

Energy Efficiency Measures in an average Scandinavian Kraft Pulp Mill with Hemicelluloses Pre-Extraction Hot Water and Dilute Acid Extraction

Master's Thesis

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Department of Energy and Environment Division of Heat and Power Technology CHALMERS UNIVERSITY OF TECHNOLOGY Göteborg, Sweden, 2011 MASTER'S THESIS

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Abstract

Rapid increase in energy demand results in conventional sources of energy e.g. fossil fuels, becoming limited. This issue has been shown to cause an impact on both the energy cost and the environment. Likewise, industry's irrational energy use can decrease revenues and increase the environmental impacts. The economic and environmental issues are crucial for energy intensive industries like pulp and paper industries in North America and Europe. Moreover, lower costs for pulp and paper production accompanied with the fast growth rate of mainly Asian and South American forests calls for modifications in the older mills. Converting a conventional Kraft pulp mill into an *Integrated Forest Biorefinery (IFBR)* has been mentioned in the literature as a potential to compensate the older mills production and energy costs. The IFBR provides co-production of a wider range of products such as ethanol, carbon fibers, polymers and diesel fuel with pulp (Fernando, et al. 2006, Van Heiningen 2006, Huang, et al. 2010, Berntsson, et al. 2008).

In this thesis, a biorefinery concept focusing on hemicelluloses pre-extraction for co-production of pulp and ethanol was studied. In the pre-extraction process, hemicelluloses are extracted from hardwood chips prior to cooking and with further purifications are converted into ethanol. During the extraction, acetic acid is formed as byproduct. Several hemicelluloses pre-extraction processes have been studied in literature; the focus of this thesis is, however, on hot water and dilute acid extraction methods. Opportunities to implement the pre-extraction process in an average Scandinavian Kraft Pulp Mill have been analyzed. The studied mill is a model mill developed in the FRAM program: Bleached Market Kraft Pulp mill – Type mill. The objective of this Thesis is to investigate opportunities for increasing energy efficiency in the mill, and, evaluate the integration potential of the pre-extraction process into the mill.

The results of pinch analysis for the mill shows a pinch temperature of 107°C and a minimum hot utility demand of 164.3 MW while the current hot utility demand of the mill is 179 MW. This results in 14.7 MW potential for steam savings. All pinch violations were identified, they mainly consisted in heating streams below the pinch with live LP steam. A total of 14 MW of pinch violations were solved through 3 retrofits, i.e. 95% of the total potential for hot utility savings.

The energy efficiency measures were then evaluated for the extraction process and ethanol production. The IFBR showed the lowest heating demand among other possibilities.

Major conclusion from this thesis is that an IFBR based on hemicellulose extraction and coproduction of pulp and ethanol has lower income than the conventional pulp mill manily due to a 20% overall pulp yield loss. Increasing the wood input to the process or improving the amount of pulp production, may raise the profitability of the IFBR.

Key words:

Kraft pulp mill, Hemicelluloses extraction, Dilute Acid Hydrolysis, Hot water extraction

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Preface

This master thesis aims at identifying energy efficiency measures in an average Scandinavian pulp mill with a hemicelluloses pre-extraction unit prior to cooking.

First and foremost, I would like to express my gratitude to Valeria Mora and Maryam Mahmoudkhani for their great supervision during this project. I always felt their support and big helps during past 6 months. Thank you both for teaching me lots of valuable knowledge. Valeria, I believe that you will pass your PhD career with lots of successes.

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1 Introduction

The thesis analyzes the energy efficiency measures in an average Scandinavian pulp mill when a hemicelluloses pre-extraction unit prior to cooking is implemented. In the following section, the motivation for implementing the Biorefinery concept based on hemicelluloses extraction in conventional Kraft pulp mills is addressed by describing the Kraft pulping process and various methods for hemicelluloses extraction.

1.1 Background

Rapid increase in energy demand results in conventional sources of energy e.g. fossil fuels becoming limited with respect to availability. This issue has an impact on both the economy of energy intensive industries and on the environment as the natural source for such non-renewable energy resources. These issues have become crucial for energy intensive industries like the pulp and paper industry in North America and Europe. Moreover, the lower cost for pulp and paper production accompanied with fast growth rate of forests mainly in Asia and South America calls for modifications in the older mills to have even more efficient process and therefore, higher revenues. Converting a conventional Kraft pulp mill into an *Integrated Forest Biorefinery (IFBR)* has been mentioned in the literature as a potential to compensate the older mills production and energy costs. The IFBR provides co-production of a wider range of products such as ethanol, carbon fibers, polymers and diesel fuel with pulp (Fernando, et al. 2006, Van Heiningen 2006, Huang, et al. 2010, Berntsson, et al. 2008).

1.2 Kraft pulping process

The wood consists mainly of three major components namely celluloses, hemicelluloses and lignin. The purpose of the pulping process is liberating the cellulose fibers from the wood matrix and dissolving most of the lignin contained in the fiber walls. In principle, this can be achieved in two ways, either mechanically or chemically. The chemical pulping process which is of interest in this thesis, can convert approximately half of the wood into pulp. Mechanical pulping has higher yield but demands lots of electric power. Kraft pulping is one of the most popular methods of chemical pulping in which liberating of celluloses fibers is carried out by the aid of cooking chemicals including sodium hydroxide (NaOH) and sodium sulfide (Na₂S) (Gullichsen and Fogelholm 2000, Brannvall 2006, Mimms, et al. 1993).

The Kraft process starts with steaming the wood chips to drive off the air inside the chips and also to heat up the chips. After steaming, pre-impregnation of chips is performed which helps distributing the cooking liquor into the chips uniformly. The pre-impregnated wood chips are then exposed to cooking chemicals in batch or continuous digesters at a constant temperature of approximately 160-170 °C. Produced pulp contains solid impurities, mainly incomplete delignified wood, some knots and other solid material. These impurities have to be removed from the pulp to reach market grade pulp. Cleaning the discharged pulp is done in further washing and bleaching stages. In addition, some of the remaining lignin content of the pulp will be separated in one or two oxygen delignification stages. The oxygen-bleached pulp is further bleached in a

sequence of bleaching stages by the aid of some chemical treatments that results in a brighter pulp. The bleached pulp is ready to be used after drying.

The cooking liquor that has been used for wood cooking is called black liquor. Black liquor consists of various organic components, small amounts of inorganic dissolved from the wood, some inorganic compounds originated from the cooking liquor (white liquor) and also water. Black liquor is used as a fuel in the recovery boiler to meet the electricity and steam demand of the mill. In addition, when burning the black liquor in the recovery boiler, the inorganic fraction will be recovered in the form of a smelt which produces green liquor when dissolved in water. The white liquor is formed from the green liquor in the white liquor preparation plant. It should be noticed that, to be able to burn the black liquor it is necessary to increase its dry content in an evaporation plant (Mimms, et al. 1993, Gullichsen and Fogelholm 2000, Theliander 2006). Figure 1 shows a conventional Kraft pulp mill.



Aker Kvaerner Mill

Figure 1 - Kraft pulping process (Industrial Energy Systems course material)

1.3 Integrated Forest Biorefinery (IFBR)

Different biorefinery concepts can be implemented in conventional pulp and paper mills with coproduction of pulp as the main product. The concepts such as separation of lignin from black liquor to produce either fuel or other added-value products or extraction of hemicelluloses prior to cooking have been addressed in the literature. Figure 2 presents various Biorefinery paths that can be implemented in pulp mills. In this thesis, the focus is on extraction of hemicelluloses prior to cooking of hardwood chips and aiming at production of ethanol. The existing extraction methods found in the literature are briefly described in the following section.



Figure 2 - A schematic diagram of an IFBR (Huang, et al., 2010)

1.4 Hemicelluloses pre-extraction

In conventional Kraft pulping processes the largest part of hemicelluloses and lignin is dissolved during cooking or delignification of wood chips and ends up in black liquor which is finally burned in the recovery boiler. To produce other added-value products, in an IFBR, the hemicelluloses can either be separated from black liquor (Wallberg et al., 2006) or prior to cooking stage from wood chips. There are various methods to extract the hemicelluloses prior to cooking including *dilute acid pretreatments* (Kumar, et al., 2009), *liquid hot water extraction* (Huang et al. 2010, Carvalheiro et al. 2008), *steam explosion-based extraction* (Huang et al., 2008), *alkaline extraction* (Huang et al., 2008) and *near-neutral extraction process* (van Heiningen et al., 2008). This thesis will address the two first methods; hot water and dilute acid extraction methods. It should be mentioned that a sister Master thesis conducted by Jean-Florian Brau addressed the two latter methods; near-neutral and alkaline extraction methods. A brief summary of the extraction methods is given in the followings.

In *steam explosion-based extraction* wood is pretreated by pressurized steam and then a rapid relief of pressure causes a breakdown in the lignocellulosic structure. The result is an easy depolymerization of lignin and that also hemicelluloses can be hydrolyzed easily (Huang et al., 2008). *Alkaline extraction* method uses NaOH prior to Kraft pulping to extract the hemicelluloses of the wood and produce high quality pulp at the same time. A well done optimization along this process can result in the same yield and pulp quality as compared with a case without pre-extraction of hemicelluloses (Al-Dajani et al., 2008). The *near-neutral extraction process* starts with pre-steaming of wood chips in a steaming vessel and chips heating up to extraction temperature which is about 160° C in the presence of green liquor. This solution contains mainly Na₂CO₃ and Na₂S and it is recovered from the smelt of the recovery boiler. An important drawback of this method is less sugar content of the extracted liquor as compared with the alkaline extraction method (Van Heiningen, et al., 2008). An advantage of this method is that the pulp production after hemicelluloses extraction is not affected considerably regarding its quality and yield (Van Heiningen, et al., 2008).

Hot-water extraction

In this method, hemicelluloses can be highly recovered without any need to supply extra catalyst. The only catalyst is hydronium ion (H_3O^+) which leads to depolymerization of hemicelluloses in the first step and improving the reaction kinetics in the second step (Carvalheiro et al., 2008). This method uses compressed liquid hot water at a temperature between 140°C and 200°C to hydrolyze the hemicelluloses (Huang et al., 2008,Carvalheiro et al., 2008). In comparison with acid hydrolysis method, hot water hydrolysis has less corrosion problems due to milder pH conditions. Also due to the absence of acid during hydrolysis, there is a smaller need for an acid recycling system and the use of a cheaper reactor is possible, making the water hydrolysis method, therefore, to be more economic than the acid hydrolysis method. It should be mentioned that in hot water extraction, hydrolysis of acetyl and uronic groups result in acids formation which can catalyze the hydrolysis of links between hemicelluloses and lignin (Carvalheiro, et al., 2008). These acidic conditions may cause degradation of cellulose which results in lower pulp yield and quality in comparison with alkaline and near neutral methods (Heiningen 2006) (W.J.Frederick Jr, et al., 2008).

Dilute acid extraction

In *dilute acid extraction method* dilute solution of inorganic acids such as H_2SO_4 and HCl is used to hydrolyze the wood chips. This will, in turn, enhance the liberation of fermentable sugars. Due to the toxicity and corrosive characteristics of this method, the reactors need to be resistant to corrosion and therefore this method has the drawback of higher investment cost as compared to hot water extraction method. This process however is considered as an interesting process for industrial application because of its reasonably high yields of sugars separation. The results of experiments performed by Toven and Øyaas, show that the acid hydrolysis of hardwood will extract almost 60% of hemicelluloses of hardwood which mainly consists of pentose (Toven and Øyaas 2009 (Testova, 2006). Figure 3 presents the results of mentioned experiments.



Figure 3 - Comparison of dissolved carbohydrates in different hemicelluloses extraction methods from hardwood chips (Toven and Øyaas 2009)

It should be mentioned that some other acids like HNO_3 and H_3PO_4 can also be used in this process but using H_2SO_4 is usual. An alternative of acid addition is CO_2 addition which forms carbonic acid. This acid is particularly suitable for hydrolysis under mild pH conditions at high temperatures and pressures (Carvalheiro et al., 2008).

2 Aims and Scope

This master thesis aims at investigating opportunities for increasing energy efficiency in an average Scandinavian pulp mill. An additional goal is evaluating the integration potential of the pre-extraction process into the mill. Introducing an additional process, hemicelluloses extraction and ethanol production process, alters the energy and material balances of the Kraft pulping process Accordingly, an energy efficiency analysis for the process is crucial.

To reach this objective, several questions need to be addressed, for example:

- What is the current energy situation of the mill?
- How can the process integration of the mill be increased so that it does not need any extra cooling or heating supply? What are the possibilities to solve the pinch violations?
- How do the hemicelluloses pre-extraction methods work?
- What is the current situation of hemicelluloses pre-extraction methods from heat deficit and surplus point of view?
- How will the energy balances of both processes be affected upon integration (partly or completely)?
- Identify the potentials for integrating the hemicelluloses extraction processes into Kraft pulping process (partly or completely)?

3 Methodology

The studied mill is the FRAM bleached market Kraft pulp mill (type mill-Hardwood) which is a hypothetical mill that represents the typical Scandinavian pulp mill and its operation conditions. FRAM stands for Future Resource Adapted Mill that is a research program managed by Innventia AB¹. The mill's streams data was extracted from a simulation of the mill in WinGems. During data extraction, when some information was missing in the files, more details were asked to Christian Hoffstedt at Innventia AB. The most important parameters of each stream were its start and target temperature and also its energy content that is transferred from/to other streams. Streams data gathering ended up with a table representing the stream set of the studied mill. Performing the pinch analysis using ProPi and investigating different possibilities to solve the pinch violations of the mill took place after the stream set of the mill was prepared. More details on pinch analysis and ProPi are given in sections 4.1 and 4.4.

To study the hot water and dilute acid processes, flowsheets were constructed based on experimental data from the literature.

The integration potential of the hemicelluloses extraction process with Kraft pulping process was studied with the help of pinch analysis that was followed by a cash flow assessment. Finally, comparison between hot water and dilute acid extraction methods was carried out.

¹ Innventia is a world leader in research and development relating to pulp, paper, graphic media, packaging and biorefining (Innventia AB n.d.).

4 Pinch analysis

Pinch analysis has been used extensively in this thesis work. This method is explained more in details in the following section.

4.1 Basic description and definitions

Pinch analysis is a useful methodology to analyze the energy savings potential of a complex system with lots of streams and equipments. The aim of minimizing the need for hot and cold utility demand can be achieved through maximizing the internal heat recovery of the process. The configuration that meets this theoretical maximum internal heat recovery is called a maximum energy recovery (MER) network (Frank et al., 2008).

Pinch analysis uses some information of the streams such as temperatures and heating or cooling demand, to calculate the maximum possible internal heat recovery. To do this, it is necessary to define the hot and cold streams. The hot streams are those with a particular heat capacity that call for cooling in order to change its temperature from a start point to a target point. On the other hand, a cold stream is a stream that needs heating for changing its temperature from a start temperature to a target temperature. In pinch analysis, all the hot and cold streams are identified to see if there is any excess of heat in a given temperature interval. This excess heat can be used to meet a heat deficit at a lower temperature interval, this is called heat cascading. Normally, there is a temperature in pinch analysis above it there is deficit of heat while there is excess heat below it. This temperature is called pinch temperature. Accordingly, the part above and the part below the pinch can be seen as two thermodynamically separate systems (Frank et al., 2008) (Mora and Festin 2009). Based on these two parts, there are three golden rules namely:

- Do not cool with external coolers above the pinch. Above the pinch there is deficit of heat and adding an external cooler causes an increase in the heating demand of the process.
- Do not heat with external heaters below the pinch. Below the pinch there is excess of heat and adding an external heater causes an increase in the cooling demand of the process.
- Do not transfer heat through the pinch. Transferring heat through pinch means removing heat from a stream with heat deficit to add it to a stream with heat surplus. This will cause an increase in both cooling and heating demand of the process.

The procedure to perform a Pinch Analysis can be summarized as below:

- Preparing a list of relevant streams
- Collecting the necessary information (temperatures, heating or cooling demands, etc.)
- Definition of a minimum allowable temperature difference², ΔT_{min} , between hot and cold streams for heat exchanging internally

² The minimum temperature approach, ΔT_{min} , is the lowest temperature difference between the hot stream and the cold stream that can be accepted in a heat exchanger.

- Construction of Composite Curves and Grand Composite Curve
- Determining the minimum hot and cold utility demand and investigating maximum internal heat recovery possibilities

Composite and Grand Composite Curves play an important role in pinch analysis and process integration. They are therefore explained in the next section.

4.2 Composite and Grand Composite Curves

The Composite Curves (CC) and Grand Composite Curve (GCC) provide valuable information such as the maximum internal heat recovery, minimum hot utility demand and minimum cold utility demand. Composite curves and grand composite curve are temperature/enthalpy diagrams of the stream network. Composite curves (CC) consist of a hot composite curve and cold composite curve which are constructed based on calculations of the total heat content or demand of all the hot streams or all the cold streams respectively. Those heat contents/demands are calculated at the different temperature intervals. Both hot composite curve and cold composite curves are placed in the same diagram. The cold composite curve is moved horizontally towards the hot composite curve so that the vertical distance between the two curves is not smaller than the chosen minimum temperature difference, ΔT_{min} , at any point of the curves (Frank et al., 2008) (Mora and Festin 2009). Figure 4 is an example of hot and cold composite curves.



Figure 4 - Composite Curve sample

It is worth to mention that the area in the curve that is the overlap between hot composite curve and cold composite curve shows the possibilities of internal heat exchange. The parts of hot composite curve and cold composite curve that not overlap, represents the minimum cold utility demand and hot utility demand. The grand composite curve (GCC) is build by adding all the hot and cold streams by their corresponding heat excesses and deficits in one diagram. The dissimilarity between CC and GCC is that in the former, individual hot and cold composite curves are shown while in latter, there is only an overall curve (Frank et al., 2008) (Mora and Festin 2009). Figure 5 is demonstrating such curve.



Figure 5 - Grand Composite Curve sample

4.3 Retrofitting

Many existing heat exchanger networks were built before pinch analysis was introduced. So, from a pinch analysis point of view, most of them are not fully optimized. Accordingly, when analyzing a process, one can see that there is always more hot and cold utility demand than the minimum determined by pinch analysis. This is due to violations to the golden rules of pinch analysis. To achieve a heat exchanger network which fulfils the energy targets, one choice is to build a completely new, which is undesirable from an economic point of view. Another alternative is performing a retrofit design that uses the existing heat exchanger more effectively and requires fewer new heat exchangers. The new heat exchanger network aims at eliminating most of the pinch violations whilst the investment cost, which increases with every new heat exchanger, is also taken into account. Consequently, a good retrofit should be one that eliminates most of the pinch violations with less additional investment cost (Frank et al., 2008) (Mora and Festin 2009).

4.4 ProPi

ProPi is an excel-based add-in developed at Chalmers University of Technology for pinch analysis. This tool is widely used in this thesis work due to its fast and simple operation to construct composite curves and grand composite curves. Therefore, the heating and cooling demands, as well as the pinch temperature can be identified with the aid of this tool.

5 FRAM - The studied mill

The studied model mill represents an average Scandinavian bleached market Kraft pulp mill with typical operation data and configuration. All the information about this mill is prepared by a R&D program called "Future Resource Adapted pulp Mill-FRAM" (Delin, et al., 2005). In the following sections the studied mill is presented more in details.

5.1 Overview

The model covers the entire pulp mill from wood as feedstock to bleached and dried pulp. The feedstock wood is hardwood which is almost birch with less than 10% other hardwood species. Key data for the mill are given in two tables below:

Table 1 - Key operational data of the mill

Wood to digester t/day	2328
Annual production ADt/day	1250
5.5 effect evaporator 72% dry solid content	
201.8 MW steam production by recovery boiler	
3.8 MW steam production by bark boiler	
No condensing turbine	
Separate stripper (not integrated in evaporation plant)	
Lime kiln fuel is oil	
Backpressure turbine is too small (Part of HP steam reductio	n by
PRVs (pressure reducing valves)	

Table 2 - Summary of steam demand

SUMMARY STEAM CONSUMPTION (MW)	
High Pressure (HP)-steam at 450 °C	19.1
Medium Pressure (MP)-steam at 200 °C	38.7
Low Pressure (LP)-steam at 150 °C	129.2
TOTAL STEAM CONSUMPTION (MW)	

The mill produces the entire amount of steam demand. Additionally, 24 MW is utilized in back pressure steam turbine. The main user of MP-steam is the digester that uses almost 56% of total MP-steam. Also the evaporation plant and pulp machine use most of the LP-steam in the mill.

5.2 **Process description**

Wood logs from woodyard are converted into bleached pulp through a multi-stage process which is described in following parts.

5.2.1 Wood handling

Debarked wood chips should be supplied to the cooking stage. The purpose of debarking is to improve the final product quality. Debarking will differ according to different types of pulp required (Gullicbsen et al., 2000). Among 297.5 t/day bark production in FRAM mill, 41.3 t/day is sent to bark boiler and the rest are sold in the market. In order to improve the cooking efficiency, the wood will be chipped before going to digester (Delin et al., 2005).

5.2.2 Cooking and blowing

In the FRAM mill, the wood chips are steamed with LP-steam before being pre-heated to 120 °C by flash steam. Then the wood chips will be mixed up with white liquor that enters the chip chute at 85 °C before the final mixture enters the pre-impregnation vessel. The objective of steaming of the wood chips is driving off the air in wood pores and also heating it up while the pre-impregnation step aims at distributing the cooking liquor within the wood chips uniformly (Delin et al., 2005).

From top to bottom, there are two zones in the digester: a cooking zone and a washing zone. The impregnated wood chips at 120 °C and fresh white liquor at 85 °C enter the top of the digester. The cooking takes place in the top zone of the digester that calls for a constant temperature around 160 °C. In order to keep this target temperature of the cooking zone, there is a circulation loop in which the cooking liquor enters at 158 °C and is heated up to 163 °C by the aid of an external heat exchanger which utilizes MP steam. Similar heat exchanging occurs in the bottom zone of the digester. The washing liquor enters the digester from the bottom side at 106 °C. In order to keep the temperature of the washing zone at its target value, washing liquor passes through a circulation loop in which it is heated up from 123 °C up to 157 °C; again by the aid of an external heat exchanger that utilizes MP steam (Delin et al., 2005).

The wood chips leave the digester from the bottom side at 113 °C while the spent cooking liquor, Black liquor, exits the digester at 162 °C. The black liquor will continue towards the flash vessels and the chemical recovery cycle that will be described later. The wood chips should pass through a blowing step to be converted into pulp which is done in a blow tank. Before being blown, the wood chips are washed with washing liquor at around 82 °C. This washing liquor has been cooled down from 85 °C by the aid of an external heat exchanger which utilizes cooling water. The pulp produced after the blow tank is screened and deknotted (Delin et al., 2005).

5.2.3 Bleaching

The produced pulp has to be deknotted in order to separate the large particles from the pulp. These particles are uncooked chips, large knots or stones that will harm the downstream equipments. The screened pulp then goes to two oxygen delignification stages to be further delignified. These stages use oxygen and alkali to remove a considerable fraction of the lignin remaining after cooking (Gullicbsen et al., 2000; Mimms et al., 1993). Afterwards, the delignified pulp flows to bleaching sequences.

The bleach plant is designed with four bleaching stages in this mill in the sequence of (D1) (EPO) (D2) and (D3). The bleaching in all three D stages takes place at similar temperatures of about 70 °C while in the EPO stage; it is performed at 90 °C. In the first and second D stages,

the washing liquor is being cooled down by water in external heat exchangers. The bleached pulp is then ready to enter the pulp dryer (Delin et al., 2005).

5.2.4 Pulp drying

The pulp dryer is of floating web dryer type, which dries the pulp by keeping it floating on a cushion of hot air. The air that is used in this dryer is heated up by LP steam. The pulp is dried from 50% up to 90% dryness. The pulp dryer is one of the biggest LP steam users in pulping process (Delin et al., 2005).

5.2.5 Chemical recovery cycle

The black liquor, flows towards two flash vessels to be flashed, which results in two flash steams that are used for steaming the wood chips and producing hot and warm water in Hot and Warm Water System (HWWS). The black liquor passes then through a 5.5 effect economy evaporation plant to be concentrated up to 72% dry solid content. This is done in order to increase the heating value of the black liquor that is going to be burnt in the recovery boiler. Evaporation plant is another big user of the LP steam in the process. The condensates of LP steam used in evaporation are distributed to different consumers within the mill based on its contamination degree. The concentrated black liquor which is called strong black liquor is burnt in the recovery boiler. Consequently, HP steam at 450 °C and 60 bars is produced. In the recovery boiler, the combustion air is distributed in different levels to assist complete combustion and minimize NOx formation. Currently, the flue gases are discharged at 175 °C which can be seen as a non-utilized high temperature heat source (Delin et al., 2005).

Beside steam production, a molten smelt is produced that leaves the bottom of the recovery boiler at 800 °C. The smelt is then mixed with wash water from the causticising plant to form green liquor. Due to this mixing, steam is produced which is condensed by water in an external heat exchanger. The generated green liquor contains particles such as unburned carbon. These particles are called dregs which should be removed from the green liquor in order to have pure white liquor. This removal takes place in green liquor clarifier. The clarified green liquor is then mixed with some burnt lime from lime kiln and also some fresh lime in a slaking stage which is followed by a series of causticising vessels. The obtained white liquor is ready to be sent back to the pre-impregnation vessel and digester after being filtered. The lime mud resulted from white liquor filtration can be sent to the lime kiln after being washed and dewatered to recover the lime. The lime kiln in the FRAM mill consumes oil as fuel. The flue gases of the lime kiln exit at 170°C that are discharged to stack as well as the recovery boiler flue gases (Delin et al., 2005).

5.2.6 Steam system

The HP steam produced by recovery boiler is used in a backpressure turbine in order to generate electricity. The backpressure turbine is not big enough and part of the HP steam is reduced directly to lower pressures by PRVs (Delin et al., 2005). A summary of steam consumption of different units in the mill is available in table 3.

Table 3 - Summary of steam consumptions

	Heat effect MW
HP-steam	
Soot blowing recovery boiler	19.1
Total HP-steam	19.1
MP-steam	
Digesting	22.5
Bleaching	11.0
Oxygen stage	2.8
Chemical preparation	0.4
Miscellaneous, losses	2.1
Total MP-steam	38.7
LP-steam	
Woodyard	1.9
Digesting	7.5
Pulp machine	39.6
Pulp machine, white water system	<mark>2.4</mark>
Evaporation	55.9
Stripper	7.7
Hot water production	<mark>4.8</mark>
Chemical preparation	1.0
Causticising	<mark>0.8</mark>
Heating etc	1.0
Miscellaneous, losses	6.5
Total LP-steam	129.2
TOTAL STEAM CONSUMPTION (MW)) 187.0

The hot and warm water system (HWWS) of the mill was constructed when the mill started operating. The mill has, however, been facing changes in operation since then; the hot and warm water system requires therefore, modifications to overcome the imbalances. The imbalances are caused mostly by poor monitoring, insufficient buffer tanks, and improper heat exchanging network design. Accordingly, LP steam is partially used in the HWWS to meet the mill's hot water demand. This additional 8 MW LP steam consumption is showed by yellow color in table 3 The HWWS imbalances are not considered a relevant stream for the pinch analysis and neither for the pinch violations. However, different retrofit options have been studied and a retrofit is proposed in the Results chapter that could eliminate this steam demand.

6 Hemicelluloses extraction methods

In this section the extraction methods and the process flowsheets are given. The advantages and disadvantages for each method are discussed from an energy perspective as well as pulp quality and quantity perspective. The studied methods are also compared with near-neutral method for which a un-change pulp production yield has been reported in the literature.

No detailed flowsheets for the two extraction methods can be found in the literature, therefore in this thesis, the schematic flowsheet for these processes was constructed by the author. The flowsheets were developed mostly based on reported experimental data and process design in the literature. Concerning the process sequences, these three methods are more or less similar after producing monosaccharides from hemicelluloses. Thus, this part of the process is presented in detail in hot water extraction method only.

6.1 Hot water extraction method

Figure 6 illustrates a schematic flowsheet for the hot water extraction process which is mainly based on the process described by Mendes and co-authors (Mendes et al., 2009). Some differences from the original version have been proposed to allow simpler comparisons between other extraction methods. The major changes are done mainly in the ethanol production process based on the process flowsheet available in Mao's Master Thesis (Mao, 2007).



Figure 6 - Schematic flowsheet of hot water extraction process

In the extraction vessel wood chips are exposed to hot water with a total liquid to wood ratio of 4:1 that is reached by recycling part of the extraction liquor. The extraction is carried out at

temperature of 150 °C with a duration time of 180 minutes. It should be mentioned that there are different values for the duration time and also the extraction temperature available in literature. Here the most common values are considered. The extracted chips are washed and sent to the preimpregnation vessel and digester. The extraction liquor which contains water and dissolved solids is recycled partly to the extraction vessel in order to increase the solid content and also increase the rate of reaction due to the presence of acetic acid. Acetic acid is generated during the extraction and can catalyze the hemicelluloses hydrolysis when being recycled to extraction vessel (Yonghao et al., 2010). The rest of the extraction liquor is flashed in a flash vessel to increase the sacharides concentration and to recover heat. The extraction liquor is then hydrolyzed in a secondary hydrolysis stage, in which sulfuric acid is used to convert oligomeric saccharides to monosaccharides. Performing the second hydrolysis is carried out at a total sulfuric acid concentration of 0.4% w/w at 120 °C for 180 minutes.

Beside the hemicelluloses, some lignin will be separated during extraction. The separated lignin is assumed to be precipitated after acid hydrolysis which can be removed by filtration. Separated lignin is sent back to the recovery boiler. As the heating value of lignin is reported to be double as much as for hemicelluloses, recycling the separated lignin back to recovery cycle is beneficial from energy perspectives. Removing hemicelluloses from the wood chips results in higher lignin to hemicelluloses ratio in black liquor which may lead to a higher heating value of black liquor (Kautto et al. 2010). This should be considered in further energy analysis.

The extraction liquor which is called hydrolyzate after the secondary hydrolysis stage contains water soluble sugar degradation products, such as furfural, hydroxymethyl furfural and acetic acid. These products will have an inhibitory impact on the yeast growth and fermentation process (Mendes et al., 2008). Consequently, adequate chemical, physical, biological or combined processes are needed to decrease the concentration of these inhibitors. In the proposed hot water extraction method, the inhibitors concentration is decreased by a liquid-liquid extraction and distillation. Acetic acid and furfural are then separated as the by-products. The temperature at which the distillation takes place is not available in the literature so accordingly to the boiling temperature of acetic acid which is 168°C and water, it can be assumed that distillation is taking place at a temperature above 100°C and below 168°C. In the distillation column, water is the top product and acetic acid is the bottom product. The operation temperature of distillation column is assumed to be 120°C, hereafter, in all calculations. The hydrolyzate should be neutralized before fermentation. The neutralization is performed at about 50°C by adding lime, (i.e. over liming), during which sulfur is removed as gypsum. (Aden et al., 2002). After removing the inhibitors, the hydrolyzate is fermented by a suitable microorganism. In this thesis, Pichia stipitis is considered as the appropriate microorganism. This microorganism is selected due to its ability to ferment a variety of sugars and mostly for fermenting pentoses such as xylose into ethanol with a high yield (Mendes et al., 2009). The microorganism is more effective at a temperature about 30°C. After fermentation, the ethanol and water mixture goes through final distillation until reaching ethanol's azeotrope concentration. The operation temperature of this distillation column is in the range of 78°C (boiling point of ethanol) and 100°C (boiling point of water). A temperature of 90°C is assumed.

6.2 Dilute acid extraction method

Dilute acid extraction followed by ethanol production operates similar to hot water extraction. Only the extraction part of the process up to monosaccharides production is explained in this section, as the ethanol production is assumed to be similar to the hot water method.

Figure 7 shows a schematic flowsheet of dilute acid extraction and ethanol production with same wood charge as hot water.



Figure 7 - Schematic flowsheet of the dilute acid extraction process

Dilute sulfuric acid with a concentration of 0.4% w/w is charged and extraction is performed at 150 °C for 120 minutes. The preliminary studies of Mendes and co-author show that the saccharides obtained from dilute acid extraction does not need any further hydrolysis for conversion of oligomers to monomers (Mendes et al., 2009). After solid and liquid separation, the extraction liquor is directly flashed in the flash vessel to increase concentration of saccharides and to recover heat. Similarly to hot water extraction, lignin is precipitated and recycled to Kraft recovery cycle. The resulting hydrolyzate is purified via liquid-liquid extraction, distillation and over liming, before being fermented.

6.3 Near neutral extraction method

A brief description of near-neutral extraction process is given in this section and the flowsheet is illustrated in Figure 8. The heat integration potentials for integrated near neutral pre-extraction method with the FRAM mill has been studied by Jean-Florian Brau in a sister master thesis. For further details the reader is referred to (Mao, 2007 and Brau, 2010)



Figure 8 - Schematic flowsheet of near neutral extraction process (Brau, 2010)

In this process, the oligomers are not converted to monomers completely after the extraction with green liquor. Thus, similar to hot water method, the extracts from the extraction vessel is submitted to a secondary hydrolysis step by sulfuric acid at 126 °C. The resulted hydrolyzate contains precipitated lignin that is removed by filtration.

The rest of the process from lignin recycling to Kraft pulping process, to ethanol production, operate in a similar way as hot water extraction and dilute acid extraction processes.

7 **Results and discussions**

As it was mentioned earlier in the methodology section, pinch analysis has been done for the FRAM bleached market pulp mill to find the theoretical minimum hot utility demand and also possible retrofits to the process. The results of the pinch analysis and possible retrofits are presented in this section. The results for possible retrofits for hemicelluloses extraction process are also presented. Finally, the integration potential for hemicelluloses extraction process with FRAM bleached market pulp mill are discussed from energy and economic perspectives.

7.1 FRAM mill

7.1.1 Pinch analysis results

For the pinch analysis, defining the minimum temperature difference is crucial. For example, with smaller minimum temperature difference, more heat can be transferred but on the other hand, larger heat exchanger area is needed. In this thesis, individual minimum temperatures have been used. Individual temperature differences allow considering the heat transfer characteristics of the different fluids studied (Axelsson 2008). In Table 4 the chosen values for individual minimum temperature differences of the various streams are presented.

Stream type	$\Delta T_{min}/2$ (K)
Clean water	2.5
Contaminated water	3.5
Live steam	0.5
Contaminated steam	2
Steam with non-condensable gases	4
Air	8

Table 4 - Minimum temperature difference for FRAM mill streams

The stream set which is used in this pinch analysis is presented in Table 5. It should be mentioned that detailed calculations for heating water to different temperature levels in hot and warm water system and also about the effluents are available in appendix 1 and 2.

St.number	Description	T start	T target	Q (MW)
1	Soot blowing recovery boiler (HP steam)	449.0	450.0	19.1
2	MP to bleaching	200.0	201.0	11.0
3	MP to oxygen stage	200.0	201.0	2.8
4	MP to chemical preparation	200.0	201.0	0.4
5	MP to rest	200.0	201.0	2.1
6	LP to woodyard	18.0	30.0	1.9
7	LP to digesting	119.0	120.0	22.2
8	LP to evaporation	149.0	150.0	55.9
9	LP to stripper	149.0	150.0	7.7
10	LP to heating etc.	149.0	150.0	1.0
11	LP to rest	149.0	150.0	7.5
12	Pulp machine (LP)	95.0	120.0	39.6
13	White liquor digester loop (MP)	158.0	163.0	12.1
14	Wash liquor digester loop (MP)	123.0	157.0	10.5
15	Make-up boiler water	18.0	75.0	6.0
16	WW to 50 C	18.0	50.0	40.7
17	WW to 75 C	50.0	75.0	28.9
18	WW to 85 C	75.0	85.0	7.2
19	Wash liquor blow tank	85.6	82.0	2.0
20	Loop DQ1	72.0	67.0	3.4
21	Loop DQ2	64.0	60.5	2.5
22	BL to evap	105.0	89.0	6.9
23	Vapour from smelt dissolver	76.0	75.0	3.4
24	Surface condenser (hot stream evaporation)	61.0	60.0	57.3
25	General cooling	40.0	35.0	13.1
26	Chemical preparation	48.0	47.0	1.8
27	Stripper condenser	100.0	99.9	6.2
28	Stripper secondary Condenser	90.0	89.9	0.7
29	Effluents DQ1 & DQ2	63.4	41.7	12.8
30	Effluent after DQ1	96.6	71.0	6.7
31	second flash condensate	104.0	70.0	0.8
32	Flue gas RB	175.0	115.0	5.8
33	Flue gas Lime kiln	170.0	115.0	0.6
34	first flash steam	127.0	120.0	14.7
35	second flash steam	109.0	104.0	13.3
36	continue of Effluent after DQ1	71.0	35.0	9.4
The Grand Composite Curve of the process is shown in figure 9. This Grand Composite Curve (GCC) gives a pinch temperature of 107 °C with minimum hot utility demand of 164.3 MW.



Figure 9 - Grand composite curve of FRAM mill

As can be seen in section 5.1, the total steam demand of the FRAM mill is 187 MW. By excluding the steam consumption of the HWWS due to imbalances (see section 5.2.6), a steam demand of 179 MW is obtained. This steam demand does not match the theoretical minimum hot utility demand obtained by pinch analysis. As it is described in section 4.3, the 14.7 MW difference in heating demand is due to pinch violations. Table 6 shows the identified pinch violations and it can be seen that most of the pinch violations are due to transferring heat through the pinch point. More detailed calculations for pinch violations can be found in appendix 3.

Table 6 - Pinch violations of FRAM mill

Pinch Violation	ation Type	
LP steam to Woodyard	Heat transferring through the pinch	1.9
LP steam to pulp dryer	Heat transferring through the pinch	6.3
Flue gas recovery boiler	Cooling above pinch	5.8
Flue gas lime kiln	Cooling above pinch	0.6
	TOTAL	14.7

The flue gases from lime kiln are discharged to stack without any heat recovery in the current design. It is, however, listed as one of the pinch violations in Table 6. As the corresponding potential heat source from this stream is comparatively small, 0.63MW, it was not considered in the retrofits. In addition to pinch violations, there are also some preheating opportunities resulting in steam savings. These are some heat sinks that are currently heated with steam (that are not a pinch violation in the current situation of the mill) but that can be heated by other heat sources. For example heat provided by MP and LP steam to pre-heat water and air to recovery boiler can be provided from other heat sources. These steam saving potentials are explained in following sections.

It is worth to mention the LP steam consumption, which arises according to imbalances in the mill, is analyzed separately in this thesis. This comes from the fact that this steam consumption cannot be replaced by other heat sources in current operating conditions of the mill. Accordingly, it is not considered as pinch violation while reconfiguration of the HWWS results in a significant steam saving in the mill. So, before going through the pinch violations, redesigning the HWWS of the mill is described in next section.

7.1.2 New hot and warm water system

As it was mentioned earlier, because of some imbalances in the mill, LP steam is partially used in HWWS to meet the mill demand. This increase in LP consumption is called LP steam due to imbalances in this master thesis, which correspond to LP steam consumption by hot water production, pulp dryer – white water system and causticising. The current HWWS diagram is available in appendix 4.

A new design for the hot and warm water system is proposed in order to eliminate this LP steam consumption. The new configuration has been designed using CC (Composite Curve) for the hot and warm water system. In designing this new arrangement, the minimum temperature difference of 5°C was used. This minimum ΔT grants heat exchange between heat sinks and heat sources in a more efficient way and provide the necessary amount of hot and warm water to the mill. This new configuration is available in appendix 5.

With the new HWWS design, the hot and warm water demand of the mill are met and the excess heat has been liberated which can be utilized in other retrofits. It is worth to mention that with the new HWWS design, the turpentine condenser is not used any more for providing the warm water. Instead of turpentine condensate, the effluent after stage DQ1 is used to provide warm water. The starting temperature of this stream is 96.6°C, which can provide 16MW of heat when cooling down to 35°C. In this retrofit, however, the effluent is cooled down to 71°C and therefore about 6.7 MW of its available heat is used in the HWWS.

7.1.3 Wood yard as a heat user

In wood yard, wood needs to be deiced during winter. The amount of required heat for deicing, presented in FRAM report, is an average value of heating demand during a year. The heat is provided by LP steam. Using LP steam at such low temperature is a pinch violation that can be solved by replacing the steam by other means of heat available. In this proposed retrofit, effluent

after loop DQ1 and DQ2 in bleaching plant can be used for wood deicing. This effluent is originally sent to an overall effluent system and the temperature at the discharging point is 63.4 °C. By using this effluent in wood yard, the heat demand of the wood yard is met and the effluent will be discharged to the effluent system at the temperature of 60 °C.

7.1.4 Pulp dryer modification

In the pulp dryer, air at 120°C is used to dry the pulp. In order to heat the air from 95°C to the target temperature of 120°C, 39.6 MW of LP steam are used at the current design. About 15% of the heat demand (6.34MW) is a pinch violation by means of heat transfer through the pinch. To eliminate this pinch violation, it is necessary to replace the LP steam by other heat source at high temperature. The only heat available is excess steam from the second flash vessel which was previously used to heat water in the turpentine condenser. This steam is at 109°C with 13.33 MW heat available that is not used for providing warm water in new HWWS anymore. So all the heat available can be utilized in other cold streams e.g. pulp dryer machine.

7.1.5 Recovery boiler flue gas heat recovery

Another heat source at high temperature, 175° C, which is discharged directly to stack in the current design of the mill, is flue gas from recovery boiler. This flue gas can be cooled, for example down to 115° C (according to pinch temperature and the minimum temperature difference). An important concern about the flue gas is the risk of sulfuric acid condensation at temperatures below the dew point of sulfuric acid, i.e. 135 °C. It was reported by Sharp that, since no acid corrosion occurs above the water dew point in the recovery boiler, the target temperature of 115° C should not cause any risk for acid precipitation (Sharp, 1992). Consequently, 5.83 MW of heat can be available in the mill from cooling the flue gases from 175° C down to 115° C.

At the current mill design, the air to recovery boiler is pre-heated up to 146°C by 6.5 MW of LP steam (from 30°C to 100°C) and 4.3 MW of MP steam (from 100°C up to 146°C). Using flue gases to pre-heat the air, all the MP steam, and 1.5 MW of LP steam will be saved at the mill.

7.1.6 More steam saving potential

The new HWWS configuration provides the opportunity of using all the heat available of blowthrough steam and second flash steam, which was going to turpentine condenser in old configuration. In addition, the condensate can provide extra heat available when cooled down to 70°C. Part of this available heat has been used in the pulp dryer machine to pre-heat the air. Furthermore, 5 MW of its available heat can be utilized to pre-heat the air that goes to recovery boiler from 31°C up to 84°C. As it was mentioned in previous section, the air can be heated up from start temperature of 84°C, by flue gases from the recovery boiler. Accordingly, 5 MW of LP steam consumption can be decreased at the mill.

In this section, usage of the mixture of blow-through steam and second flash steam has been discussed. Table 7 is summarizing the utilization of this steam in different applications.

Table 7 - Applications of available heat in mixture of blow-through steam and second flash steam

Heat available in the blow-through and second flash steam	13.3	MW
Heat available in condensate of this steam	0.8	MW
Total available heat	14.1	MW
Heating the air to pulp dryer	6.3	MW
Pre-heating the air to recovery boiler	5	MW
Total available heat used	11.3	MW

7.1.7 Retrofit summary and practical concerns

In Table 8 the summary of different retrofits which have been done in FRAM mill and described in previous sections are presented

Table 8 - Summary of all retrofits in FRAM mill

Mill configuration	Hot utility demand (MW)	Steam saving (MW)
Original mill	179	
Wood yard as heat user	177.1	1.9
Modified pulp dryer	170.8	6.3
Recovery boiler heat recovery	164.9	5.8

As can be seen in the table 8, there are three possibilities to eliminate the pinch violations in FRAM bleached market pulp mill. Accordingly, 14 MW of pinch violations can be eliminated that corresponds to about 95% of all pinch violations and 7.5% of total heating demand of the mill. In addition, there are 8 MW LP steam savings by redesigning the HWWS of the mill and also 5 MW of steam saving possibility by pre-heating the air to recovery boiler with blow-through and second flash steam.

The main steam saving opportunity which has been described is designing new hot and warm water system (HWWS). In the new configuration, the minimum temperature difference is chosen equal to 5°C which is lower than in conventional HWWS. This small ΔT may imply high investment costs. Also in comparison with the old configuration, there is more water that goes in each heat exchanger (The total fresh water consumption is decreased but the flow rate of water in each heat exchanger has been considerably increased). On the other hand, the 8 MW LP steam demand of this system has been eliminated by re-arranging it in a more efficient way.

Accordingly, this retrofit has both advantages and drawbacks and a detailed economical assessment would be needed. This is beyond the scope of this thesis.

Another retrofit which contributes significantly to the hot utility savings is referred to as "modified pulp dryer" in Table 8. In this retrofit the LP steam used for heating air to pulp dryer, is replaced by both blow-through steam and second flash steam. This retrofit would lead to 6.3 MW of LP steam savings. Regarding the quantity of heat exchangers, in the old arrangement, there was a condenser, turpentine condenser, which was producing warm water by cooling down the excess steam. In the new arrangement, there is one heat exchanger to pre-heat the air to pulp dryer and one heat exchanger to pre-heat the air to the recovery boiler. As a result, changing the path of blow-through and second flash steam cooling from the old configuration into the new one, two new heat exchangers are needed (as compared with one heat exchanger in the old case).

7.2 Hot water extraction process

Three scenarios have been discussed and compared for energy integration potentials in the mill and the extraction process. The first scenario (base case) considers the stand-alone hemicelluloses extraction process and stand-alone FRAM mill without any retrofit. In the second scenario, both the FRAM mill and the hot water extraction process are retrofitted separately, taking into account all the steam saving potentials. Finally, the IFBR scenario which represents the fully integrated hemicelluloses extraction process with the mill. Each of these scenarios is described more in the details in the followings sections.

7.2.1 First scenario: Original FRAM mill and stand-alone extraction process

The heat demand in the original mill design is 187 MW. In order to estimate the heat demand in the extraction process, the stream set in Table 9, has been identified.

St.number	Description		T target	Q (MW)
1	MP steam to extraction vessel	199	200	44.4
2	LP steam to LL extraction and distillation		150	4.4
3	LP steam to ethanol distillation	149	150	4.8
4	Hydrolyzate between acetic acid distillation and over liming	120	50	13.8
5	Hydrolyzate between over liming and fermentation		30	3.8
6	Flash steam	127	126	7.3

Table 9 - Str	eams set of Ho	t water extract	ion process
1 a O O - O U	cams set of 110	i water extract	Ion process

The heat loads which are shown in the table 9 correspond to wood consumption as FRAM bleached market pulp mill. The calculations in more detail are available in appendix 6.

Total heating demand of the extraction process is 53.6 MW that is the sum of the steam demand in the extraction vessel and two distillation stages, streams 1 to 3.

7.2.2 Second scenario: retrofitted FRAM mill and retrofitted extraction process

The heat demand can be decreased from 187MW in the original mill to 164.9MW in the modified mill with new HWWS and three retrofits. The extraction process based on hot water method demands 53.6MW when no retrofit is implemented. There are, however, potentials for energy savings in the process. The most important heat sources in this process are the heat available in hydrolyzate stream (after acetic acid distillation) and the flash steam. The flash steam can potentially provide 7.3 MW high grade heat, i.e. available at the temperature of 127°C. This available heat can be utilized to pre-heat the water entering to extraction vessel. The water can be heated up to 91.5°C by transferring 13.8 MW heat from the hydrolyzate. Note that water is assumed to enter at 20°C. The other retrofit is to utilize the flash steam for use in both LL extraction/distillation column and partly in ethanol distillation column. In the former, 4.4 MW heat at 120°C is needed that can be met by flash steam. In the latter, 4.8 MW heat should be provided at 90°C which can partly be provided by flash steam.

In the extraction process, a total steam demand of, 21.1 MW can be replaced by other heat sources available through the retrofits. Accordingly, the heating demand of the extraction process can decrease from 53.6 MW to 32.5 MW.

7.2.3 Third scenario: Integrated Biorefinery

The last scenario represents fully integrated hemicelluloses pre-extraction with the mill. The heat integration potentials between the two processes are therefore, identified in this scenario.

One of the units in which potentials for heat integration between the two processes can be identified for, is the steaming and pre-impregnation of wood chips. In FRAM mill, the wood chips enter at 15°C and after being steamed and pre-impregnated using LP steam and flash steam, are sent to the digester at 120°C. In this unit, the white liquor is also pre-heated from 85°C up to 120°C. By implementing the hemicelluloses extraction process, the wood chips will be discharged from the extraction vessel at the temperature of about 90°C (Mao, 2007). Accordingly, less LP steam and flash steam are required to reach 120°C in the integrated process. In FRAM original mill, this area is using about 22.2 MW LP and flash steam. About 4 MW of the total LP and flash steam is blow-through steam that cannot be altered in the process. Moreover, about 6 MW of the total LP and flash steam is the heat demand for heating up the white liquor 120°C; this 6MW cannot be changed either. The rest of 22.2 MW, i.e. 12.2 MW, is the heating demand for wood chips, which can be decreased to 3.4MW by implementing the extraction process prior to cooking. Accordingly, total heating demand of this area will decrease to 13.4 MW instead of 22.2 MW.

Pre-impregnation heating demand in Pre-impregnation heating demand in FRAM stand-alone case IFBR case 4 MW blow-through steam Constant 4 MW blow-through steam 6 MW white liquor heating demand Constant 6 MW white liquor heating demand 12.2 MW wood chips heating demand Decrease 3.4 MW wood chips heating demand Total: 22.2 MW Total: 13.4 MW

This heat saving is due to receiving wood chips at higher temperature in the pre-impregnation zone. The less steam demand in the pre-impregnation zone would liberate the heat available in the black liquor to be used elsewhere. As it was mentioned earlier, the black liquor exits the digester at 162°C and is flashed in to two flash vessels at 127°C and 105°C. One potential retrofit for the integrated processes is to use the heat content of black liquor in the hi-washing zone to increase the wash liquor temperature from 123°C up to 157°C. Accordingly, black liquor can transfer 10.5 MW of its available heat to wash liquor and then enter the flash vessel at the temperature of 142°C. In this way, 10.5 MW of steam savings are achieved.

To provide the heating demand of pre-impregnation zone in IFBR case, 4 MW heat content of the first flash steam can be used. It should be mentioned that the heat content of second flash steam is, however, not affected by this retrofit. So the corresponding retrofits, discussed earlier in section 7.2.2, are still valid in this case. By providing the 4 MW of pre-impregnation zone heating demand, by the aid of first flash steam, there will be only 9.4 MW left to cover the steam demand of the extraction vessel completely. As it was mentioned in previous sections, the hydrolyzate flash steam in the extraction process has 7.3 MW heat load that is used in different heat sinks in the retrofitted extraction process. Since the temperature of this flash steam is the highest temperature among all heat sources, its available heat can be used in the pre-impregnation zone in Kraft pulping process. Consequently, the retrofit possibilities in extraction process need to be changed. One of the changes is ignoring the usage of flash steam in distillations columns anymore that will give 7.3 MW heat available. Accordingly, the LP steam demand of the extraction process will increase 7.3 MW in comparison with second scenario. In addition, there will be 2.1 MW more LP steam demand in the IFBR. Accordingly, a total amount of 9.4 MW LP steam demand is added to the heating demand of IFBR. Although there will be higher amount of LP steam demand in IFBR, the MP steam saving in Hi-heat zone (wash liquor circulation loop) is significant that is 10.5 MW.



Difference in heating demand of Kraft mill: -10.5 MW + 2.1 MW= - 8.4 MW

Difference in heating demand of extraction process: + 7.3 MW

As result, the total heating demand of the FRAM bleached market pulp mill will decrease 8.4 MW which will result in 155.9 MW steam demand. Besides, the heating demand of the extraction process will reach a final value of 39.8 MW.

It should be noted that in all three scenarios that are described in this section, the effect of implementing hemicelluloses extraction on the load of recovery boiler is not considered

7.3 Effect of introducing hemicelluloses extraction on the Kraft pulping process

Hot water extraction of hemicelluloses generates acidic conditions due to release of acetic acid from hemicelluloses. These acidic conditions may cause degradation of cellulose which is not desirable in an IFBR that produces pulp as one of its key products. To maintain the same pulp production, more wood must be charged to the process which will affect the loads of process equipments (W.J.Frederick Jr 2008). Degradation of cellulose in wood chips results in lower pulp yield than the conventional Kraft pulping process (Heiningen 2006). The degraded celluloses can either follow the hydrolyzate and being converted to ethanol or follow the extracted wood to the digester and eventually being burned in the recovery boiler. In this thesis, the increased amount of ethanol production due to celluloses conversion is considered in final cash flow assessments. But the increased load of the evaporation plant or recovery boiler is not considered.

In this master thesis, the wood input in the IFBR is unchanged compared to the original FRAM mill. Therefore, the pulp production in IFBR would not be the same as FRAM bleached market pulp mill, due to cellulose degradation during extraction process. In the IFBR, delignification rate can be faster and more effective due to the fact that wood chips have already been heated up and been "wetted" in the extraction vessel. (DeMartini, 2008). This can result in a shorter cooking time and also decreasing the digester utilization. Mao reported a relatively 8% decrease in the heat load of digester when extracting 10% of wood mass with the near neutral method prior to cooking (Mao, 2007). No information can be found in the literature for the effect of hot water

extraction on the digestion at the mill. The calculation in this master thesis is, therefore, based on a scaling up of the values from the near-neutral extraction process. Based on this scaling assumption, a 12.8% decrease in digestion heat load is considered in hot water extraction case when 16% of wood mass is extracted. In addition, removing hemicelluloses results in using less white liquor charge in digester that generates less black liquor respectively. A decreased amount of black liquor may thus decrease the load of the evaporation plant.. Mao reported a decrease rate of 6.8% in the near neutral process (Mao, 2007); the value is used to estimate the load decrease in hot water extraction in this thesis, i.e. a 10.9% decrease in evaporation load. In addition to digestion heat load and evaporation load, changes in stripper and pulp dryer are also expectable which give us a totally 20.6 MW drop in heating demand of the FRAM mill. All the calculations are available in appendix 7. Consequently, the minimum hot utility demand of the mill in original case will be 166.4 MW instead of 187 MW which is equivalent to almost 11% decrease.

Another effect is the higher heating value of black liquor that arises from the higher ratio of lignin: hemicelluloses in IFBR as compared with stand-alone Kraft mill (DeMartini, 2008). On the other hand, since a relatively large part of the hemicelluloses in the wood is removed, a significant decrease in recovery boiler load is expected. Mao reported 10% decrease in steam production in recovery boiler that is a significant reduction in recovery boiler load (Mao, 2007). In this study, since the extraction rate is 16% of wood mass, 16% less steam production is assumed in recovery boiler.

FRAM bleached market pulp mill is producing 211 MW steam in the recovery boiler and bark boiler. Of these 211 MW, 24 MW are directly sent to the back pressure turbine to generate 22.8 MW electricity for the mill. In addition, the mill purchases 13.1 MW electricity from the market grid. By implementing a hemicelluloses extraction process, 16% less steam will be produced which would result in about 177.2 MW steam production.

It is also worth to mention that, by implementing hemicelluloses extraction process the HWWS diagram will be also affected. In this master thesis, based on the scope of the project, the changes in HWWS diagram are not considered.

7.4 Summary and discussion

7.4.1 Technical assessment

In section 7.2, different plant configurations were discussed without considering the effect of hemicelluloses pre-extraction. In this section, the changes which are expected to be observed in both heating demand and heat supply are considered. Table 10 is comparing three scenarios that have been explained with respect to steam deficit/excess.

	Scenario 1	Scenario 2	Scenario 3
Pulp mill heating demand (MW)	166.4	143.7	135.3
Extraction heating demand (MW)	53.6	32.5	39.8
Global heating demand of IFBR (MW)	-220	-176.3	-175.2
Electricity generation steam demand (MW)	-24	-24	-24
Steam production by mill (MW)	177.2	177.2	177.2
Steam deficit/excess (MW)	-66.8	-23.1	-22

Table 10 - Summary of heating demands in three different scenarios

Based on the information available in table 10, the steam production at the mill is not enough to meet the steam demand in any scenario. In the first scenario, there will be 66.8 MW steam demand for the process. The second scenario, that represents the retrofitted pulp mill and retrofitted extraction process, has 23.1 MW deficit of steam which is a significant amount. The last scenario shows that fully integrating the extraction process with pulp process will not make the IFBR self sufficient regarding steam demand.

It should be noted that, regarding the price of steam and electricity, it is always important to keep the electricity production constant rather than selling excess steam. Here, it is assumed that, the steam demand of the back pressure turbine is met by the steam production of mill in all three scenarios. Accordingly, a part of steam demand of the process must be purchased from the market.

It is worth to mention that in all scenarios, the electricity consumption of the mill is assumed to be constant due to lack of information about possible changes.

According to the table, since the third scenario needs less steam to be purchased than other scenarios, it is more interesting to implement the fully integration of extraction process with pulp process. Obviously, the investments costs will be affected which is not considered in this study.

7.4.2 Cash flow assessment

A cash flow assessment for the IFBR is presented in this section. Here, the IFBR is compared against the FRAM stand-alone mill regarding income and expenses per year. In the cash flow assessment, only the IFBR (i.e. third scenario) is studied due to the fact that the IFBR is more interesting than other scenarios presented in the previous section. So the FRAM mill and IFBR are compared with respect to: wood consumption, pulp production, steam consumption, steam production, ethanol production, acetic acid production and steam purchase. All the calculations with the different references for prices are available in appendix 8 in more detail. An overview of the results are summarized in table 11 in which the annual income of IFBR is compared with FRAM mill.

	F	FRAM mill IFBR with 10% pulp IFBR with same yield loss pulp production		IFBR with 20% pulp yield loss		IFBR with same pulp production				
	Amount	Income/Expense (M€/year)	Amount	Income/Expense (M€/year)	Amount	Income/Expense (M€/year)	Amount	Income/Expense (M€/year)	Amount	Income/Expense (M€/year)
Wood consumption (t/day)	2328	-51,2	2328	-51,2	2560,8	-56,4	2328	-51,2	2793,6	-61,5
Pulp production (Adt/day)	1250	287,8	1125	259,0	1250	287,8	1000	230,2	1250	287,8
Steam production (MW)	211		177,2				177,2			
Steam consumption (MW)	187		199.2				199.2			
Steam purchase (MW)	0	0	22,0	-3,4		-3,4	22,0	-3,4		-3,4
Bark selling (t/day)	256,2	7,8	256,2	7,8	281,82	8,6	256,2	7,8	307,44	9,4
Ethanol production (t/day)	0	0	99,5	16,9	109,8	18,6	128,7	21,9	155	26,3
Acetic acid production (t/day)	0	0	77,5	12,7	77,5	12,7	77,5	12,7	77,5	12,7
Total income (M€/year)		244,4		241,8		268,0		218,0		271,3

Table 11 - Summary of cash flow assessment

As it was mentioned in previous sections, implementing the hemicelluloses extraction process by hot water extraction method will decrease the pulp yield of the mill. Based on different studies by different authors, there are two ways to express the pulp yield decrease. One is cooking (or digester) loss which represents the pulp yield decrease after cooking stage, i.e. cooking yield. With 12% extraction rate, the cooking yield loss varies from 4.4% or 5.8% (Mendes, et al., 2009) to 7.7% (Testova, 2006). Another term for yield decrease which has been used in literature is called overall yield decrease that represents the drop in pulp yield after bleaching. The overall yield decrease is higher than cooking yield loss due to several treatments that are done after cooking and before selling the pulp. This loss is reported to be 17.7% by Mendes and co-authors (Mendes, et al., 2009) for 12% extraction rate. Also, Testova reported 19.3% overall yield loss with almost the same extraction rate (Testova, 2006). Al-Dajani and co-authors claimed a decrease in overall yield of 23.2% overall yield decrease in the case that 19% of wood mass is extracted in hot water method (Al-Dajani, et al., 2009). For 16% extraction rate, which is considered in this thesis, no literature data about the overall yield decrease could be found. Therefore, a value of about 20% was estimated for the overall pulp yield decrease and the cash flow analysis in Table 11 is based on this value. As can be seen in table 11, the IFBR with 20% pulp yield loss has about 11% lower income than FRAM that is mainly due to its less pulp production. Although an accurate economic assessment with regards to capital costs has not been performed in this study, the results show that for the studied mill, implementing hemicelluloses extraction process with hot water method could not be profitable for the mill. This result could be predictable as the pulp production is decreased drastically. Also it is noticeable that due to lack of information about the electricity consumption of IFBR case and also the price of chemicals that are used in the extraction process, these important factors are not considered in this cash flow assessment. If appropriate treatments can be made to minimize the pulp yield loss, the hot water extraction method could become competitive. Therefore further investigation about improving the overall pulp yield is crucial. To emphasize on the importance of the overall pulp yield, a case of 10% overall pulp yield loss is compared with 20% loss.

One way to maintain constant pulp production is to compensate the pulp loss by increasing wood input to the process. Table 11 shows the comparison in terms of cash flow.

7.5 Dilute acid extraction process

Concerning dilute acid extraction process, available data is not enough to make a precise investigation about energy integration opportunities. Hence, a discussion based on available data is included in this part which is mainly a comparison between the hot water extraction processes with dilute acid extraction process.

7.5.1 Heat integration opportunity

The dilute acid extraction process is almost similar to the hot water extraction process. Accordingly, there are similar integration possibilities for dilute acid extraction with the pulp mill. For example, the wood charge to extraction process is the same as in hot water extraction with same moisture content. Consequently, the amount of flash steam that is exiting the flash vessel in dilute acid process has almost the same heat load as in the hot water process. This means that there will be more or less similar heat integration possibility for this process as well as hot water extraction process.

7.5.2 Advantages and disadvantages in comparison with hot water extraction

The most important advantage of hot water extraction in comparison with dilute acid extraction is milder extraction conditions. In hot water process, the wood materials are treated in less severe conditions while in acidic conditions; the cellulose structure is exposed to more severe conditions, i.e. lower pH levels. This will result in even lower pulp yield as compared with the hot water method. So in the case of dilute acid extraction, the overall pulp yield loss is higher than the hot water extraction (Mendes, et al., 2009). In addition, acid extraction process has the drawback of corrosion that may happen in the extraction vessel or other equipments. Therefore, all the equipments in this process need to be resistant to corrosion which results in higher investment costs (Huang, et al., 2008).

Dilute acid extraction has, however, the advantage of higher hemicelluloses extraction rate (Huang, et al., 2008). This is also confirmed by Toven and Øyaas who reported 60% of total hemicelluloses extraction from hardwood chips in dilute acid extraction method (Toven, et al., 2009). Moreover, Chirat and co-authors presented similar results for softwood (Chirat, et al., 2009). Consequently, in the case in which ethanol production is more important than pulp production, the desired way would be dilute acid extraction that yields higher amount of sugars.

8 Conclusions

The first part of this Thesis concerned the FRAM mill: Bleached Market Kraft Pulp Mill, operating with hardwood. The following conclusions can be drawn from the results:

- The minimum hot utility demand of the mill is 164.3 MW, which gives potential heat savings of 14.7 MW.
- All pinch violations were identified; the majority of these 14.7 MW is caused by heating streams below the pinch and transferring the heat through the pinch.
- Out of 14.7 MW, 14 MW of pinch violations were solved through measures described in this report, i.e. 95% of the total heat saving potential.

In addition to pinch violations, there are some more steam saving potentials in the mill which are not pinch violations but preheating opportunities i.e. the current steam consumption can be replaced by other heat sources like blow-through and second flash steam.

Even greater savings can certainly be found if the digesting and evaporation areas are studied in detail.

The second part of the report investigated the hemicelluloses extraction by hot water process and further ethanol production. Conclusions of this part can be summarized as:

- Hot utility demand for the process as it was designed amounts to 53.6 MW if adapted to FRAM mill's wood consumption.
- Opportunities were identified to reduce steam consumption in the process by using heat available in hydrolyzate after acetic acid distillation and flash steam.
- 21.1 MW steam saving potential has been identified after retrofitting the process.
- 69.4 t/day ethanol and 77.5 t/day acetic acid are produced in extraction and ethanol production process only by considering the conversion of hemicelluloses.
- When the retrofitted pulp mill is integrated with the retrofitted hemicelluloses extraction process, the IFBR is NOT self sufficient with respect to steam production and consumption anymore.

Although a detailed economic assessment regarding capital costs of retrofits and integration was not performed in this Thesis, a cash flow analysis showed that the IFBR with 20% overall pulp yield decrease has lower income than FRAM stand-alone mill per year. This can be overcome by improving the overall pulp yield or charging more wood to the process. This calls for thorough investigations about changes in process loads.

9 Further work

Based on the scope of this master thesis, a whole economic analysis, i.e. determine investment cost has not been performed. So, the first idea that could be worth considering is carrying out an extensive economic analysis including investment costs, modified operating costs and etc.

As the overall pulp yield is defined as an important parameter which has a significant effect on yearly income, it is crucial to investigate different methods to increase it. So it is highly recommended to go through this issue further in detail.

The impact of hemicelluloses pre-extraction on the chemical recovery cycle and also digester and evaporation plant could also be determined in a more accurate way. This can be done by running the WinGems model of FRAM mill with incoming wood chips having a different composition, i.e. the composition reported at the output of the extraction vessel.

Also, it could be interesting to look into other products from hemicelluloses to assess the viability of the process, or even into hemicelluloses themselves as a product for sale. Other products could be for example polyesters (Heiningen, 2006).

In the final distillation column in ethanol production, ethanol reaches its azeotrope concentration. After distillation, the ethanol is exiting at rather high temperature. This ethanol should be cooled down to be able to be sent to market. Also, there is water that is leaving distillation at high temperature. Accordingly, another possible further work is determining the temperature of distillation column accurately and calculating the heat available in ethanol and water for internal heat recovery.

Finally, a work similar to the one performed with hot water extraction could be carried on concerning dilute acid extraction, allowing a comparison between the two processes. If more details could be accessed concerning the dilute acid extraction, the calculations could be updated, thus providing results for the comparison.

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Appendixes

Appendix 1: Hot and Warm Water calculations

Hot/warm water is needed in four units in the mill: Pulp drying machine, Bleach plant, Causticising and Pulp washing. Three temperature levels are used: 50°C, 75°C and 85°C; three cold streams are therefore required for Pinch Analysis. It is important to notice that some of the demand for 75°C hot water is met by using condensates from the evaporation plant. Those streams must not be included as cold streams in Pinch Analysis; therefore the causticizing plant does not appear here since it uses only condensates.

Data extracted from the hot and warm water diagram is summarized in the table below:

Unit	Temperature level (°C)	Mass flow (t/h)
Dulp dwying mashina	85	344.5
Pulp drying machine	50	98.9
Pleash plant	85	206.7
Bleach plant	75	371.7
Pulp washing	85	72.6

This data allows determining the different heat loads for each of the three streams in Pinch Analysis. Heat loads are calculated using an average value for water specific heat capacity of $4.18 \text{ MJ/t} \,^{\circ}\text{C}$ with the following equation:

 $Q=F.c_{p}\Delta T$ with F mass flow (t/s) and ΔT temperature difference (°C)

Pinch Analysis stream	Mass flow (t/h)	Q (MW)
WW 18 to 50°C	1094.5	40.7
WW 50 to 75°C	995.6	28.9
WW 75 to 85°C	623.9	7.2

Appendix 2: Effluent calculations

The current effluent treatment system implies mixing all effluents regardless of their respective temperatures. This mixing produces a stream at 55°C which then needs to be cooled to 35°C, temperature at which a biological treatment is carried out. It is obvious that this configuration leads to an exergy waste: effluents ranging from 18°C to 97°C are mixed and cooled away in a cooling tower.

In this Thesis, calculations were performed to recover heat from these effluents. Since biological treatment must be carried out, the temperature of 35°C must be reached by the global effluent stream. But heat can be recovered from the warmest streams before they are mixed with the colder ones. This allows using energy to heat other streams in the mill and decreases the cooling demand. Indeed, if the stream to biological treatment reaches 35°C right away instead of being warmer, the need for a cooling tower is eliminated.

Heat loads are calculated using the same equation as in Appendix 1: Hot and Warm Water Calculations. First step is mixing streams 1 and 2 (see diagram below): the resulting stream has a temperature of 27°C. The whole heat content of stream 2 is used to reach this temperature; this configuration was chosen because this is the smallest and coldest of streams 2 to 4.



The energy needed to heat the resulting stream from 27°C to 35°C is then calculated and allows determining which part of the energy in stream 3 can be used for other purposes. It was therefore found that the whole heat content of stream 4 from 96.6°C to 35°C can finally be used in the mill.

Appendix 3: Pinch violations

Detailed calculations for pinch violations are provided here.

One of the pinch violations is caused by heating streams below the pinch with live LP steam. In this case in the table below, both T_{start} and T_{target} are below the pinch so the whole heat content of the stream constitutes a pinch violation.

Pinch Violation	Туре	Q (MW)
LP steam to Woodyard	Heating below pinch	1.9

Heating below the pinch also happens in the pulp dryer. In this case, only the part of the heat content that is below the pinch constitutes a pinch violation.

LP steam to pulp dryer:

 $T_{start} = 95^{\circ}C$ $T_{target} = 120^{\circ}C$ Pinch temperature for this stream = $T_p - 8 = 107 - 8 = 99^{\circ}C$ So Q will be: $Q = F.Cp.\Delta T = 1.58 \times 1 \times (99 - 95) = 6.32$

Pinch Violation	Туре	Q (MW)
LP steam to pulp dryer	Heating below pinch	6.3

Two other pinch violations were found concerning flue gases. In the current mill configuration, their heat is not recovered, which constitutes a pinch violation: cooling above the pinch. Heat content calculations for flue gases were carried out using Cp for CO_2 with a value of 0.85 kJ/kg °K (Universal Industrial Gases). Mass flows were found in the model's Excel file.

Flue gas recovery boiler:

 $T_{\text{start}} = 175^{\circ}\text{C}$ $T_{\text{target}} = 115^{\circ}\text{C}$ So Q will be: $Q = F.Cp.\Delta T = 411.5 \times 0.85 \times (175 - 115) = 5.8$

Flue gas lime kiln:

 $T_{start} = 170^{\circ}C$ $T_{target} = 135^{\circ}C$ So Q will be: $Q = F.Cp.\Delta T = 48.5 \times 0.85 \times (170 - 115) = 0.6$

Pinch Violation	Туре	Q (MW)
Flue gas recovery boiler	Cooling above pinch	5.8
Flue gas lime kiln	Cooling above pinch	0.6



Appendix 4: Current Hot and Warm Water System (HWWS) diagram

Appendix 5: New HWWS

To meet the mill's hot and warm water demand, save 8 MW of LP steam and make hot streams available for retrofits, a new Hot and Warm Water System was designed. The new design meets the whole cooling demand of the process and covers the need in hot and warm water. The new HWWS system was designed with the aim of reducing minimum temperature differences in heat exchangers and maximizing vertical heat exchange. Composite Curves representing all concerned streams were constructed and allowed determining the optimal configuration, by identifying streams in the curves.

In the new HWWS, the effluent after loop DQ1 is partly used instead of turpentine condenser. Also the effluent after loop DQ1 and DQ2 is used in wood yard which is not shown in current diagram.





Appendix 6: Hot water extraction stream calculations

All the streams flow rate in hot water extraction are calculated based on the values in near neutral case and the extraction rate of 16% is taken into account. Also it is assumed that 8% of wood mass is extracted in the form of xylan that can be converted to ethanol. The efficiency of acid hydrolysis is considered 90% and the conversion rate is assumed to be 46% in fermentation step.

To identify the amount of hydrolyzate that goes to distillation columns, the output streams of the process need to be defined. One of the most important streams is the lignin which precipitates after acid hydrolysis. In this hot water extraction, it is assumed that 3.4% of wood mass is precipitated in the form of lignin that is sent back to Kraft pulping process (Tunc and Van Heiningen 2008).

Another important assumption which is made in these calculations is related to the distribution rate of dissolved solid. When Mao is reporting almost 80% of total dissolved solid goes in ethanol production process (Mao 2007), there are other authors who report only 60% of dissolved solid content in the stream which goes to produce ethanol (Kautto, et al. 2010). Here in this study, it is assumed that 60% of total dissolved solid is sent to ethanol production process.

St.number	Description	T start	T target	Q (MW)
1	MP steam to extraction vessel	199	200	44.4
2	LP steam to LL extraction and distillation	149	150	4.4
3	LP steam to ethanol distillation	149	150	4.8
4	Hydrolyzate between acetic acid distillation and over liming	120	50	13.8
5	Hydrolyzate between over liming and fermentation	50	30	3.8
6	Flash steam	127	126	7.3

As it was mentioned, the mass flows of the streams are calculated based on the near neutral case. By the aid of specific heat of water and assuming the inlet and outlet temperature of each stream, the cooling or heating demand of the streams can be determined.

The steam demands of both distillation columns are calculated based on near neutral case. To calculate the steam demand of the wood which goes to digester, the specific heat of the wood is assumed as 2.1 Kj/Kg°K (Simpson and TenWolde 2009).

Appendix 7: Effect of hemicelluloses extraction on pulp mill

The following effects on the loads of Kraft pulp mill are calculated based on near neutral extraction method. All the values are identified based on scaling up the corresponding value in near neutral method.

	FRAM	IFBR	Difference	
Digester heating demand (MW)	22.2	19.4	2.8	-12.8%
White liquor loop (MW)	12.1	10.6	1.5	-12.8%
Wash liquor loop (MW)	10.5	9.2	1.3	-12.8%
Evaporation plant (MW)	55.9	49.8	6.1	-10.9%
Stripper (MW)	7.7	6.9	0.8	-10.9%
Pulp dryer (MW)	39.6	31.7	7.9	-20%
Total decrease in heating demar		20.6		

Accordingly, 20.6 MW less heating demand in Kraft pulp mill will be expectable after implementing the hemicelluloses extraction process.

Appendix 8: Cash flow calculations

Income calculations used in the cash flow analysis for hot water IFBR are accounted for in this Appendix. Figures for Ethanol and Acetic Acid production are calculated mainly based on scaling hot water process to near neutral process. The IFBR is assumed to operate 24h/day and 355 days/year when the availability of the mill is 0.92. As the M€year is used as income unit in this analysis, where the prices are SEK, the change rate of $1SEK = 0.104 \in is$ used (June 2010).

The prices of Ethanol, Bark and steam are taken from (Brau, 2010). The sources of other prices are also available. For example pulp price, that is available in (Paper Age website) and it is considered as 704.99 €metric ton.

The other prices are:

- Ethanol: 4 SEK/liter, ethanol density is considered 0.8 kg/m³
- Acetic acid: 500 €t (ICIS Pricing 2010)
- Bark price: 170 SEK/MWh fuel, the heating value of bark is 19 $MJ/kg DS^2$
- Steam: 19.75 €MWh
- Electricity: 49€MWh (Axelsson and Harvey, Scenarios for assessing profitability and carbon balances of energy investments in industry 2010)