., 11 cases for the model mills and 4 cases for the real mill. The cases varied depending on the critical parameters that were evaluated. The studied parameters included the following:

a) Use of the hydrolysate: exporting the hydrolysate to a hemicellulose upgrading plant or combusting it in the recovery boiler.

b) Three pulp production levels were studied: L (low) - 1474 ADt/d, M (medium) - 1986 ADt/d and H (high) - 2303 ADt/d.

c) Method for debottlenecking the recovery boiler: no debottlenecking (NO) or debottlenecking via lignin separation (LIG) or recovery boiler upgrade (RB).

d) Level of heat integration: no heat integration (0), simple heat integration (1) or ambitious heat integration (2).

e) Choice of by-products produced: back-pressure and condensing power (el) or back-pressure power and lignin (lig).

In this thesis, the results that are most relevant for answering the research questions (presented in *Chapter 4*) are presented. The complete set of results for all of the cases can be found in the appended papers (**Papers II-IV**).

3.2.3 Integration of a high-solids ethanol process to a kraft pulp mill

This lignocellulosic ethanol production process is based on alkaline pretreatment of the biomass. According to experimental trials, alkaline pretreatment is an effective method to fractionate lignocellulosic biomass and allows for early separation of lignin in the process, which enhances enzymatic hydrolysis and results in a high-quality lignin fraction that can be sold as a valuable co-product (von Schenck et al., 2013).

Alkaline-based ethanol production can advantageously be integrated with a kraft pulp mill because potentially interesting heat integration opportunities arise between the processes (Fornell et al., 2012) and the chemicals used during pretreatment can be effectively recovered in the recovery cycle of the pulp mill; if spare capacity is available for all the pieces of affected equipment. In this project, it was assumed that the total wood input (at the pulp mill and biorefinery) is increased by ~25% upon implementation of this biorefinery concept. This level was chosen to result in ethanol production (~130 000 m^3/year) of the same order of magnitude as existing commercial lignocellulosic ethanol plants (Decker, 2009). Moreover, it was assumed that a modern pulp mill may be able to handle the increased load in the recovery cycle (possibly after some debottlenecking).

The first unit operation in the ethanol plant is an alkaline fractionation step that uses oxidized white liquor, which is possible to import from the pulp mill. The aim of the pretreatment step is to dissolve the lignin with hydroxide ions as the main cooking chemical, resulting in a relatively pure carbohydrate stream and a weak black liquor stream containing a large portion of the lignin. The weak black liquor formed in the pretreatment step is evaporated to approximately 35% dry solids in the ethanol plant evaporation plant (EPEP); thereafter, lignin is extracted in a lignin separation plant. Filtrates from the lignin separation process contain water, non-precipitated lignin, dissolved organic material and chemicals, which must be sent back to the pulp mill, evaporated in the pulp mill evaporation plant (PMEP) and subsequently combusted in the recovery boiler. From the lignin separation plant, a high-quality lignin product is extracted that could be upgraded to valuable products or sold as a renewable fuel.

Before entering the SSF (simultaneous saccharification and fermentation) reactor, the slurry from the pretreatment is washed, the pH is adjusted, and the slurry is diluted to a concentration of approximately 13% WIS (water-insoluble solids) for the conventional case or to 30% WIS for the high-gravity case, which is followed by cooling to approximately 37 °C. Yeast used in the SSF procedure is assumed to be produced in-house using some of the sugars available in the hydrolysate as substrate.

After SSF, the ethanol broth enters a distillation step to concentrate the formed ethanol. The material present in the bottom of the distillation column, which is called stillage, enters a dewatering step. A press filter is used to separate the solid material (filter cake) from the dissolved material (thin stillage). The solid material containing non-fermentable lignin, yeast and some un-hydrolyzed organic material is sent to the pulp mill for combustion, while the thin stillage containing mainly water and minor amounts of dissolved components is assumed to be handled by the existing effluent treatment system of the pulp mill.

Mass streams are exported from the pulp mill to the ethanol plant and vice versa (see Figure 8). Cooking chemicals are exported from the pulp mill to the ethanol plant; stillage and filtrates from the ethanol plant are sent back to the pulp mill for evaporation in the pulp mill evaporation plant (PMEP) and combustion in the recovery boiler.

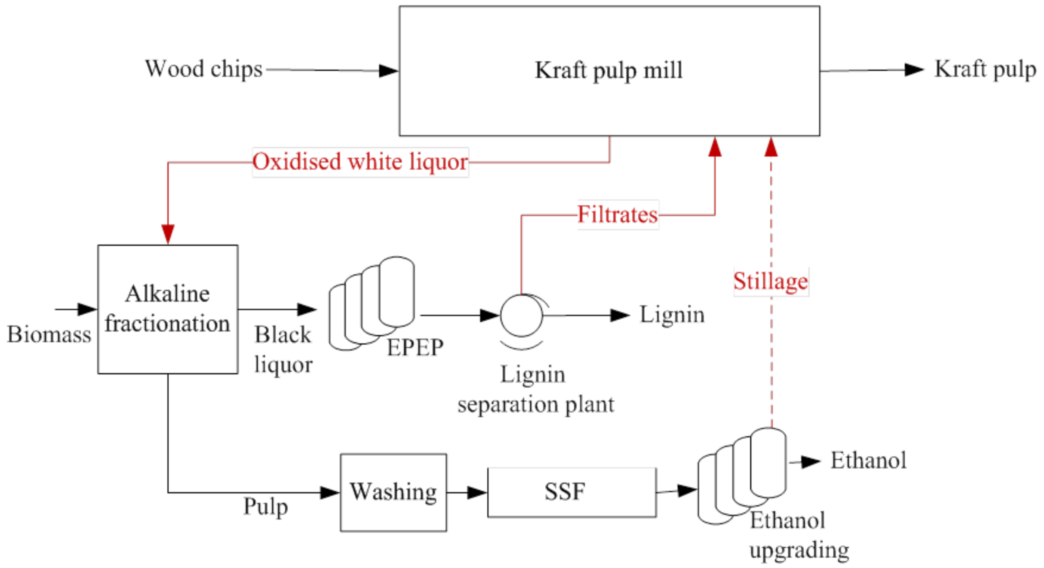

Figure 8 Alkaline-based high-solids ethanol process.

The ethanol concentration of the feed has been claimed to largely affect the steam demand resulting in significant cost effects during distillation (Hoyer et al., 2013; Katzen et al., 1999; Zacchi & Axelsson, 1989a). Accordingly, two configurations of the distillation plant were studied for both conventional and high-gravity feed concentrations. The studied configurations were as follows:

a) 3 distillation columns integrated with one another: The ethanol feed is split and sent to two stripper columns. The distillates are subsequently mixed and sent to a rectification column where they are concentrated to 92% (w/w). The operating pressures of the columns are chosen so that the heat available in the condenser of the first stripper can be used as a heat source for the reboiler of the second stripper; the condenser of the second stripper can be use a heat source for the rectifier reboiler.

b) 2 distillation columns integrated with the EPEP: The distillation plant consists of two columns in series. The pressure is chosen so that the large excess heat available in the surface condenser of the EPEP can be used as a heat source for the reboilers.

The two configurations were chosen to represent a conventional distillation sequence design and a design aiming to maximize the heat integration with the EPEP (and consequentially minimize the steam demand for distillation). In this thesis, only the results of the two-column design are presented because the results presented in **Papers V** and **VI** suggest that this design is preferable over the three-column design from heat integration and economic performance perspectives. Moreover, the results of the two-column design are sufficient to answer the proposed research questions (presented in *Chapter 4*). The results of the three-column design can be found in the annexed papers (**Papers V** and **VI**).

High-gravity conditions are expected to affect the overall ethanol yield of the process. However, the exact extent to which the yield is affected for a particular concept is highly uncertain. Consequently, the distillation configurations were tested for three different scenarios: a scenario with a conventional solids loading and two high-solids loading scenarios. In the first of the high-solids loading scenarios, a reasonable overall yield reduction was considered (from 19% for the conventional solids loading to 15% for the high-gravity concept), whereas a best case scenario is represented for the second scenario. In this latter case, the same ethanol yield as the conventional process is maintained at high-gravity conditions.

4 Objectives

The general objective of this PhD project was to increase our knowledge of process integration for chemical and biochemical biorefinery concepts in kraft pulp mills. To evaluate a particular biorefinery concept and to compare these concepts, it is necessary to evaluate the impact of the expected changes in energy and mass streams on the economic and climate performance for the pulp mill and the biorefinery. This evaluation can be performed by answering the following research questions:

Q1 What are the most important factors to consider when choosing the size of the biorefinery?

Q2 How is the steam production and demand of the pulp mill affected by the implementation of the biorefinery concept (base case: before process integration)?

Q3 What is the heat integration potential of the pulp mill and biorefinery? Are there any advantages of pursuing heat integration between the pulp mill and biorefinery?

Q4 What is the potential for by-products generation, e.g., lignin and power?

Q5 What are the consequences of changes in composition/flowrates of material streams at the pulp mill that arise from implementing the biorefinery concept, e.g., consequences on the Na/S balance and consequences on the pulp production capacity?

Q6 What are the major factors that affect the profitability of the biorefinery concept?

Q7 What are the CO_2 *consequences of implementing the biorefinery concept?*

In Table 3, a summary of the research questions investigated for each of the three biorefinery concepts included in this thesis is presented.

Table 3 Research questions addressed in each of the papers

	Q2	*Q3*	*Q4*	*Q5*	*Q6*
Hemicellulose extraction at a kraft pulp mill and upgrading the hydrolysate to ethanol	Paper I	Paper I		Paper I	
Conversion of a kraft pulp mill into a dissolving pulp mill	Paper II and Paper IV	Paper II and Paper IV	Paper II and Paper IV	Paper II, Paper III, and Paper IV	Paper III and Paper IV
Integration of a high-solids ethanol process to a kraft pulp mill	Paper V	Paper V	Paper V		Paper VI

Choosing the size of a biorefinery (*Q1*) is an important and complex task that affects both the process integration potential and the economic performance of the biorefinery. The optimal size of a stand-alone biorefinery is a trade-off between the costs for processing (which decrease as the plant size increases) and the feedstock transportation costs (which increase as the plant size increases) (Wright & Brown, 2007). Moreover, other factors, e.g., the effect that biorefinery size has on the operability of the pulp mill, should be considered when choosing the size of a biorefinery integrated to a pulp mill.

In this project, biorefinery size was not optimized. However, the size of each biorefinery was chosen so that the negative impacts on the quality of the produced pulp and other negative impacts on the pulp mill e.g., bottleneck risks or disruptions in Na/S balance, were minimized. The principles used for each of the studied biorefinery concepts are described in *Sections 3.2.1*, *3.2.2* and *3.2.3*.

The implementation of the studied biorefinery concepts could have positive or negative environmental effects depending on the types of products and by-products produced, the type of fuel used and the level of heat integration. For example, the biomass-based products produced in these biorefineries could replace fossil-based products (e.g., bioethanol replacing fossil ethanol) or products with a bad environmental performance (e.g., dissolving pulp replacing energy and water intensive cotton). However, the biomass used in the biorefinery could have been used for other purposes (e.g., to replace coal in a power generation plant), which could bring higher environmental benefits than if used at the biorefinery. Depending on the level of heat integration, the implementation of biorefinery concepts could result in an increased demand for fossil fuel to generate steam or could result in excess steam that could be used for green power generation.

Despite the importance of research question 7, no environmental assessments were conducted in this PhD project due to several methodological difficulties, such as the need to develop methods to assess the environmental impact of material streams (e.g., dissolving pulp) and the need to increase knowledge regarding the potential upgrading routes for the by-products produced in these biorefineries (e.g., lignin or hydrolysate).

5 Methods

In Table 4, the methods chosen to address each of the research questions are presented. Thereafter, each method is described; the input data and major assumptions are also discussed.

Table 4 Methods used to address each of the research questions

Research question	Methods
Q2	5.1 Combustion calculations 5.2 Gathering of input data
Q3	5.3 Process integration
Q4	5.4 Power production calculations 5.5 Estimation of lignin extraction potential
Q5	5.6 Bottleneck analysis 5.7 Calculation of sodium and sulfur balances
Q6	5.8 Input data to the economic performance indicators - Investment cost estimates - Downtime cost estimates - Operating cost estimates - Estimations of by-product revenues 5.9 Economic performance indicators - Annual earnings - Break-even dissolving-to-kraft-pulp price ratio - Profit opportunity

5.1 Combustion calculations

Implementing biorefinery concepts affects the steam production of the pulp mills. In the “near-neutral” ethanol plant (**Paper I**), hemicellulose is extracted from wood chips that would otherwise have been combusted in the recovery boiler, which results in a decrease in steam production. However, in the case of the high-solids loading ethanol plant (**Papers V** and **VI**), organic material found in filtrates and stillage from the ethanol plant is exported to the pulp mill, where it is combusted, resulting instead in an increase in steam generation.

In the cases of conversion into dissolving pulp production (**Papers II-IV**), the wood intake to the pulp mill is increased to maintain the pulp production at the same level as the unconverted kraft pulp mill. As a consequence, the amount of organic material in the black liquor increases, which also increases the steam produced in the recovery boiler.

However, if lignin extraction is used to debottleneck the recovery boiler, this could instead result in a decrease in organic material for combustion.

Accordingly, implementing biorefinery concepts can result in either an increase or a decrease in organic material combusted in the recovery boiler. The following heating values were used to calculate the resulting steam production at the studied pulp mills (Table 5).

Table 5 Heating values of hemicellulose and lignin

Low heating value of hemicellulose in black liquor	13.5	GJ/t_{DS}
Low heating value of lignin in black liquor	24.7	GJ/t_{DS}

In the cases in which hemicellulose or lignin is extracted from wood chips or from the black liquor, it was assumed that the rate of organic material extracted must not exceed the maximum limit that would affect the operability of the recovery boiler (i.e., the temperature required for the endothermic reactions in the smelt to occur). For lignin extraction (softwood, black liquor 80% DS), the maximum extraction rate was ~0.42 t/ADt (corresponding to an adiabatic combustion temperature of ~1450 °C) (Delin, Wadsborn, et al., 2005). A constant marginal efficiency of the recovery boiler of 92% was assumed (because the allowed rate of organic material extracted was always below the critical limit).

5.2 Gathering of input data

The studied kraft pulp mills and biorefinery concepts were combined as described in *Chapter 3* (Figure 5). With the exception of the case study mill (**Paper IV**), all of the pulp mills studied in this PhD project were modeled using the WinGEMS simulation software (Metso, 2014), which is specifically design for the pulp and paper industry. By using model mills, it was possible to work with a complete and consistent set of input data.

The choice of the pulp mill type for each biorefinery concept was based on the best model available when each study was conducted and on specific biorefinery characteristics. For example, for the first biorefinery concept (near-neutral based ethanol plant), a model of an average pulp mill was chosen to be representative of as many existing pulp mills as possible. However, by the time the high-solids ethanol production study was conducted (2014), a model for a state-of-the-art pulp mill was available, which was updated and allowed for more relevant comparisons with previous studies (Fornell et al., 2012) than an average pulp mill. In the case of the kraft-based dissolving pulp mill, a state-of-the-art pulp mill model was chosen, although a case study was conducted to compare with an existing pulp mill.

For the case study, the data were gathered when possible from the internal control system of the mill for a period (January 2012) during which production was stable. This period was representative of mild winter conditions in Scandinavia without extremely high or low outside temperatures. For instances in which data were unavailable, the temperatures and flowrates were estimated in collaboration with the mill personnel.

Regarding the studied biorefinery processes, the mass and energy balances of the "near-neutral" based ethanol plant (**Paper I**) were conducted in MS Excel. Most of the process steps in the high-solids ethanol plant (**Papers V** and **VI**) were modeled in WinGEMS except for the ethanol upgrading section (i.e. distillation and molecular sieves), which was simulated in Aspen Plus (Aspentech, 2014).

5.3 Process integration

Process integration has been defined by the IEA as follows (Gundersen, 2000):

> *"Systematic and General Methods for Designing Integrated Production Systems ranging from Individual Processes to Total Sites, with special emphasis on the Efficient Use of Energy and reducing Environmental Effects."*

Process integration methods can be broadly classified as (1) heuristics-, (2) thermodynamics- and (3) mathematical programming-based methods. Because heuristics-based methods have become more redundant, thermodynamic-based methods and mathematical programming have become the two major methodological schools for conducting process integration studies. The two methodologies have strengths and weaknesses; therefore, these approaches may potentially complement one another well (Klemeš & Kravanja, 2013).

Pinch analysis, which is the most commonly used process integration method in industry and academia (Klemeš & Kravanja, 2013), was used in this PhD project for energy targeting and for retrofit design. Although no optimization tools were used to find the most profitable design, for most of the studied biorefinery concepts, various levels of heat integration were investigated and the economic performance of each level was evaluated. Therefore, the results can be expected to be close to the global optima.

Pinch analysis (Kemp, 2007; Klemeš et al., 2010; Linnhoff & Boland, 1982) uses the first and second laws of thermodynamics to determine the theoretical minimum heating and cooling demand for a process and to identify potential energy efficiency improvements. Since the introduction of pinch analysis in the late 1970s, several industries, including the pulp and paper industry, have benefited from this technique (Atkins et al., 2011). Moreover, the heat integration methodology has been extended by numerous contributions (Friedler, 2010) and various methodologies for retrofit situations have been developed (Asante & Zhu, 1997; Varbanov & Klemeš, 2000). The basics of pinch analysis are presented in *Appendix I*.

The proposed modifications to the heat exchanger network of the processes studied in this PhD project were based on general pinch analysis heuristics, e.g., to solve the largest pinch violations, heat-exchange streams located close to one another, and re-use existing equipment.

5.4 Power production calculations

Increased heat integration in a process results in a reduced demand for external heating and cooling. In the processes studied in this PhD project, heat is supplied via steam. To produce the steam, fuel (most often black liquor) is combusted in a boiler to generate high-pressure steam, which is then passed through back-pressure turbines and/or let-down valves to reach the desired pressure. By increasing heat integration, both the steam demand and the need to combust fuel in the boiler decrease. The process manager could choose to maintain constant steam production and use the excess steam for condensing power generation or to reduce the fuel input to the boiler and to export the excess fuel.

For the power generation calculations, it was assumed that the excess steam passes through back-pressure turbines and condensing turbines generating as much power as possible based on the pressure level of the steam. It was also assumed that the efficiency of the existing turbines is unaffected by partial-load operation (isentropic efficiency, η_{is}=88%, and mechanical/generator efficiency, η_{m+g}=97%). For the cases in which new turbines are needed, it was assumed that they can be purchased in any required size and with the same efficiency as the existing ones.

5.5 Estimation of lignin extraction potential

When the steam produced by black liquor combustion in the recovery boiler exceeds the steam demand for a particular process, lignin can be extracted from black liquor, which decreases the fuel input to the recovery boiler. In this PhD project, it was assumed that lignin separation is performed according to the “LignoBoost” concept, in which lignin is precipitated from black liquor by injecting CO_2, which lowers the pH and causes an agglomeration of lignin molecules. The precipitated lignin is separated and washed with acidified condensate from the evaporation plant (H_2SO_4 is used as the acidifier). The filtrates from the lignin separation plant are recirculated to the evaporation plant. Details about the LignoBoost process can be found elsewhere (Tomani, 2010).

The method for estimating the maximum amount of extracted lignin that ensures sufficient organic material remains to satisfy the steam demand of the heat-integrated mill is necessarily iterative because the steam demand of the pulp mill depends on the amount of extracted lignin. The method utilized in this work to estimate the amount of extracted lignin was described by Olsson et al. (2006).

5.6 Bottleneck analysis

Implementing biorefinery concepts can affect the recovery system of the pulp mill in different ways. The biorefinery concepts studied in this PhD project affect the pulp mill either by disrupting the Na/S balance or by limiting the pulp production capacity.

Biorefinery concepts that require a larger wood input to maintain the same pulp production level (e.g., dissolving pulp production) result in a higher flowrate of black liquor and of all the streams in the recovery cycle. Similarly, biorefinery concepts that export residual streams to the pulp mill for combustion in the recovery boiler (e.g., export of filtrates and stillage from the high-solids ethanol plant to a pulp mill) use the capacity of the recovery cycle. The recovery cycle and in particular the recovery boiler is often considered as to be bottleneck for pulp production; therefore, implementing any biorefinery concept that results in extra loads in the recovery cycle may negatively affect the pulp production capacity.

In this PhD project, a detailed bottleneck analysis was conducted for the conversion of a kraft pulp mill to dissolving pulp production (**Papers II-IV**) because this biorefinery concept largely affects the recovery cycle. Recirculation of stillage and filtrates from the high-solids ethanol plant to the pulp mill (**Papers V** and **VI**) has a comparatively lower effect in the recovery cycle and was not studied in the same detail.

For the bottleneck analysis, it was assumed that either the pulp production level was adjusted (i.e., reduced) so that the load of the recovery boiler remained constant or that all equipment with limited capacity (including the recovery boiler, the evaporation plant, digester[3] and causticization plant) were upgraded or supplementary equipment was purchased.

5.7 Calculation of sodium and sulfur balances

The recovery cycle of the pulp mill may also be affected by disruptions in the Na/S balance. In the "near-neutral" ethanol plant (**Paper I**), green liquor is exported from the pulp mill to the biorefinery process. To investigate the consequences of using green liquor in the ethanol plant, sodium and sulfur balances were configured for different process units.

The procedure to calculate the Na/S balances for this biorefinery concept was developed by consultants from the consulting firm ÅF AB (Delin, 2010) and is outlined in Figure 9. This procedure considers that the net Na/S balance depends on the export of Na and S ions in green liquor from the pulp mill to the biorefinery, on the properties and flowrates of the streams that are recirculated back to the mill from the biorefinery and on S lost in the form of gypsum. The amounts of Na and S that are recirculated depend on the reactivity of S (whether it is bound to lignin or not, which is relevant because the lignin present in the hydrolysate is separated and sent back to the pulp mill for combustion) and on the amount of sulfuric acid added during acid hydrolysis to neutralize green liquor components and to lower the pH hydrolysate to pH=1 before L/L extraction (because the stillage waste from the ethanol plant is returned back to the mill for combustion).

[3] The digester is not a part of the recovery cycle of the mill but is also affected by increased wood input.

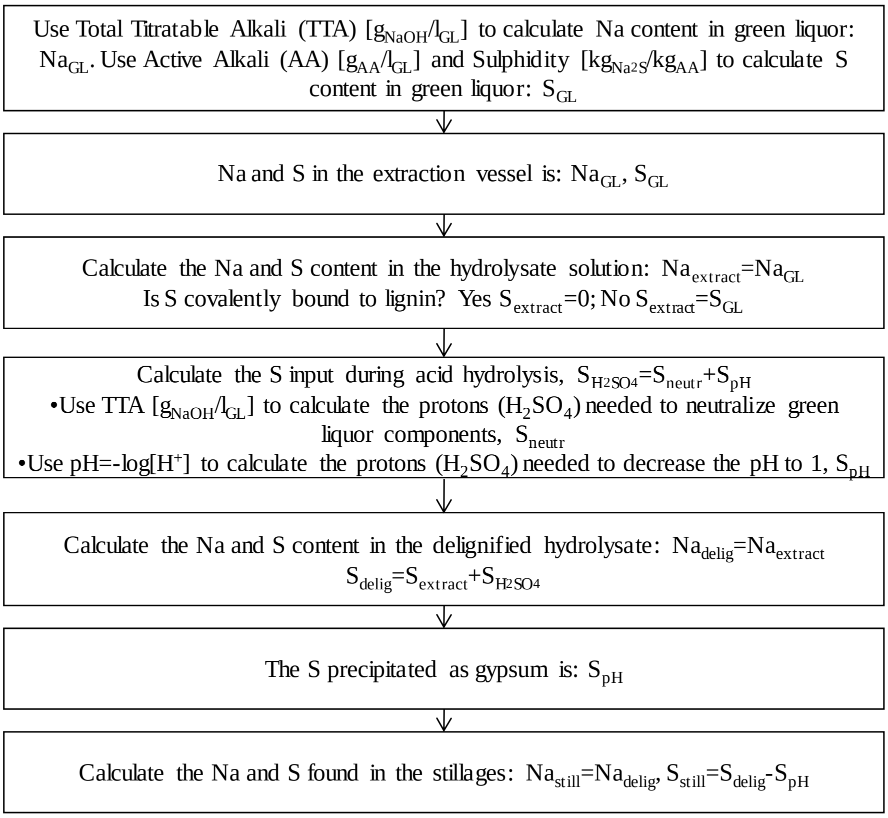

Figure 9 Method to develop Na/S balances.

The export of chemicals from the pulp mill to the biorefinery plant is also a characteristic of the third biorefinery concept studied in this project: the high-solids ethanol plant (**Papers V** and **VI**). In this case, oxidized white liquor is exported from the pulp mill to the biorefinery, and residual streams are sent back to the pulp mill for combustion. The Na/S balances for this process were calculated in WinGems and showed that the differences between the high-gravity and the conventional processes are negligible. However, these results were intentionally left out of this thesis and the publications due to large uncertainties regarding the upscaling of the chemicals used in the experimental settings to industrial scale operations.

5.8 Input data to the economic performance indicators

Three economic performance indicators were used in these studies: annual earnings, break-even dissolving-to-kraft-pulp price ratio and profit opportunity. To estimate these indicators, investment costs, operating costs, downtime costs and by-products revenues were calculated.

❖ INVESTMENT COST ESTIMATES

The investment costs were either estimated by correlations, upscaled/downscaled from reference equipment costs according to the six-tenth rule (Sinnott, 2005), or estimated using the online cost estimator (Peters et al., 2014) provided together with the book "Plant design and economics for chemical engineers" (Peters et al., 2003). The six-tenth rule is defined as follows:

$$\frac{c_A}{c_B} = \left(\frac{s_A}{s_B}\right)^{0.6}, \quad [1]$$

where c_X is the equipment cost with a corresponding size s_X.

The correlations and reference equipment costs are presented in Table 6.

Table 6 Investment cost correlations and reference equipment costs

Investment costs			Source
Heat exchangers			
Liquid-liquid	47,91 €+479 €/m^2	(for year 2005)	Laaksometsä et al. (2009)
Gas-water/steam	200 €/m^2	(for year 2005)	Laaksometsä et al. (2009)
Air-air	100 €/m^2	(for year 2005)	Laaksometsä et al. (2009)
Back-pressure turbine	$1.09 \cdot P^{0.6}$ [M€]	P= generated power [MW] (for year 2005)	Olsson et al. (2006)
Condensing turbine	$1.96 \cdot P^{0.6}$ [M€]	P= generated power [MW] (for year 2005)	Olsson et al. (2006)
Lignin separation plant	$5.95 \cdot LR^{0.6}$ [M€]	LR= lignin separation rate [kg/s] (for year 2005)	Olsson et al. (2006)
Digester plant	450 [MSEK]	(for a pulp production of 2000 ADt/d, year 2003)	Delin et al. (2005b)
Pre-hydrolysis unit	35%	increased capacity in the digester plant	Mateos-Espejel et al. (2013)
Evaporation plant	400 [MSEK]	(for a pulp production of 2000 ADt/d, year 2003)	Delin et al. (2005b)
Digester plant	450 [MSEK]	(for a pulp production of 2000 ADt/d, year 2003)	Delin et al. (2005b)
Causticization plant and lime kiln	470 [MSEK]	(for a pulp production of 2000 ADt/d, year 2003)	Delin et al. (2005b)
Pulp line	399 [MSEK]	(for a pulp production of 2000 ADt/d, year 2003)	Delin et al. (2005b)
Recovery boiler	750 [MSEK]	(for a steam production of 441 MW, year 2003)	Delinet al. (2005b)
Bark boiler	290 [MSEK]	(for a steam production of 45 MW, year 2003)	Delin et al. (2005a)

For the investment cost calculations of the different distillation sequences studied in **Papers V** and **VI**, estimations of the column diameter and number of trays for each column were used as input for the online estimator (Peters et al., 2014); "Purchased cost of distillation columns including installation and auxiliaries; 15-15; Bubble plate towers" was used with the selection of stainless steel. The investment cost was subsequently adjusted for design pressure using a correction factor (Smith, 2007). To estimate the costs for the heat exchangers, the online estimator (Peters et al., 2014) was used; "Purchased cost of fixed-tube-sheet heat exchangers; 14-18" of stainless steel. All of the investment cost estimations were converted from USD to € using the exchange rate 1.36 USD/€.

All costs were updated using the Chemical Engineering Plant Cost Index (Chemical Engineering, 2014):

$$cost_{updated} = cost_{original\ year} \cdot \frac{CEPCI_{updated\ year}}{CEPCI_{original\ year}}. \quad [2]$$

❖ DOWNTIME COST ESTIMATES

To implement biorefinery concepts in pulp mills, substantial retrofitting and process modifications may be required. In simple cases, such changes could be performed in a scheduled maintenance production stop. However, for larger modifications, a dedicated stop may be required, which would result in downtime costs (i.e., costs due to pulp sale losses). Downtime costs were calculated for the conversion of a kraft pulp mill to dissolving pulp production (**Papers II-IV**), which is the most substantial modification for the pulp mills studied in this PhD project, see Table 7.

Table 7 Downtime costs

Downtime costs[1]			Source
Retrofits and turbines/ lignin separation	1 week		Olausson (2013)
Debottlenecking equipment	1 week	(except for recovery boiler)	Olausson (2013)
Recovery boiler upgrade[2]	10 weeks		Olausson (2013)

[1] Based on losses in kraft pulp production.
[2] The recovery boiler capacity could be increased by purchasing a modular complementary recovery boiler (Wilcox, 2013). The downtime of such an option would be shorter.

❖ OPERATING COST ESTIMATES

The operating costs of a pulp mill increases upon integration of a biorefinery concept, e.g., increased wood input or raw materials required in the biorefinery. The operating cost estimates are presented in Table 8.

Table 8 Operating costs

Operating costs			Source
Wood cost[1]	75 €/ADt		Jansson et al. (2010)
Percentage of wood cost in total operating costs[2]	50%		Jylhä et al. (2010)
Lignin separation plant	33 €/t- lignin	(equivalent to 5 €/kWh- lignin)	Olsson et al. (2006)

[1] Input to **Papers III**, **IV** and **VI**.
[2] Input to **Papers III** and **IV**.

❖ ESTIMATIONS OF BY-PRODUCT REVENUES

The sales of by-products can substantially affect the profitability of the pulp mill and the biorefinery. The prices used for the by-product revenue estimate are presented in Table 9.

Table 9 By-product prices

By-products prices			Source
Lignin price [1]	23 or 35 €/MWh-lig[2]	(representing low-grade wood fuel or heavy fuel oil, respectively)	Harvey and Axelsson (2010)
Electricity price [1]	57±33% €/MWh-el[3]		Harvey and Axelsson (2010)
Ethanol price	500-650 €/m^3		Harvey and Axelsson (2010)

[1] The prices of electricity and lignin represent values for 2010, which were extracted from an in-house scenario tool developed to estimate possible prices of various energy products based on fossil fuel prices on the European commodity market and policy instruments (Harvey & Axelsson, 2010).
[2] Input to **Papers III** and **IV**. By the time the study presented in **Paper VI** was conducted, a new version of the price estimation tool was released (E. Axelsson & Pettersson, 2014) the input data were updated to 20 €/MWh-lig (low-grade wood fuel) and 35 €/MWh-lig (heavy fuel oil).
[3]Input to **Papers III** and **IV**. A sensitivity analysis on the electricity price was conducted in **Papers III** and **IV**, in which the base case price 57 €/MWh-el was varied by ±33%. In **Paper VI,** the electricity price was updated to 60 €/MWh-el.

5.9 Economic performance indicators

❖ ANNUAL EARNINGS

Annual earnings were used as a profitability indicator for the conversion of a kraft pulp into dissolving pulp production (**Papers II-IV**). The annual earnings were calculated using the annuity method:

$$annual\ earnings\ = \\ annual\ revenues - operating\ costs\ \ - a\ \cdot (investment\ costs + dowtime\ costs), \qquad [3]$$

where

$$a = \frac{i}{1-(1+i)^{-n}} \quad . \qquad [4]$$

The annual earnings are dependent on the annual revenues, the operating costs, the total investment costs and the downtime costs associated with the change to dissolving pulp production. Note that the investments and downtime costs were annualized with the annuity factor, a, which depends on the interest rate (i) and the economic lifetime (n) of the project. An annuity factor equal to 0.1 was used (corresponding to i = 5% and n = 14.2 years), which reflects a strategic, long-term investment.

The annual revenues include revenues from the sales of pulp and by-products. The operating costs include the costs of wood and, when relevant, the lignin separation plant operating costs (e.g., the cost of chemicals for lignin separation and make-up chemicals for the mill).

The investment costs include the costs for the pre-hydrolysis unit for hemicellulose extraction, costs for debottlenecking equipment, downtime costs and the costs for achieving energy savings.

❖ BREAK-EVEN DISSOLVING-TO-KRAFT-PULP PRICE RATIO

Because the long-term price of dissolving pulp is uncertain, a special performance indicator was defined in **Papers III** and **IV**, which does not require the price of dissolving pulp as an input. The break-even dissolving-to-kraft-pulp price ratio is the price ratio at which the conversion investment would break even:

$$\frac{price_{diss}}{price_{kraft}} = \frac{prod_{kraft}}{prod_{diss}} + \frac{\Delta wood \cdot price_{wood} - \Delta byprod \cdot net\ price_{byprod}}{price_{kraft} \cdot prod_{diss}} + \frac{a \cdot (inv. + dowtime\ costs)}{price_{kraft} \cdot prod_{diss}}, \qquad [5]$$

where

$\Delta wood =$ wood input for dissolving pulp mill $-$ wood input for kraft pulp mill,

$\Delta byprod =$ byproduct production in dissolving pulp mill $-$ byproduct production in kraft pulp mill,

and the annuity factor is set to 0.1.

Accordingly, lower ratios correspond to a better economic performance of the converted pulp mill. The break-even dissolving-to-kraft-pulp price ratio depends on the production of kraft and dissolving pulp, the price of kraft pulp, the net revenues from changes in wood consumption and by-product production, and the annualized investment costs for conversion, including the downtime costs associated with the conversion. Depending on the pulp production level, wood costs and by-product revenues may be higher or lower than for the original kraft pulp mill.

❖ PROFIT OPPORTUNITY

Assessing the performance of a high-solids ethanol plant (**Papers V** and **VI**) is particularly challenging because several costs are unknown. Nevertheless, a performance indicator called profit opportunity was used to compare the high-gravity case with the conventional solids loading. This profit opportunity represents the known (calculated) economic benefits of high-gravity conditions compared to conventional process conditions and is defined as follows:

$$Profit\ opportunity = \Delta revenues_{EtOH} + \Delta revenues_{Elec} - a\ \Delta inv_{Dist+Retrofit}, \qquad [6]$$

where

$\Delta revenues_{EtOH}$ = revenues of ethanol sales in high gravity – revenues of ethanol sales in conventional,

$\Delta revenues_{Elec}$ = revenues of electricity production in high gravity – revenues of electricity production in conventional,

$\Delta inv_{Dist+Retrofit}$ = investment cost for distillation + retrofits in high gravity – investment cost for distillation + retrofits in conventional,

and the annuity factor is set to 0.1.

Many of the contributions to the total production costs are the same for the high-gravity and the conventional cases; therefore, these contributions cancel each other out when calculating the profit opportunity. Other costs are associated with large uncertainties and are intentionally left out of the calculations. Therefore, the profit opportunity can be interpreted as the maximum allowed value of the uncertain cost differences for the high-gravity case to be more economical than a conventional process, i.e., the following condition is necessary for the high-gravity case to become economically feasible:

$$Unknown\ costs\ for\ high\ gravity - corresponding\ costs\ for\ conventional < Profit\ opportunity. \qquad [7]$$

This relationships means that the high-gravity case can become feasible even if the profit opportunity is negative, provided that the unknown costs for the high-gravity case are lower than their corresponding costs for the conventional case.

6 Results and discussion

In this chapter, a selection of the most important results for each of the biorefinery concepts is presented. In addition, the results are discussed, while the research questions are answered.

6.1 Hemicellulose extraction at a kraft pulp mill and upgrading the hydrolysate to ethanol

By extracting ~10% of the wood mass in the studied pulp mill, the steam production in the recovery boiler decreases by 12% (due to the removal of organic material that would otherwise have been combusted), which is shown in Table 10 (results from **Paper I**). However, the combined steam demand of the studied pulp mill and ethanol plant is significantly larger than the original pulp mill alone. As a consequence, the implementation of this biorefinery concept results in a net deficit of steam of 48 MW (steam production = 197 MW; steam demand = 245 MW).

Table 10 Steam balance before and after implementing the biorefinery concept [MW]

	Before	After
Steam production		
Recovery boiler	216	192
Bark boiler	5	5
	221	**197**
Steam demand		
Kraft pulp mill		
Steaming	5	0
Evaporation plant	56	55
Digester	12	8
Rest of the pulp mill, including back-pressure turbine	148	148
	221	211
Ethanol plant	0	34
Total	**221**	**245**

To assess the potential for steam savings, grand composite curves of the studied mill and ethanol plant were constructed (Figure 10, results from **Paper I**). The mill has a theoretical minimum heating demand (Q_{Hmin}) of 175 MW and therefore a potential steam savings of 36 MW (the steam demand after implementing the biorefinery concept is 211 MW, Table 10). The bioethanol plant has a minimum heating demand of 17 MW, which corresponds to a steam savings potential of 17 MW (the non-process-integrated plant has a steam demand of 34 MW, Table 10). Accordingly, there is a total steam savings potential of 53 MW, which is sufficient to compensate the steam deficit.

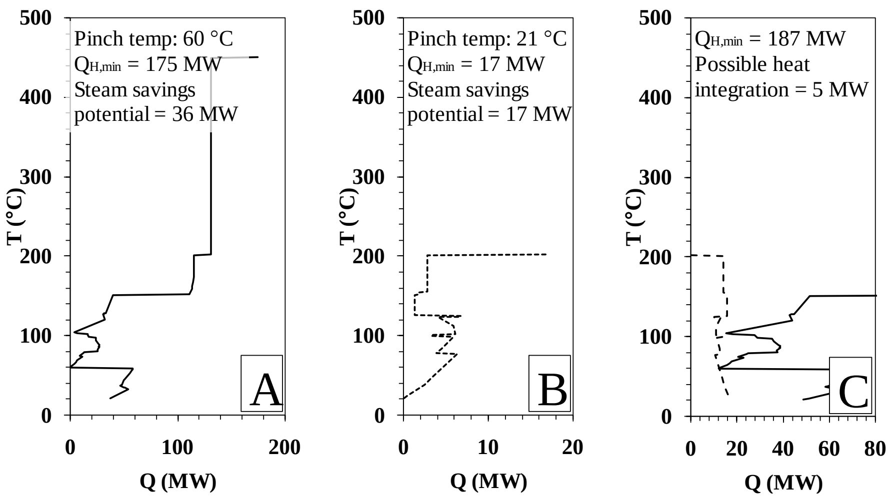

Figure 10 Grand composite curves. 13A, Left: Pulp mill. 13B, Middle: Bioethanol plant. 13C, Right: Foreground-background analysis.

Reasonable retrofits were suggested to increase the heat integration of the pulp mill and ethanol plant on a stand-alone basis, with the potential to save 45 MW of steam (85% of the total theoretical potential), which is shown in Table 11 (results from **Paper I**). The most important retrofit measure is to rebuild the hot and warm water system (HWWS) of the pulp mill so that process water can be heated with waste heat (e.g., from effluents). In turn, this makes it possible to release heat at a higher temperature, which can be used for other purposes than heating process water. Modifying the HWWS in this way requires additional heat exchanger area due to a smaller driving force in the heat exchangers. The released excess heat at a high temperature could be used to replace steam in other parts of the pulp mill. Similarly, at the ethanol plant, the construction of a heat recovery heat exchanger network could result in steam savings. A more detailed description of the retrofit measures can be found in **Paper I**.

The suggested retrofit of 45 MW is nearly sufficient to compensate the increase in steam demand that would otherwise have been obtained (48 MW). The net deficit of 3 MW can be addressed by burning excess bark in the bark boiler (the boiler capacity can possibly allow for a load increase from the current 5 MW to 8 MW). Alternatively, further heat integration may be pursued between the mill and the bioethanol plant, i.e., total integration. However, the benefits of achieving this level of integration should be weighed against the drawbacks of increasing the complexity of the retrofit.

To investigate the potential energy savings in a total integration mode, a background/foreground curve, which is also called a split GCC, was constructed (Figure 10C). The basic idea of the background/foreground analysis is to plot a certain portion of a process separately from the rest of the process in the same temperature-enthalpy diagram. In this way, the heat integration potential between the two portions can be graphically identified. In Figure 10C, the background curve (right curve) represents the pulp mill and the foreground curve (left curve) represents the ethanol plant.

According to the background/foreground analysis, an additional 5 MW of steam savings can be achieved by exporting heat from the pulp mill to the ethanol plant and vice versa. In practice, this result means that it is possible to export excess warm water from the pulp mill to the ethanol plant and to release excess heat at a high temperature from the ethanol plant to replace 3 MW of steam at the pulp mill. Thus, total heat integration eliminates the steam deficit - the original produced steam at the pulp mill (197 MW, Table 10) is sufficient to satisfy the steam demand of both the mill and the ethanol plant. The resulting steam balances are presented in Table 11.

Table 11 Steam savings potential and resulting steam demand [MW]

Steam savings	
Stand-alone	
At the pulp mill	28
At the ethanol plant	17
	45
Additional steam savings due to total integration	
Between the pulp mill and ethanol plant	3
	48
Resulting steam demand after steam savings	**197**

Although the heat integration study shows that implementing this biorefinery concept can be achieved without major disturbances in the steam balance of the pulp mill, hemicellulose extraction with green liquor severely affects the Na/S balance of the pulp mill. The continuous withdrawal of Na and S ions (in the green liquor) from the pulp mill and the export to the ethanol plant results in large deficits in those ions at the pulp mill.

The results of the Na/S balance calculations are shown in Table 12 (results from **Paper I**). A deficit of 31 kg/ADt of sodium and between 0 and 4[4] kg/ADt of sulfur is expected at the mill. By using make-up chemicals, the deficit can be compensated. For example, Na_2SO_4 could potentially compensate for the loss of sodium; however, this would insert excess sulfur in the cycle (18-22 kg/ADt). If a sulfur-free chemical, e.g., NaOH, were added as a make-up chemical, the loss of sodium could be compensated without introducing new sulfur into the system. However, the increase in chemical costs when using NaOH as a make-up chemical would be nearly twice the cost for Na_2SO_4 due to higher market prices. It can easily be shown that the cost of make-up chemicals is significant when compared with the revenue from the value-added products, i.e., ethanol and acetic acid (see Table 12).

[4] At different parts of the ethanol plant with low pH, sulfur could be covalently bound to lignin as thiolignin. If sulfur is covalently bound to the lignin, then it may be re-incorporated in the chemical recovery cycle of the mill. Whether and to what extent sulfur will be bound to lignin must be further investigated. The first number of the interval presented refers to the case in which all S from green liquor is bound to lignin. The second number refers to the case in which S is not bound to lignin.

Alternatively, the studied process could be designed so that these ions are recovered and sent back to the mill. However, this is complicated from a practical perspective because the lost sodium and sulfur are found in substantially diluted stillage that would require large steam consumption to become concentrated before being recirculated, thus causing an increase in evaporation demand. Moreover, the amount of sulfur recycled back to the mill would be excessive if all of the sodium was recovered, i.e., 22 kg/ADt, due to the use of sulfuric acid in the acid-hydrolysis unit.

Additionally, other costs may worsen the profitability of the studied process. To detoxify the raffinate prior to fermentation from the sodium sulfate formed during the pH adjustment step, purchased lime (or produced at the lime kiln) is added, forming excessive amounts of gypsum with an associated disposal fee. For the studied pulp mill, it was estimated that as much as 27 tons of gypsum is generated daily, i.e., 22 kg/ADt. According to the open literature, the Na/S balance issue remains unsolved for the "near-neutral" extraction process.

Table 12 Possible solutions to the Na/S balance problem and associated costs

	Deficit	Na_2SO_4 is added	NaOH is added	Stillage is recirculated
Na, kg/ADt	-31	0	0	0
S, kg/ADt	0/-4	+22/+18	0/-4	+22/+22
Increased steam demand, MW		0	0	+13
Revenues from ethanol and acetic acid sales[1], €/ADt		45	45	45
Make-up chemicals/steam costs[1], €/ADt		12	22	12

[1] The following prices were assumed: 533 €/ton EtOH, 727 €/ton HAc, 125 €/t Na_2SO_4, 205 €/t NaOH 50 w% sol, and 38 €/MWh steam.

6.1.1 Answers to the investigated research questions

Q2 How is the steam production and demand of the pulp mill affected by the implementation of the biorefinery concept (base case: before process integration)?

During the hemicellulose extraction step, most of the hemicellulose in wood chips (and some lignin) that would otherwise have been combusted in the recovery boiler is removed. Accordingly, the steam production decreases. This decrease in steam production, in combination with an increased total steam demand, results in a large steam deficit (48 MW) if heat integration is not increased.

Q3 What is the heat integration potential of the pulp mill and biorefinery? Are there any advantages of pursuing heat integration between the pulp mill and biorefinery?

By increasing the heat integration within the studied pulp mill and ethanol plant, it is possible to significantly reduce the steam demand (45 MW) and almost completely eliminate the steam deficit. Increasing the level of retrofit complexity by pursuing heat integration between the pulp mill and the ethanol plant should be weighed against its (rather limited) potential for further steam savings (3 MW). As an alternative, steam production could be increased by burning bark, provided that the bark boiler has spare capacity.

Q5 What are the consequences of changes in composition/flowrates of material streams at the pulp mill that arise from implementing the biorefinery concept, e.g., consequences on the Na/S balance and consequences on the pulp production capacity?

The export of green liquor from the studied pulp mill to the ethanol plant results in severe disruptions in the Na/S balance, which may prohibit the implementation of this biorefinery concept unless products with higher market value (compared to ethanol) are targeted from the extracted hemicellulose.

6.2 Conversion of a kraft pulp mill into a dissolving pulp mill

Unlike the other two biorefinery concepts studied in this PhD project, kraft-based dissolving pulp production is not conducted by erecting a new process beside an otherwise rather unchanged pulp mill and exchanging material and energy streams between them. Dissolving pulp production requires the total transformation of the pulp mill to produce a different main product. Accordingly, the pulp mill and biorefinery steam balances cannot be presented independently (as with the other biorefinery concepts). For the same reason, the heat integration potential cannot be studied for stand-alone and total heat-integrated processes. Instead, two levels of heat integration are studied, a simple heat integration and a more ambitious heat integration. The two levels of heat integration differ largely in the number of modifications and new heat exchangers required.

The steam and water demands of the unconverted kraft pulp mill and the dissolving pulp mill are similar except for some process units (see Table 13, results from **Paper II**). Due to the different wood chip treatment, the total pulp yield is expected to decrease from approximately 43% to 33% upon the conversion from kraft to dissolving pulp production, which is a decrease of approximately 25%. As a result, pulp production would be reduced for a constant wood input. Alternatively, the wood input may be increased to compensate for the lower yield.

The main difference between the pulp mills is that a pre-hydrolysis unit is added to the dissolving pulp mill prior to cooking to remove most of the hemicellulose. The steamed chips are exposed to the extraction water in the pre-hydrolysis vessel, and the mixture is heated to approximately 175°C. Even a very simple configuration with heat integration between the process streams to/from the pre-hydrolysis vessel would significantly reduce the steam demand compared with the case in which the heat demand is satisfied by steam. Hence, a case with no heat integration is highly unlikely to be considered for implementation, although for the purpose of comparing results, the steam demand for extraction presented in Table 13 represents the case with no heat integration as a reference case.

In **Paper II**, it was assumed that the recovery boiler is the bottleneck for pulp production, which is motivated by the fact that the recovery boiler is a very expensive unit to purchase or upgrade and, in some cases, has already been upgraded to its limit. Consequently, it is assumed that other equipment that may limit the capacity for pulp production must be upgraded upon conversion and that the pulp production capacity is determined solely by the capacity of the recovery boiler. Therefore, the load of the recovery boiler is constant both before and after the conversion (441 MW, Table 13). However, due to pulp yield losses, pulp production is decreased from 2000 to 1474 ADt/d, which results in higher steam production per ton of produced pulp (25.8 GJ/ADt).

In terms of the energy balance, the most important changes are found in the extraction step, digester, evaporation and soot blowing. All of these units are affected by the fact that a higher wood input is required to produce dissolving pulp; consequently, an increase in the specific steam demand is observed. Otherwise, the rest of the mill is unaffected and has the same steam demand per ton of produced kraft or dissolving pulp (shown as "Heat demand for the rest of the process" in Table 13; 4.1 GJ/ADt).

Even without increased heat integration (case A-0 in Table 13), the mill has enough steam (25.8 GJ/ADt) to satisfy the steam demand of the studied process (18.9 GJ/ADt) and the back-pressure turbine (5.1 GJ/ADt). Consequently, the dissolving pulp mill also has excess available steam (1.7 GJ/ADt). However, the excess available steam decreases upon conversion into dissolving pulp production.

Table 13 Steam and water demand of the kraft and dissolving pulp mills

	Kraft pulp mill		**Dissolving pulp mill (Case A-0)**[1]	
	[ADt/d]	[BDt/h]	[ADt/d]	[BDt/h]
Wood consumption	4605	173	4467	168
Pulp production	2000	75	1474	55
Yield		43%		33%
STEAM PRODUCTION	[GJ/ADt]	[MW]	[GJ/ADt]	[MW]
Recovery boiler	19	**441**	25.8	**441**
STEAM DEMAND				
Extraction	0	0	6	103
Digesting	1.2	27	1.6	27
Evaporation	4.3	100	5.9	101
Soot blowing	1	23	1.3	22
Heat demand for the rest of the process	4.1	95	4.1	71
Sub-total process heat	10.6	245	18.9	323
Sub-total including preheating of boiler water and combustion air[2]	(12.6)	(291)	(21.6)	(368)
Back-pressure turbine	4	93	5.1	88
Excess steam, e.g., steam to condensing turbine	4.4	103	1.8	30
Total	19	441	25.8	441
WATER DEMAND	[t/ADt]	[t/h]	[t/ADt]	[t/h]
Water demand for extraction	0	0	6.1	374
Water demand for rest	20.9	1738	20.5	1263
Total	20.9	1738	26.6	1637

[1] A mill configuration with no heat integration and with a pulp production corresponding to a constant load in the recovery boiler. The different studied cases are described in the following section.
[2] Boiler water and combustion air are not net steam consumers but are included in the pinch study because they can still be heat integrated to provide excess steam.

In **Paper II**, two dissolving pulp mill cases were studied: a case in which the hydrolysate was upgraded (beyond the system boundaries) and a case in which the hydrolysate was evaporated in the PMEP and combusted. The GCCs of the kraft pulp mill and the dissolving pulp mill(s) are very similar (see Figure 11). The main differences in the curves can be explained by the larger LP and MP steam demand in the digester, the pre-hydrolysis unit and evaporation plant of the dissolving pulp mill(s). As expected, the steam demand for evaporation increases if the hydrolysate is combusted in the recovery boiler compared to the case in which it is sent to an upgrading facility.

The theoretical minimum heating demand of the dissolving pulp mill is 14.1 GJ/ADt if the hydrolysate is sent to be upgraded and 17.3 GJ/ADt if the hydrolysate is burned in the recovery boiler. The large difference between the theoretical minimum heating demand and the steam demand of the non-integrated processes (21.6 GJ/ADt for the first case[5], which is shown in Table 13 as "Sub-total including preheating of boiler water and combustion air") indicates that there is great potential for internal heat integration.

Although the potential for internal heat integration is large, the relatively low pinch temperature of the processes indicates that the possibilities for exporting heat from process streams in the dissolving pulp mill(s) to other facilities, e.g., hemicellulose upgrading facilities, are limited.

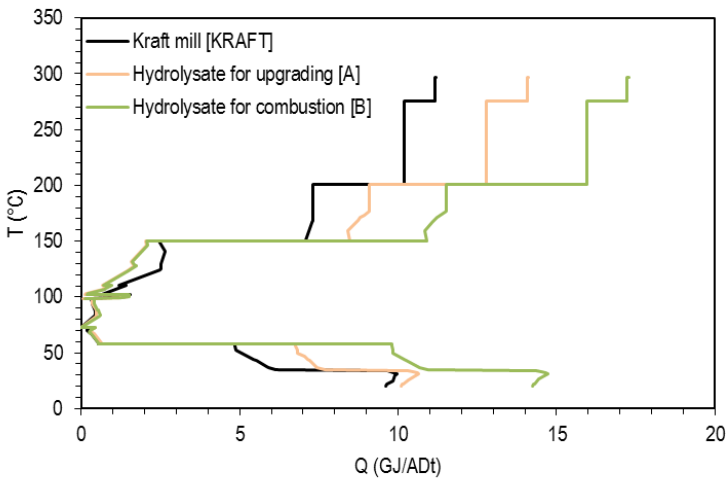

Figure 11 Grand composite curves for the kraft pulp mill, the dissolving pulp mill when the hydrolysate is sent to be upgraded and the dissolving pulp mill when the hydrolysate is burned in the recovery boiler.

Two levels of heat integration were investigated: a simple heat integration and a more ambitious heat integration. In both cases, heat integration with the streams to/from the extraction unit was considered. In practice, this means that the hot hydrolysate that exits the extraction unit is used to preheat the extraction water entering the extraction unit. The main difference between the two heat integration levels is the way in which the extraction water is preheated prior to the previously mentioned heat exchanger. In the simplest case, excess heat, which is readily available at the mill (through cooling of the surface condenser), is used. In the more ambitious case, preheating of the extraction water is performed in a step-wise manner with other sources of excess heat at a higher

[5] To simplify the presentation and understandability of the results, case B-0, i.e., the case in which the hydrolysate is burned in the recovery boiler, is not shown in Table 13. The steam demand of the non-integrated process is 24.7 GJ/ADt.

temperature, which requires a more complex heat exchanger network design. Additional steam savings are achieved using some of the excess heat available in flue gases or hot extracted wood chips to heat other process streams, e.g., combustion air and the dryer.

In summary, the simple heat integration retrofit requires new piping and one new heat exchanger, whereas ambitious heat integration requires new piping, upgrading two existing heat exchangers and purchasing 6 new heat exchangers. For a detailed description of the retrofits, the reader is referred to **Paper II**. Very similar heat integration measures were also possible for the case study mill (**Paper IV**). The resulting heat integration potential for both heat integration approaches and for both pulp mill configurations is presented in Table 14 (results from **Paper II**).

Table 14 Heat integration potential for different levels of heat integration [GJ/ADt]. The numbers presented in parentheses represent the achieved steam savings in comparison to the total steam consumption (21.6 for the case of upgrading the hydrolysate and 24.7 GJ/ADt for the case of combusting the hydrolysate)

HEAT INTEGRATION LEVEL	A: Hydrolysate for upgrading	B: Hydrolysate for combustion
Simple heat integration	*4.0 (19%)*	*3.1 (13%)*
Ambitious heat integration	*6.3 (29%)*	*6.3 (25%)*
Theoretical heat integration potential	*7.4 (35%)*	*7.4 (30%)*

The different cases, including different process configurations and levels of heat integration, have different pulp production capacities. Dissolving pulp production requires larger amounts of wood per ton of produced pulp compared to kraft pulp production, which increases the risk for bottlenecks in pulp production. In the case in which the hydrolysate is sent for combustion, additional water and organic material enters the recovery cycle of the pulp mill, which may limit the pulp production capacity even more. Extracting lignin from black liquor has the potential to debottleneck the recovery boiler. While this is true for any level of heat integration, a more ambitious heat integration design enables more lignin to be extracted without compromising the steam balance of the pulp mill.

In Figure 12 (results from **Paper II**), the variation in pulp production capacity for the different process configurations is shown. For the cases without heat integration (A-0 and B-0), the pulp production capacity decreases significantly compared with the kraft mill if the recovery boiler is the bottleneck. All of the cases with maximum power generation (A-1-el, A-2-el, B-1-el and B-2-el) also exhibit this dramatic decrease in pulp production capacity, which can be explained by the fact that the load in the recovery boiler is solely determined by the fuel input to the recovery boiler and not by the steam demand of the mill. In the cases with lignin separation (A-1-lig, A-2-lig, B-1-lig and B-2-lig), the recovery boiler is debottlenecked, which allows a much higher pulp production than in all of the other cases.

When hydrolysate is sent to be upgraded, simple heat integration (A-1-lig) would allow a pulp production to be similar to the kraft pulp mill if lignin separation is implemented. More ambitious heat integration (A-2-lig) has the potential to increase the pulp production capacity to a higher level than the kraft pulp mill. However, this production increase also requires debottlenecking of equipment in the pulp line downstream of the digester. The cases in which the hydrolysate is sent for combustion are worse than the cases in which it is sent for upgrading in terms of the pulp production capacity. Nevertheless, ambitious heat integration (B-2-lig) is able to produce nearly the same amount of pulp as the kraft mill.

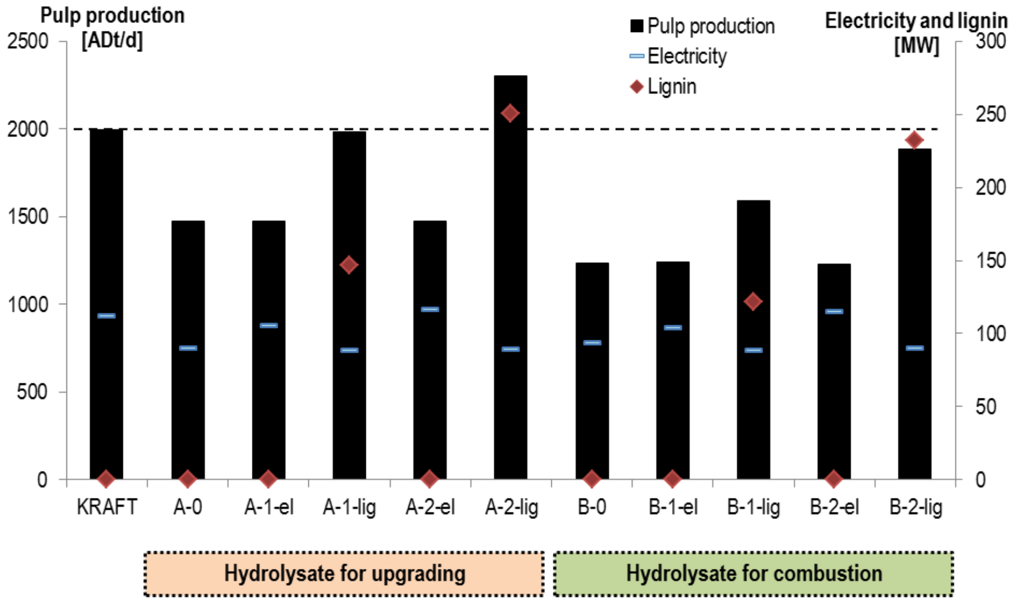

Figure 12 Pulp production capacity (left axis) and energy outputs (right axis) when the recovery boiler is the bottleneck for pulp production.

Clearly, debottlenecking equipment is vital for maintaining high pulp production levels upon conversion to dissolving pulp production. In the previous results, lignin separation was used as a way to debottleneck the recovery boiler. However, the debottlenecking can be performed via other means. In **Paper III**, the case in which the recovery boiler is debottlenecked by boosting its capacity (e.g., by rebuilding or purchasing a modular complementary boiler) was studied.

Figure 13 (results from **Paper III**) presents the capital investment required for conversion to dissolving pulp production for three different cases with the same level of heat integration (i.e., steam savings per ADt) but with different levels of pulp production. Case L-NO-2-el (same as case A-2-el in Figure 12) represents a mill in which the recovery boiler is not debottlenecked and consequentially has a low level of pulp production (1474 ADt/d). Cases H-LIG-2-lig (same as case A-2-lig in Figure 12) and H-RB-2-el (new case studied in **Paper III**) are debottlenecked to achieve a high level of pulp production (2303 ADt/d) by separating lignin (H-LIG-2-lig) and upgrading the recovery boiler (H-RB-2-el). It is shown that debottlenecking requires a large capital investment, which is significantly higher than the investment required for simply extracting hemicellulose (pre-hydrolysis). This finding emphasizes the importance of lifting the focus from the pulp line to the entire mill (including the energy system) when evaluating the profitability of the conversion.

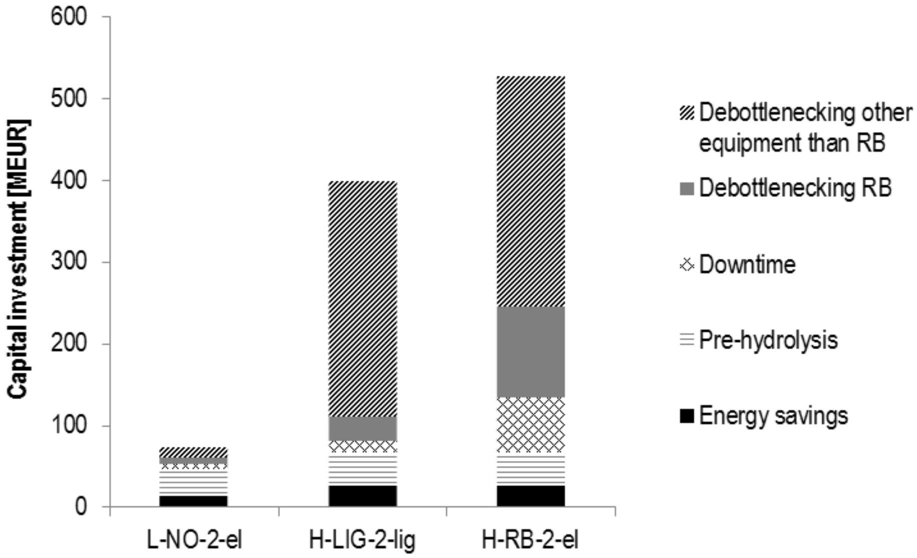

Figure 13 Capital investments [M€] for cases L-NO-2-el, H-LIG-2-lig and H-RB-2-el.

Despite the comparatively higher investment costs of the debottlenecked cases, the overall economy of these cases may be favorable because increased pulp production is possible. However, the long-term price of dissolving pulp is uncertain; therefore, the annual earnings of each case are also uncertain. Figure 14 (results from **Paper III**) illustrates the necessary ratio between dissolving and kraft pulp prices required to achieve a profitable conversion, i.e., the ratio required so that the converted mill has the same annual earnings as the kraft pulp mill, including the investments required for conversion (see Eq. 5 in *Section 5.9*).

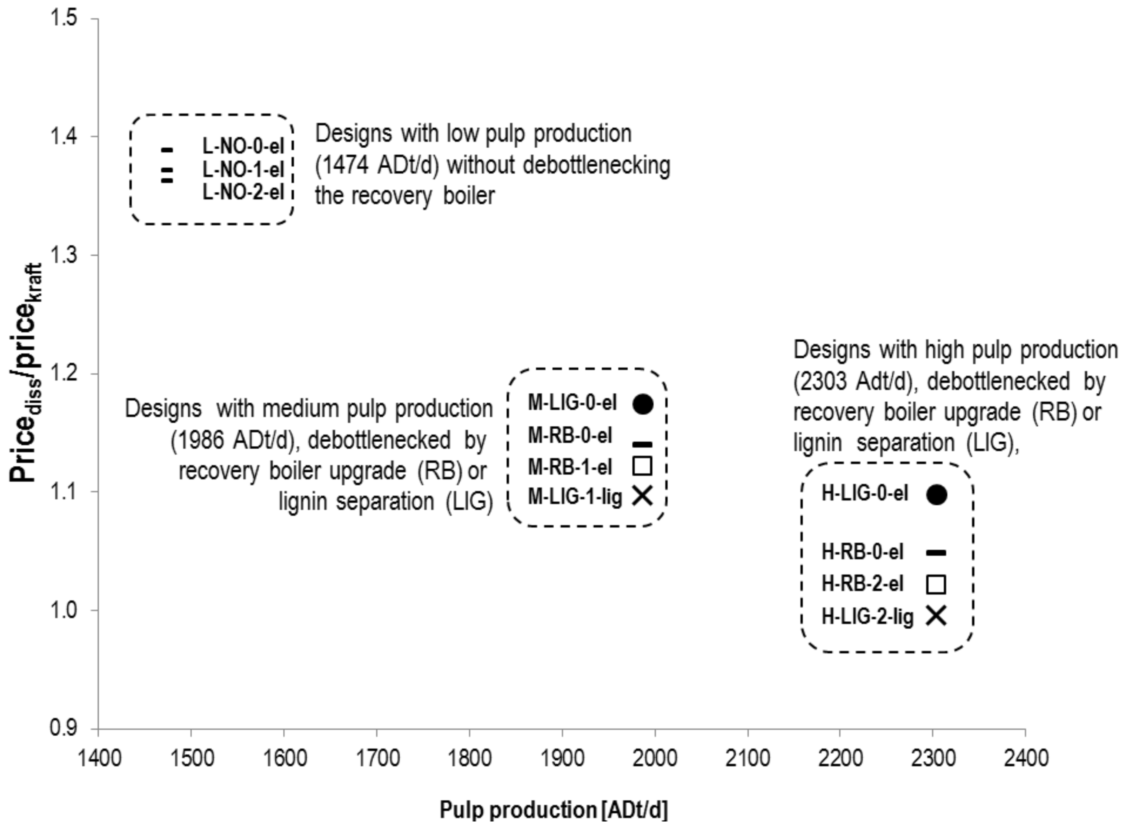

Figure 14 Ratio between dissolving and kraft pulp prices that makes the annual earnings equal for both the kraft and the dissolving pulp mill. To calculate the revenues from lignin sales, a lignin price of 35 €/MWh-lig was used (valued as heavy fuel oil).

Despite the major capital investments required for debottlenecking, the results show that achieving higher pulp production is more profitable (the break-even dissolving-to-kraft pulp price ratio decreases) than lower pulp production. However, **Paper IV** challenged the notion that debottlenecking is always profitable. In this study, the benefits of debottlenecking the pulp production were compared against the investments required for debottlenecking equipment, considering more pieces of equipment and a larger range of pulp production. The results of this investigation are presented in Figure 15 for two dissolving pulp price levels.

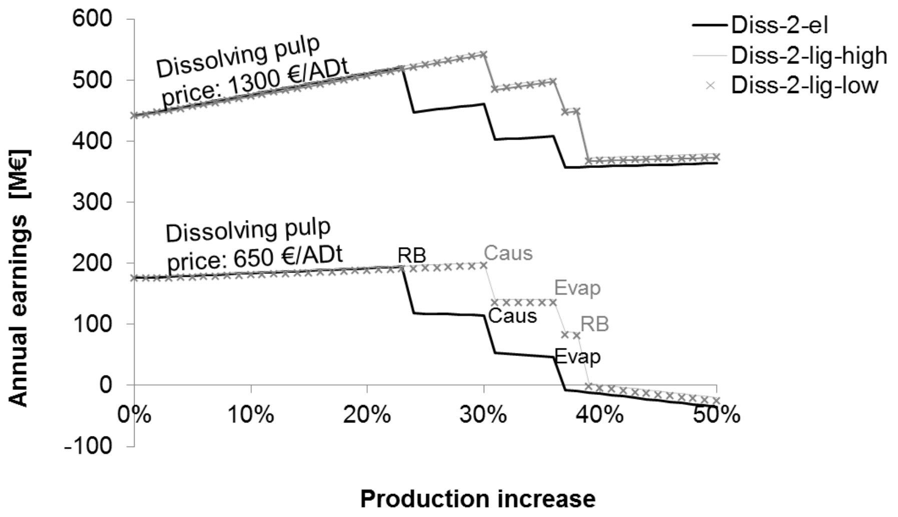

Figure 15 Relationships between annual earnings and increased pulp production for two different dissolving pulp prices.

For small increases in pulp production, the annual earnings increase for both dissolving pulp prices (as also shown in Figure 14). However, the annual earnings peak (at approximately ~23-30%) before decreasing again in a step-wise manner. Each step is associated with the need for large debottlenecking equipment investments. The steps represent requirements for debottlenecking the recovery boiler, causticization plant, and evaporation plant. The large investments required to debottleneck these pieces of equipment cannot be economically justified by the increased pulp sales. Interestingly, for the low dissolving pulp price, a production increase larger than ~36–39% results in negative annual earnings. Based on the results shown in Figure 15, there is a trade-off between the potential gains associated with increasing pulp production and the investments required to debottleneck the equipment.

Several of the parameters required to perform an economic evaluation of the conversion to dissolving pulp production are uncertain, e.g., the prices of dissolving pulp, wood and by-products. Moreover, the required investment to debottleneck the pulp production of a particular pulp mill is also uncertain. Accordingly, in **Paper III**, the influence of the uncertainty in various parameters on the annual earnings was investigated (see Table 15). The cost of upgrading equipment is one of the most important parameters for achieving profitability; only the dissolving pulp and wood prices are more important. The price of wood significantly affects profitability. Nevertheless, an increase in wood price would affect both a converted mill and an unconverted kraft pulp mill. Therefore, it is reasonable to assume that despite the large influence in overall profitability, the wood price would have a small influence on deciding to convert to dissolving pulp production. Electricity and lignin prices have a smaller influence on the annual earnings of the mill. However, they are influential enough to affect the choice of the best debottlenecking method for the recovery boiler (see **Paper III**).

Table 15 Influence of the uncertainty in different parameters on the annual earnings of the converted mill. The ranges are calculated for cases with the same pulp production (i.e., 2303 ADt/d)

Parameter	Worst scenario	Best scenario	Uncertainty
Dissolving pulp price	Same price as kraft pulp	50% higher than the price of kraft pulp	250 M€/y
Wood price	25% increase relative to the current wood price (72 €/ADt)	25% decrease relative to the current wood price (72 €/ADt)	168 M€/y
Required investment to upgrade equipment	The units that must be debottlenecked cannot be upgraded and must be completely replaced	All critical equipment has sufficient capacity to handle the conversion; therefore, no modifications are required	81-96 M€/y
Price of electricity	Low price of electricity (40 €/MWh-el)	High price of electricity (80 €/MWh-el)	25-58 M€/y
Price of lignin	Low price of lignin (lignin valued as low-grade fuel, 23 €/MWh-lig)	High price of lignin (lignin valued as heavy fuel oil, 35 €/MWh-lig)	0-24 M€/y

6.2.1 Answers to the investigated research questions

Q2 How is the steam production and demand of the pulp mill affected by the implementation of the biorefinery concept (base case: before process integration)?

The conversion to dissolving pulp production requires more wood per ton of produced pulp. Therefore, more organic material enters the pulp mill and the recovery cycle. Considering that the recovery boiler is often the bottleneck for pulp production, this means that pulp production must be adjusted (i.e., reduced) to maintain a constant steam production if no investments are made to increase the capacity of equipment in the recovery cycle. The dissolving pulp production process is more energy and water intensive than kraft pulp production. Accordingly, the steam demand increases, whereas the surplus steam decreases per ton of produced pulp.

Q3 What is the heat integration potential of the pulp mill and biorefinery? Are there any advantages of pursuing heat integration between the pulp mill and biorefinery?

Substantial steam savings are achievable using relatively simple heat integration measures. More ambitious heat integration significantly increases the investment costs of the retrofit; however, this measure has a positive effect on the amount of produced by-products.

Q4 What is the potential for by-products generation, e.g., lignin and power?

Ambitious heat integration increases the potential for by-products generation. In particular, ambitious heat integration in combination with lignin extraction is advantageous because it increases the potential for recovery boiler debottlenecking[6].

Q5 What are the consequences of changes in composition/flowrates of material streams at the pulp mill that arise from implementing the biorefinery concept, e.g., consequences on the Na/S balance and consequences on the pulp production capacity?

The conversion to dissolving pulp production may result in a drastic decrease in pulp production if the capacity of certain equipment in the mill is limited. The critical pieces of equipment identified include the recovery boiler, the evaporation plant, the causticization plant and the digester. Generalizations regarding the best way to debottleneck and to what extent should be avoided. A detailed bottleneck analysis should be conducted for any mill that is interested in the conversion.

Q6 What are the major factors that affect the profitability of the biorefinery concept?

The major factors affecting the profitability of the conversion are the dissolving pulp price and the particular needs of a pulp mill for debottlenecking equipment.

6.3 Integration of a high-solids ethanol process to a kraft pulp mill

In this biorefinery concept, filtrates and stillage that contain organic material from the ethanol plant are sent to the pulp mill for evaporation in the PMEP and combustion, which are assumed to have spare capacity. Accordingly, the net organic input to the recovery boiler is increased, which also increases steam production (see Table 16; results from **Paper V**).

The additional material streams in the pulp mill also result in an increased steam demand in the PMEP and for the recovery boiler operation (feed water and air preheating, soot blowing and blowdown are lumped together under "Other changes at the pulp mill" in Table 16). Because the studied pulp mill is a modern and efficient mill, there is a surplus of steam both before and after implementing the biorefinery at both solids loadings. Accordingly, the excess steam is sent to a condensing turbine for power generation.

[6] This statement is based on the assumption that the maximum rate of lignin extraction is set so that it still leaves sufficient amounts of organic material in the black liquor such that the steam demand of the mill and the pre-hydrolysis unit are solely satisfied by the recovery boiler. Lignin separation beyond this limit was studied in **Paper III**.

Table 16 Steam demand for ethanol production and by-product production before retrofits

	Conventional solids loading	High-gravity case
Ethanol production [t/h]	12.8	10.3
Total steam production [t/h]	1089.4	1093.6
STEAM DEMAND		
Extra load at the PMEP [MW]	13.8	13.7
Other changes at the pulp mill [MW]	12.4	12.6
Ethanol plant [MW]	103.5	86.4
Total steam demand before retrofits [MW]	**129.7**	**112.7**
Total steam demand before retrofits [MJ/l_{EtOH}]	**29.1**	**31.3**
BY-PRODUCT PRODUCTION		
Power generation [MW]	204.9	210.0
Lignin extraction [t/h]	12.0	11.9

In **Paper V**, the potential for heat integration within the pulp mill was studied using the GCC shown in Figure 16A. The theoretical minimum heating demand of the mill is 463 MW. Compared with the total steam demand (478 MW), this value provides a theoretical potential steam savings of 15 MW (3% of the total steam demand). To achieve this level of steam savings, large modifications to the flue gas system of the recovery boiler would be required, which include preheating combustion air with excess heat from process streams (instead of being performed inside the boiler house with steam) and recovering heat from stack gases at a lower temperature than in traditional operations. Although research has been conducted to solve some of the technical difficulties (Ketonen et al., 2013; Mostajeran-Goortani et al., 2011) and the development of new designs may enable the recovery of heat from stack gases in the near future, the potential to increase heat integration at the pulp mill was considered to be very limited in this study.

For the ethanol plant, foreground/background curves were constructed to study the potential for heat integration between the distillation and upgrading plant (left curves – foreground curves) and the remainder of the ethanol process (right curves – background curves), Figure 16B. More importantly, the foreground/background curves made it possible to illustrate how the analyzed processes could be designed to improve the integration between them, e.g., by setting the operating pressure (and thereby the operating temperature) of the distillation plant to a level that would allow maximum heat integration with the EPEP.

The background curves are nearly identical for the processes with conventional and high solids concentrations. However, the differences in the foreground curves are more remarkable. Clearly, the steam demand for distillation (at 79 °C) in the conventional process exceeds that of the high-gravity process. However, the heat available in the surface condenser of the EPEP is sufficiently large to cover the heat demand of the reboilers under both ethanol concentration conditions. Accordingly, the steam demands for distillation are both 0 MW for conventional and high-gravity conditions. In fact, the two processes have nearly the same theoretical heating demand: ~53 MW.

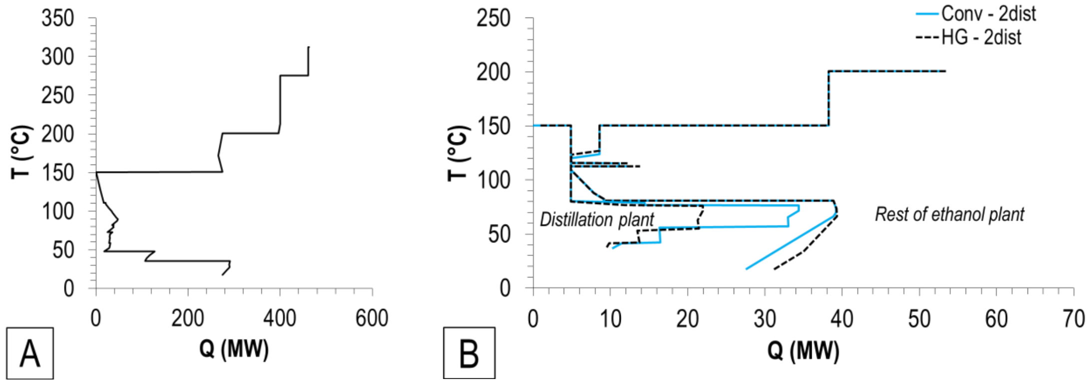

Figure 16 Potential for heat integration. 19A, Left: GCC of the pulp mill. 19B, Right: Foreground/background analyses of the distillation plant and the remainder of the ethanol plant.

Substantial steam savings can be achieved by integrating the reboilers of the distillation towers with the surface condenser of the EPEP. In addition, steam savings are possible with relatively simple retrofits, such as utilizing waste heat available in the stillage to preheat other process streams, e.g., the feed to the distillation towers. A detailed description of the heat integration retrofits can be found in **Paper V**. The resulting steam savings for both concentrations of solids are presented in Table 17.

According to the GCC of the pulp mill (Figure 16A), there are approximately 17 MW of excess heat for T≥110 °C that could be theoretically exported to the ethanol process. If heat integration is not conducted at the pulp mill, the amount of excess heat at these temperatures would be even higher. However, releasing this excess heat would also require the recovery of waste heat from the flue gases of the recovery boiler. Assuming that this would be performed, heat could be delivered to the ethanol plant. The potential users of this heat are the reboilers of the distillation plant. However, as previously shown, very efficient heat integration within the ethanol plant is possible, which makes the excess heat available in the flue gases redundant. Although the investments needed to integrate the reboilers of the distillation plant with the flue gases would certainly be different than those of the configuration proposed herein (integration with the EPEP), no benefits in terms of the total steam demand would be obtained by pursuing heat integration between the pulp mill and the ethanol plant (see Table 17).

Table 17 Steam savings potential for the retrofits

Steam savings	Conventional solids loading	High-gravity case
Stand-alone		
At the pulp mill [MW]	0	0
At the ethanol plant [MW]	49	34
	49	34
Additional steam savings due to total integration		
Between the pulp mill and ethanol plant [MW]	0	0
	49	34

The steam demand for ethanol production after retrofits is presented in Table 18 (results from **Paper V**). Note that the resulting steam demand of the high-gravity process is only marginally lower than for conventional solids loadings (in MW) and significantly higher per liter of produced ethanol. Moreover, the performance of the high-gravity concept is only marginally better than the conventional case in terms of by-product production (see “Power generation”, Table 18). Because the separation of lignin is conducted before the high solids concentration is introduced, the same amount of lignin is extracted for the same wood input.

Table 18 Steam demand for ethanol production and by-product production after retrofits

	Conventional solids loading	High-gravity case
Ethanol production [t/h]	12.8	10.3
Total steam production [t/h]	1089.4	1093.6
STEAM DEMAND		
Extra load at the PMEP [MW]	13.8	13.7
Other changes at the pulp mill [MW]	12.4	12.6
Ethanol plant [MW]	54.4	52.5
Total steam demand after retrofits [MW]	**80.6**	**78.7**
Total steam demand after retrofits [MJ/l_{EtOH}]	**18.1**	**21.9**
BY-PRODUCTS PRODUCTION		
Power generation [MW]	216.8	218.2
Lignin extraction [t/h]	12.0	11.9

The results of these studies indicate that the potential advantages of the high-gravity case over a process with a more conventional solids loadings are not related to the by-product potential. Interestingly, the advantages are also not related to the steam demand of the ethanol plant. The results challenge the popular belief that high ethanol concentrations would translate into a significant steam demand decrease in the distillation plant and consequentially reduce production costs (Galbe et al., 2007; Humbird et al., 2010; Modenbach & Nokes, 2012, 2013; Zacchi & Axelsson, 1989b). This belief is based on specific assumptions, e.g., ethanol upgrading is conducted in a single distillation step or that the same ethanol yield can be maintained under high-gravity conditions. However, the results show that the steam demand for distillation at varying ethanol feed concentrations depends greatly on the design of the distillation plant and how it is integrated with the rest of the process. It has been stated that feed concentrations exceeding 4% (w/w) are the minimum requirement to achieve an economically attractive process (Galbe et al., 2007; Hoyer et al., 2013; Kristensen, 2009). This statement could be supported by the findings presented in Figure 17 (results from **Paper V**). However, for the particular process studied in this project, the benefits of increasing the ethanol concentration beyond that minimum limit are very questionable.

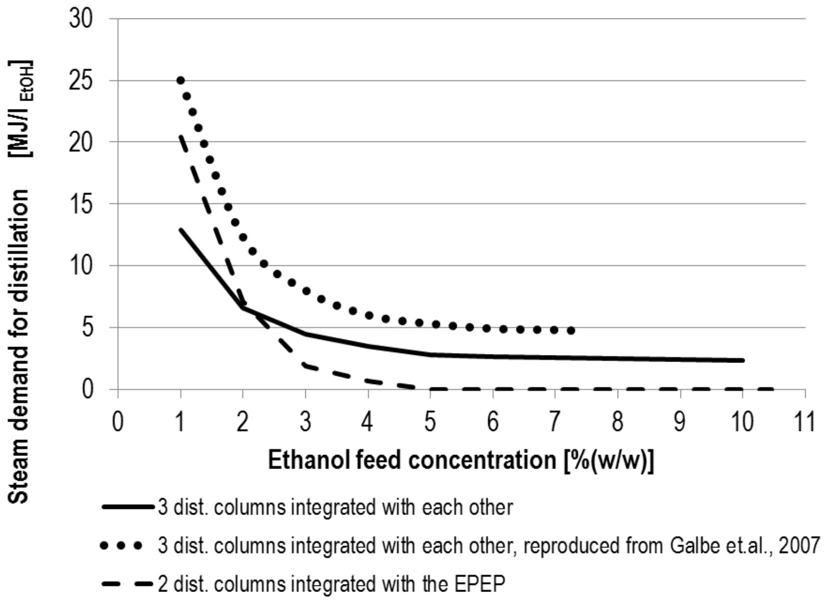

Figure 17 Resulting steam demand in the distillation plant.

Instead, two other process parameters appear to have the largest significance for the economic performance of this biorefinery process: the overall process yield and the way the stillage is treated. In Figure 18 (results from **Paper VI**), the profit opportunity (see Eq. 6 in *Section 5.9*) for the high-gravity process is presented for two stillage treatment alternatives. Clearly, the profit opportunity decreases very rapidly as the overall process yield decreases. In Figure 18A, the case in which the stillage is sent to the effluent treatment plant of the pulp mill is presented. The profit opportunity is 0.34 M€/year when the yield for the high-gravity process is maintained at the same level as in the conventional case, which is equivalent to an investment of 3.4 million €. Hence, there is room for allowing higher costs in other parts of the ethanol plant when using the high-gravity process, assuming that the yield is maintained at levels close to that which is expected for conventional process designs. However, Figure 18A shows that the profit opportunity rapidly approaches zero as the yield drops, indicating the importance of maintaining a high ethanol yield even under high-gravity conditions.

In Figure 18B, the case in which the stillage is sent to the PMEP for combustion is presented. In this case, the benefit of the high-gravity process is significantly increased compared to the case in which the stillage is sent to the effluent treatment plant. However, it is questionable to send the thin stillage for evaporation in this alkaline-based process.

Because the lignin is removed earlier in the process, the thin stillage contains no suspended solids and has very little heating value. Hence, there is nothing to gain by combusting the thin stillage in the recovery boiler. As a third alternative, the stillage could be recirculated and used as process water for example for dilution before SSF (Wingren, 2005), decreasing both treatment costs and water consumption. In this case, the profit opportunity of the high-gravity process is likely to resemble the results presented in Figure 18A.

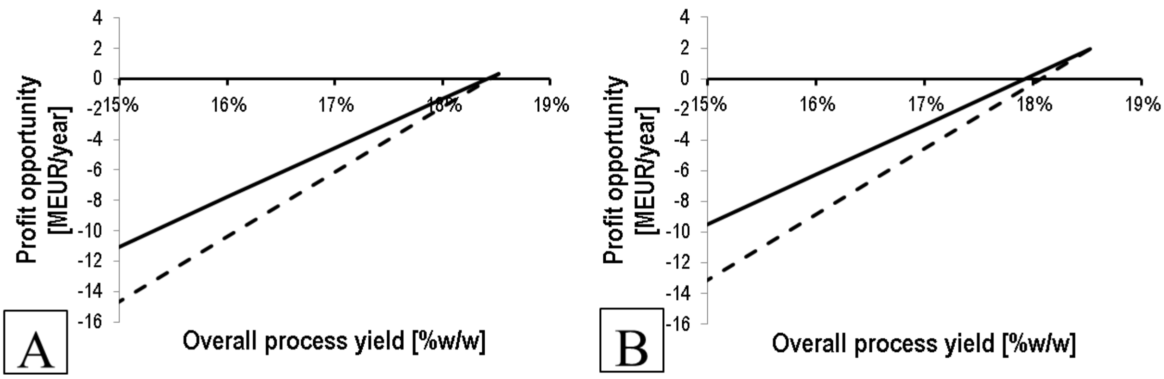

Figure 18 Profit opportunity for the high-gravity process. The solid and dashed lines are calculated with ethanol prices of 500 and 650 €/m^3, respectively. 15A, Left: stillage to effluent treatment. 15B, Right: stillage to PMEP.

6.3.1 Answers to the investigated research questions

Q2 How is the steam production and demand of the pulp mill affected by the implementation of the biorefinery concept (base case: before process integration)?

Organic material from the ethanol plant (in filtrates and stillage) is sent to the pulp mill for combustion, which results in higher steam production in the recovery boiler. However, the total steam demand increases such that the excess steam available for generating condensing power decreases upon implementation of the biorefinery concept. No significant differences in steam production are observed for the two studied solids loadings.

Q3 What is the heat integration potential of the pulp mill and biorefinery? Are there any advantages of pursuing heat integration between the pulp mill and biorefinery?

The studied pulp mill is energy efficient and has a very limited potential for further increasing internal heat integration or for exporting heat. However, large energy savings can be achieved at the ethanol plant. The heat available in the surface condenser of the EPEP is sufficient to cover the steam demand for distillation at both solids concentrations. In terms of the steam demand, no clear advantage is identified for pursuing heat integration between the pulp mill and the ethanol plant. However, investment costs for heat savings might vary depending on how heat integration is achieved.

Q4 What is the potential for by-products generation, e.g., lignin and power?

Increasing heat integration results in a larger steam surplus (although no larger than before the biorefinery concept was implemented) that can be used for generating condensing power. No significant benefits are found for the high-gravity concept compared to the conventional case.

Q6 What are the major factors that affect the profitability of the biorefinery concept?

The overall process yield has a very large effect on the economic performance of this biorefinery. Hence, it is unlikely that the high-gravity concept will be competitive with the conventional case unless the process yield can be maintained under high-gravity conditions. Ethanol production under high-gravity conditions results in a smaller flowrate of stillage, which could be advantageous if the stillage is combusted at the pulp mill. However, if the stillage is sent to the effluent treatment plant or if it is recirculated as process water, the advantages of a smaller flowrate are minor.

6.4 Summary of the results

Biorefinery concept	Heat integration potential	Consequences at the pulp mill	Remarks
Hemicellulose extraction at a kraft pulp mill and upgrading the hydrolysate to ethanol	The largest contribution to the total steam savings potential is due to stand-alone heat integration within the pulp mill and within the ethanol plant. Further heat integration between the mill and ethanol plant allows this biorefinery concept to be self-sufficient in terms of steam.	Exporting green liquor from the pulp mill to the biorefinery disrupts the Na/S balance of the mill. Because additional sulfur is introduced in the ethanol process, direct recirculation of stillage back to the pulp mill does not solve the issue.	A possible solution to the Na/S problem is to use NaOH as a make-up chemical. However, this is likely too expensive if the main product of the biorefinery is ethanol, although other products with higher added value may be produced if the process is modified.
Conversion of a kraft pulp mill into a dissolving pulp mill	Large energy savings are possible with very simple retrofits. A more ambitious approach results in a larger potential for by-products (i.e., lignin and/or power) production.	The significantly lower pulp yield of the dissolving process requires a larger wood input per ton of produced pulp. Pieces of equipment with limited capacity may become bottlenecks for pulp production upon conversion.	It is vital to keep the pulp production at a high level to achieve profitability. If the recovery boiler is the main bottleneck, it could be debottlenecked by lignin extraction (low investment costs and high operating costs) or capacity upgrade (high investment costs and low operating costs).
Integration of a high-solids ethanol process to a kraft pulp mill	Very large steam savings can be achieved by internal heat integration at the ethanol plant. Integration with the pulp mill is technically difficult and has a very limited potential for reducing the overall steam demand.	The export of organic material (filtrates and filtrate cake) from the ethanol plant to the pulp mill results in an increased load in the recovery cycle of the pulp mill, which implies a certain risk for bottlenecks. If the thin stillage from the ethanol plant is sent to the pulp mill for combustion, the high-solids ethanol process is advantageous compared to the conventional case.	This biorefinery concept remains in a very early stage of design; further research is necessary to fully evaluate the potential advantages of the high-gravity process. However, the results strongly indicate that unless the overall process yield can be maintained at a level similar to the conventional process, the advantages of the high-gravity case may be very limited (if any).

6.5 Quick reference guide regarding the effects of implementing chemical and biochemical biorefineries in kraft pulp mills

This reference guide is intended to provide general guidelines regarding the expected effects of implementing chemical and biochemical biorefineries in kraft pulp mills. Different choices regarding heat integration and debotlenecking lead to different results. A list of statements followed with a question for each statement is provided below. The answer to the question leads to another statement. Once all of the questions are answered, a warning regarding the minimum requirement for profitability (MRP) is presented, which must be considered when evaluating the feasibility of a particular biorefinery concept. A condensed overview of the tree of choices is illustrated in Figure 19.

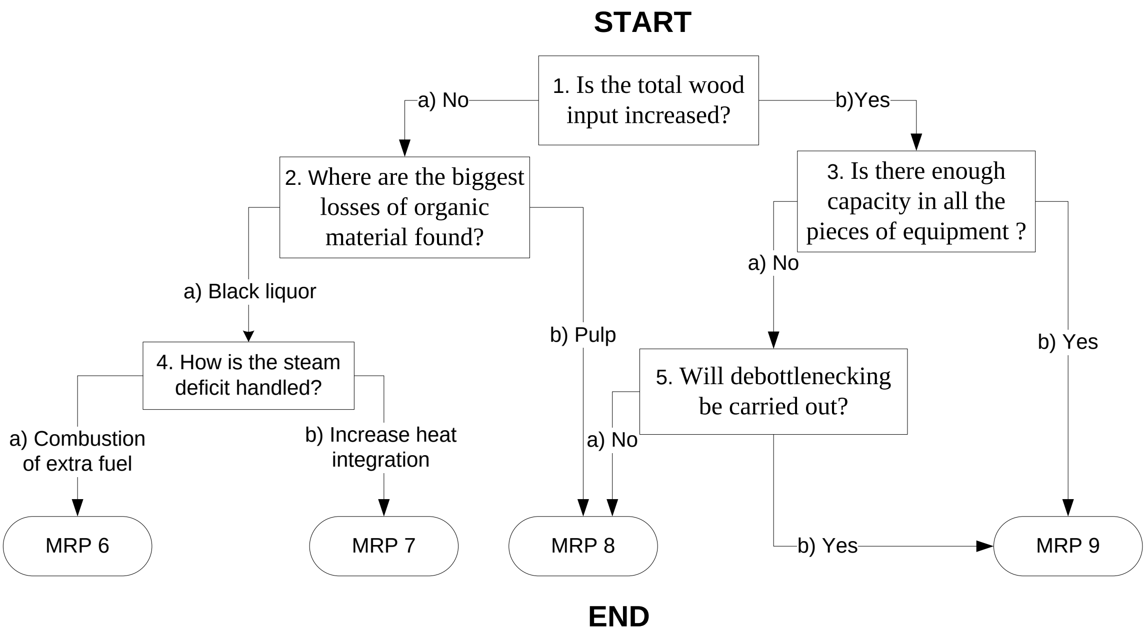

Figure 19 Quick reference guide flowchart. MRP: minimum requirement for profitability.

1. Utilization of redundant equipment at the pulp mill can be beneficial for the economic performance of a particular biorefinery. However, if there is no extra capacity in the relevant pieces of equipment, the biorefinery process will compete against pulp production for the limited capacity. This risk exists if the total wood input (pulp mill + biorefinery) exceeds the input before the implementation of the biorefinery concept. Is the total wood input increased upon implementation of the selected biorefinery concept?

   a) No (e.g., “near-neutral” hemicellulose extraction); go to statement #2.

   b) Yes (e.g., kraft-based dissolving pulp and high-solids ethanol production); go to statement #3.

2. The type and severity of the pretreatment method determines the types (i.e., cellulose, hemicellulose or lignin) and amounts of wood components that are dissolved during pretreatment and subsequent pulping. The results of laboratory trials can reveal changes in the mass balances after pulping the pre-treated wood chips compared to conventional kraft pulping. Losses in organic components can be found in the pulp (resulting in pulp yield losses), in black liquor (resulting in a decrease in its calorific value), or in both. According to the results of laboratory trials, where are the largest organic material losses found?

   a) In black liquor; go to statement #4.

   b) In pulp; go to statement #8.

3. A larger total wood input most likely means that larger amounts of organic material are handled in the recovery cycle of the mill (e.g., an increased flow of black liquor or filtrates and effluents from the biorefinery). Is there enough capacity in all of the equipment to handle the increased material throughput?

   a) No; go to statement #5.

   b) Yes; go to statement #9.

4. Removing organic material from black liquor reduces the steam production from the recovery boiler. To handle the steam deficit, two strategies are possible:

   a) Combustion of extra fuel, e.g., bark (provided that there is enough capacity in the bark boiler); go to MRP #6.

   b) Increase the heat integration at the pulp mill and/or biorefinery to reduce the steam demand; go to MRP #7.

5. Debottlenecking equipment often requires large capital investments that could significantly affect the profitability of the selected concept. Will debottlenecking investments be conducted?

   a) No; go to MRP #8.

   b) Yes; go to MRP #9.

6. MRP: The operating and investments costs will increase (due to the extra fuel and possible boiler upgrade). The minimum requirement for the selected biorefinery concept to be profitable is that the value of the main biorefinery product (e.g., ethanol) must compensate the investment costs required for erecting the biorefinery process and for the generation of steam.

7. MRP: The reduction in steam production implies a reduction in the power produced at the pulp mill (unless the turbine capacity was too small before implementing the biorefinery concept and let-down valves were used). The minimum requirement for

the selected biorefinery concept to be profitable is that the value of the main biorefinery product (e.g., ethanol) must compensate the investment costs required for erecting the biorefinery process, for heat integration retrofits and for the reduction in electricity production.

8. MRP: The implementation of the selected biorefinery concept results in decreased pulp production. The minimum requirement for this biorefinery to be profitable is that the main products (e.g., ethanol or dissolving pulp) and by-products (e.g., acetic acid or hydrolysate) must have a higher market value than kraft pulp.

9. MRP: The organic material available for steam production increases. Depending on the steam demand of the pulp mill and the biorefinery, there might be a net surplus of steam. By increasing heat integration, the steam surplus may be even larger. Consequently, there is no need to combust all of the organic material in the black liquor to produce process steam. The potential exists for extracting lignin from black liquor or for using the surplus steam to generate condensing power. The minimum requirement for the selected biorefinery concept to be profitable is that the value of the main biorefinery product (e.g., dissolving pulp) combined with the added value of the by-products (i.e., lignin and/or electricity) must compensate the investments costs required for erecting the biorefinery process and for debottlenecking equipment (if necessary).

7 Sources of uncertainty and validity of the results

This chapter presents the most important sources of uncertainties and discusses the validity of the results highlighted in this thesis. The discussion is valid for the particular systems (pulp mills and biorefineries) studied in this project. Suggestions for complementary studies and interesting future research are presented in *Chapter 9*.

7.1 Uncertainties regarding the input data and assumptions

The biorefinery concepts studied in this PhD project remain in an early stage of development which is associated with various uncertainties regarding the way the processes should be designed and operated. To perform techno-economical assessments on these innovative concepts, various assumptions were made that could affect the results presented herein.

The results regarding the process of “near-neutral” hemicellulose extraction and ethanol production are valid for the process design presented in earlier publications (e.g., Mao, 2007; Mao et al., 2008). The results suggest that implementing this biorefinery concept may result in increased chemical costs (using NaOH as a make-up chemical), which may be too excessive for the studied process. Nevertheless, this issue might not be as important if hemicellulose extraction could be performed with a lesser charge of green liquor (which reduces the need for sulfuric acid and consequentially reduces the sulfur excess) and/or if other products and by-products with a higher added value were produced.

In the case of kraft-based dissolving pulp production, it was assumed that upgrading the hydrolysate was beyond the system boundaries and that any upgrading process would operate at the break-even level, i.e., the revenues from selling the upgraded product equal the production costs. This conservative assumption was necessary due to the large uncertainties regarding the potential upgrading routes for hydrolysate. However, upgrading hemicellulose should ideally be profitable and could become an additional source of revenue for the pulp mill.

Adapting the results from experimental trials regarding high-solids ethanol fermentation to a process simulation model that was usable for conducting system studies was challenging. The experiments were conducted for diluted acid pretreated biomass, whereas the studied concept used an alkaline pretreatment stage. It is known that the type of pretreatment affects the types and amounts of inhibitors on the substrate, which in turn affect the maximum solids loading that is possible in the SSF reactor and the ethanol yield. The input data to the techno-economic assessment presented in this thesis were agreed upon after several discussions among the authors (with expertise in both acid- and alkaline-pretreated material); no laboratory trials were conducted for the studied process. The assumed solids loading level (30% WIS) can be considered to be an optimistic level that could be achieved in the future with specially designed reactors and/or tailored process conditions. On the other hand, the ethanol yield (15%) can be considered as a rather pessimistic assumption. The large uncertainties in the ethanol yield were handled by conducting a sensitivity analysis on this parameter (**Papers V** and **VI**).

7.2 Uncertainties regarding the product and by-product markets

An underlying assumption behind all of the studies highlighted in this PhD project is the time frame in which the biorefinery concepts are meant to be implemented, i.e., now (e.g., current technological development, current equipment costs, and current energy carriers' prices). In the conducted economic assessments, the prices of the produced products and by-products were found to have a major influence on the profitability of the selected biorefinery. Because some of the product markets are immature and may vary significantly over time, this assumption is quite important, which became evident during the studies of kraft-based dissolving pulp production, where the dissolving pulp price varied dramatically over only a couple of years. Nevertheless, this uncertainty was handled by evaluating the economic performance of this biorefinery concept for various dissolving pulp prices (**Paper III**).

For all of the studied biorefinery concepts, an increase in the price of produced products (e.g., dissolving pulp and ethanol) and/or by-products (e.g., power and lignin) would most likely result in a significant increase in the profitability of the studied concept, perhaps to the point where the challenges regarding make-up chemicals, debottlenecking issues and yield losses become secondary. Moreover, an increase in the price of electricity or lignin would make the process integration retrofits presented in this thesis even more attractive.

7.3 Uncertainties regarding the methods used

Integrating biorefinery concepts to kraft pulp mills implies integrating a grassroot design to an existing process, which is associated with various methodological challenges. For example, a biorefinery concept could be designed to maximize the internal heat integration and consequentially minimize internal utility consumption. Alternatively, the concept could be designed to maximize its potential for heat integration against the pulp mill to achieve a combined minimal utility consumption. Similarly, the pulp mill could be retrofitted to achieve a low utility demand, or it could be left as it is (not retrofitted) to maximize the potential for heat integration against the biorefinery.

For the biorefinery concepts studied in this PhD project, the potential for heat integration was studied both on a stand-alone basis (biorefinery and pulp mill separately) and combined. Although various retrofits were evaluated, this does not necessarily mean that an optimal design was found or that the biorefinery process could not be modified to achieve an even better integration between the processes. Although theoretically, optimization methods could be used to systematically determine an optimum overall solution, the uncertainties discussed in *Sections 7.1* and *7.2* would make it unnecessary to use these tools at this early stage of analysis.

8 Overall conclusions

8.1 Feasibility of the three studied biorefinery concepts

The results of this work show that efficient heat integration within and between the pulp mill and biorefinery can result in a significant decrease in utility demand and energy costs. However, the results also indicate that there are several challenges that must be solved for these concepts to be technically and economically feasible, even in cases where ambitious heat integration is pursued.

Of the three biorefinery concepts studied in this project, none are likely to be economically attractive in their current states. Exporting chemicals from the pulp mill to the biorefinery could destabilize the pulp mill Na/S balance, resulting in expensive make-up chemical costs that cannot be justified unless a product with a very high value-added is produced at the biorefinery (a value exceeding that of ethanol). Exporting residual streams (e.g., filtrates and stillage) from the biorefinery to the pulp mill could result in bottlenecks for pulp production that are not economically justified unless the product produced at the biorefinery has a significantly higher market value than pulp.

However, the results and conclusion presented in this thesis are valid for the particular systems and conditions studied. An increase in the price of the products and by-products produced in the biorefinery or political incentives (e.g., to promote the use of bioethanol) would make these concepts more attractive. Although a drastic change in the economic conditions would certainly affect the results of the economical evaluation, **the results from the technical and process integration studies would remain valid and could consequentially be used as input to an updated economic assessment.**

8.2 Implementation of biorefinery concepts in pulp mills

Implementing biorefinery concepts to kraft pulp mills has various potential advantages compared to stand-alone operations. The biorefinery could use redundant equipment capacity at the pulp mill, the pulp mill and biorefinery could share the same utility system, the biorefinery could have access to the pulp mill's infrastructure to handle large amounts of wood and the pulp mill could enlarge its product portfolio and enter potentially lucrative markets.

Although the possibility to fully utilize redundant equipment capacity at the pulp mill is interesting, in practice, the equipment affected by the implementation of the biorefinery process does not often have extra capacity. Chemical and biochemical biorefineries have residual streams with large organic contents that cannot be directly disposed to nature. If these streams are sent to the pulp mill for evaporation and combustion, they will compete for equipment capacity (e.g., evaporation plant and recovery boiler) that is typically already the bottleneck for pulp production. The results from this thesis suggest that the potential to use equipment capacity at the pulp mill is very limited.

Accordingly, **the implementation of biorefinery concepts will require large debottlenecking investments to maintain the same level of pulp production in many cases**. However, these investments could be smaller than the investments required for erecting the biorefinery in a stand-alone manner.

The results of this PhD project show that efficient heat integration in combination with lignin extraction enables the possibility to debottleneck the recovery boiler at a lower investment cost than upgrading capacity. However, the best way to debottleneck is dependent on the lignin and electricity prices.

Another benefit of increasing heat integration is the potential to increase the lignin extraction rate or the power generation rate. Although the revenues from by-product sales were found to only have a limited influence on the overall profitability of the three studied biorefinery concepts (compared to the cost of raw material and investments costs), for other types of biorefinery concepts (e.g., thermochemical biorefineries), the benefits of achieving ambitious heat integration and by-product production could be much larger.

8.3 General remarks

Not surprisingly, the results from these studies confirm the well-known importance of maintaining a high overall yield (from raw material to product). Although much experimental work is currently being conducted to improve the yield of these innovative biorefinery concepts, the results of this thesis are a reminder that the implementation of these concepts should not be conducted at the expense of sacrificing the pulp yield either. **It is important to lift the focus from the biorefinery reactor to the entire biorefinery and pulp mill (including the energy system and the available equipment capacity) when evaluating the profitability of biorefineries.**

The results also suggest that system studies of not fully technically developed biorefinery processes should be conducted early during the development of the concept and in parallel with experimental work. System studies can be used to identify the parameters that are most important for the overall feasibility and profitability of a particular process and to pinpoint the most important areas for further improvement and process development.

8.4 One piece of the puzzle

The results presented in this thesis can be seen as a piece of a larger puzzle. To thoroughly evaluate the potential of a biorefinery concept, the combined knowledge of researchers, policy makers and process managers is required. Techno-economic assessments can contribute to the understanding of the most important process parameters that affect the economic performance of a given process. However, this is only one part of the answer.

The implementation of biorefinery concepts may depend on other factors to an even large extent, e.g., the markets of products and by-products, the environmental policy instruments in place, the equipment capacity of a particular pulp mill, the strategic vision of the mother company, and the flexibility of their supply chain. However, the results of the techno-economic assessments can be used as input to a well-informed decision-making process that is based on as much scientific knowledge as possible.

9 Future research

9.1 Process development of biorefinery concepts

The biorefinery concepts studied in this project are all at an early stage of development. Accordingly, improvements in various critical parameters are expected to occur in the future and, in some cases, a complete makeover of the original biorefinery concept may occur.

For the “near-neutral” hemicellulose extraction process, research is needed to investigate the potential of producing other products with a market value exceeding that of ethanol. Research is also needed to develop microorganisms that can efficiently ferment hemicellulose to ethanol or other products. Experimental studies should be conducted to investigate the potential to extract hemicellulose with less green liquor to minimize the disturbances in the Na/S balance of the mill.

For the kraft-based dissolving pulp process, research is needed to investigate the possible upgrading routes for the hydrolysate. Moreover the potential to concentrate the hydrolysate using membranes (as opposed to evaporation) should be investigated for the cases in which the hydrolysate is upgraded or combusted.

For the high-solids ethanol production process, research is needed to identify the optimal combinations of feedstock, enzymes, microorganisms and detoxification methods that lead to high yields. However, this recommendation is valid for both the high-gravity case and conventional ethanol production. Research should also be conducted to investigate the potential advantages of the high-gravity process when operating in a complete stand-alone manner (as opposed to integrated with a kraft pulp mill). In this case, the advantages regarding the treatment of stillage may be more important.

9.2 Method development and complementing studies

An interesting and important dimension could be added to the results presented in this thesis by assessing the CO_2 impact of the studied biorefinery concepts. To do this, several assumptions must be made regarding the marginal use of biomass and power generation in society. Moreover, more knowledge is required about the potential upgrading routes of the by-products (e.g., lignin and hydrolysate). Additionally, methods must be developed to consistently evaluate the climate impact of material streams (e.g., dissolving pulp replacing cotton).

In addition to the climate impact of the studied biorefinery concepts, a wider environmental assessment could be performed, including land-use change and other environmental categories. Life cycle assessment could provide useful tools to handle the issues of onsite vs. offsite emissions (e.g., for the production of bioethanol at the biorefinery and subsequent combustion in a car fleet) and for allocating environmental impacts among different products (e.g., dissolving pulp, hydrolysate, lignin and power).

In the economic evaluations conducted in this PhD project, the current prices of products and energy carriers were used. In some cases, sensitivity analyses were conducted to evaluate the impact of variations in prices or economic incentives. However, it would be interesting to study the influence that environmental policy instruments could have in the economic performance of the biorefineries. For example, policy instruments designed at increasing the share of biofuels in transportation could make the biorefinery concepts with ethanol production more attractive than that shown in this thesis. Moreover, more ambitious climate policies could result in incentives to use biomass (e.g., lignin) to replace fossil fuels for power generation and make heat integration measures more attractive as a way to increase lignin extraction or power generation rates at the pulp mill.

9.3 Investigation of the ideal matches for biorefinery concepts and pulp mills

In this project, the integration of three particular biorefinery concepts to kraft pulp mills was investigated. The results and conclusions regarding the attractiveness of these concepts may differ if they were integrated to a different type of host mill. For example, integrated pulp and paper mills generally have less excess steam/heat available than market pulp mills. Therefore, the potential for heat integration within and between the pulp mill and the biorefinery may be different. Similarly, the results could differ if other types of biorefinery concepts were studied. For example, biorefineries based on biomass gasification generally have excess heat available at high temperatures that could be exported to the pulp mill or used for steam and power generation.

Accordingly, more research must be conducted to understand and quantify the advantages of choosing processes in which heat demand/excess match well compared to a less ideal match and to stand-alone operations.

Nomenclature and Abbreviations

Abbreviations

AA	Active alkali
ADt	Air dried ton (90% dryness)
BDt	Bone dried ton (100% dryness)
CO_2	Carbon dioxide
C5	Five carbon sugar e.g., xylose
C6	Six carbon sugar e.g., glucose
DS	Dried solids
EPEP	Ethanol plant evaporation plant
GCC	Grand composite curve
HP	High pressure (steam)
LP	Low pressure (steam)
MP	Medium pressure (steam)
MRP	Minimum requirement for profitability
PMEP	Pulp mill evaporation plant
SEK	Swedish crowns
SSF	Simultaneous saccharification and fermentation
TTA	Total titrable alkali
USD	United States dollar
WIS	Water insoluble solids

Symbols

h	Individual heat transfer coefficient [W/m^{2}K]
Q	Heat load [MW]
Q_{Hmin}	Theoretical minimum heating demand [MW]
w/w	Mass fraction (weight percentage)
ΔT_{min}	Minimum temperature difference [K]
€	Euro
η_{is}	Isentropic efficiency
η_{m+g}	Turbine efficiency after mechanical and generator losses

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Acknowledgements

This work was financed by the "Södra Foundation for Research, Development and Education" and the Swedish Energy Agency.

I would like to thank **Thore** for creating the economic prerequisites for me to conduct this research. I admire your helicopter perspective and your critical thinking. I also want to thank **Maryam** for helping me get started with the project and for carefully reviewing my first papers. I could not ask for better supervisors than **Erik A** and **Elin**. You rock! I am so happy I got to work with you.

I am also grateful for the opportunity to work with people from other research groups and companies. I would like to thank **Lennart Delin** and **Fredrik Lundqvist** (ÅF) for the interesting discussions about the "near-neutral" process. I also thank **Gustaf Collin**, **Linda Rudén**, and **Maria Edberg** (Södra) for supplying data and answer questions regarding the Värö pulp mill. Thank you to the many people at Innventia that helped me in one way or another. Special thanks go to **Christian Hoffstedt**, **Åsa Samuelsson**, **Ida Kulander** and **Mikael Jansson**. I would also like to thank **Charilaos Xiros** and **Lisbeth Olsson** (Industrial Biotechnology, Chalmers) for the interesting discussions about the high-gravity concept.

Thanks to my former master thesis students: **Jeff**, **Amin**, **Jon** and **Linus**; it was a pleasure to work with you. I wish you the best in your professional careers!

I would also like to thank **Kristina** for sharing an office with me for all these years. It has been therapeutic to have you around to vent and laugh. Thank you for never complaining about me eating breakfast at the office or calling my family. I thoroughly enjoyed the fun activities with the PhD students at VoM: lunch running, movie nights, after work activities, beer brewing, dancing, and so much dancing! Thank you all for that! You really surprised me with my möhippa; I will never forget it! I should particularly name **Daniella**, **Hanna** and **Erik K**, I really appreciate your friendship. Let's stay in touch!

Last but not least, I would like to thank my family of origin and my family of choice. **Daniel**, thank you for always asking me how my day at work was and for listening patiently to the same stories over and over again. I love you. **Linnea**, you turned my life upside down and I am so happy you did. Thank you for showing me what the important things in life are and for teaching me how to engage in my work in a healthy way. Te adoro nena.

"The best is yet to come…"

Appendix I: Pinch Analysis

Below is an introduction to basic pinch analysis. The material presented below is an excerpt from Wising's thesis (Wising, 2003).

Basic Pinch Analysis Concepts

Composite Curves (CC)

For construction of the Composite Curves it is necessary to know the supply and target temperatures, the heat capacity (c_p) and the flowrate (F) for each process stream. The hot composite curve is built by adding all the hot streams (heat sources) together over different temperature intervals (see Equation A:1). The hot streams supply and target temperatures define the interval temperatures.

$$Q_{interval} = T_{interval} \cdot \sum \left(Fc_p \right)_{hot} \qquad \text{(A:1)}$$

Temperature is plotted versus the enthalpy. A corresponding composite curve can be drawn for the cold streams; see Figure A1.

The region where the minimum temperature difference for heat exchange for the whole network, *global* ΔT_{min}[7] occurs is referred to as the *pinch*. The area where the hot and cold composite curves overlap reflects the amount of heat possible to recover through process-to-process heat exchange, Q_{rec}. The remaining demand for hot utility, $Q_{H,min}$, is the horizontal distance between the curves at their high-temperature endpoints. The demand for cold utility, $Q_{C,min}$, can be read from the low-temperature endpoints.

[…]

The pinch divides the flow system into two separate parts, one part over the pinch temperature and one part below the pinch. In the system above the pinch, there is a heat

[7] In the heat integration studies conducted in this project, individual ΔT_{min} values for each process stream were used to take account for differences in the heat transfer properties of each process stream (as opposed to a *global* ΔT_{min}). The minimum temperature differences can be found in *Appendix II*.

deficit, which has to be compensated from external heating. In the flow system below the pinch is a surplus of heat, which has to be cooled away with external cooling.

Three fundamental rules can be stated:

- Do not cool any flow stream above the pinch temperature using external coolers. If this is done, then the same heat quantity has to be supplied to the process from external heaters.
- Do not heat any flow stream below the pinch using external heaters. If this is done, then the same heat quantity has to be cooled by external coolers.
- Do not transfer heat from a flow stream above the pinch to another stream below the pinch, which means that streams situated above and below the pinch should not exchange heat with each other. If this is done the corresponding heat quantity has to be supplied in external heaters above the pinch and has to be cooled by external coolers below the pinch.

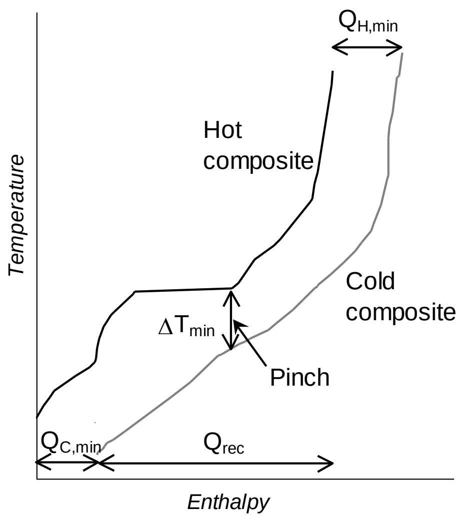

Figure A1: Example of Composite Curves.

Grand Composite Curve (GCC)

The Grand Composite Curve (GCC) is also drawn in a temperature vs. enthalpy diagram. The GCC shows the net heat versus temperature after all feasible heat-exchanging between process streams has been carried out. The curve can be constructed from the Shifted Composite Curves; see Figure A2. These curves are simply the Composite Curves that have been shifted with half-global ΔT_{min} (T - 1/2 *global* ΔT_{min} for hot streams and T + 1/2 *global* ΔT_{min} for cold streams). The curves touch at the pinch.

The GCC (see Figure A3) is the profile of the horizontal width (enthalpy) between the Shifted Composite Curves. At the pinch temperature, the curve touches the temperature axis. The profile above the pinch represents a heat sink, whereas the profile below represents a heat source. The GCC can be used as a tool for selecting the best utility or mix of utilities.

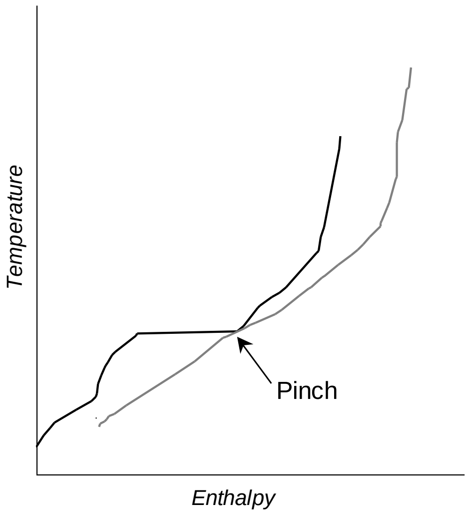

Figure A2: Example of shifted Composite Curves.

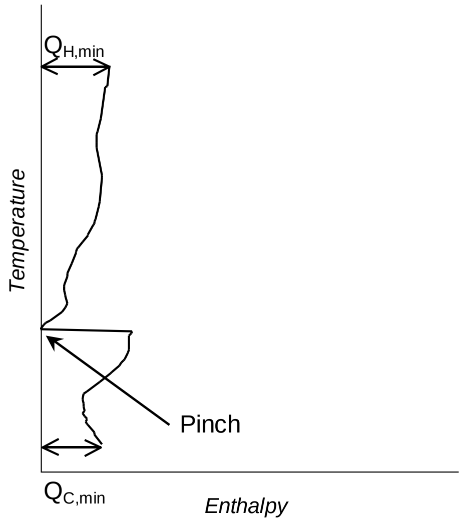

Figure A3: Example of Grand Composite Curve.

Appendix II: Minimum temperature difference and heat transfer coefficients

In this project, individual ΔT_{min} values for each process stream were used to account for differences in the heat transfer properties of each process stream. For estimating the heat exchanger area required, individual heat transfer coefficients, *h*, were specified. The minimum temperature differences and heat transfer coefficients used in the studies are presented in Table 19.

Table 19 Minimum temperature difference and heat transfer coefficients used in this thesis project

	ΔT_{min} K	h W/(m^2 K)
Clean water	2.5	3000-4000
Contaminated water	3.5	1000-3000
Black liquor	3.5	550-1000
Condensing steam	0.5	10000
Evaporating water	2	6000
Air/flue gases	8	100
Condensing organics	5	2500