Process integration study of a biorefinery producing ethylene from lignocellulosic feedstock for a chemical cluster

Master's Thesis within the Innovative and Sustainable Chemical Engineering programme

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CHALMERS UNIVERSITY OF TECHNOLOGY
Göteborg, Sweden 2011

MASTER’S THESIS

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ABSTRACT

A chemical cluster producing a variety of products is situated in Stenungsund, Sweden. In 2010 the ethylene consumption of the cluster (currently covered by import and a steam cracker converting e.g. naphta) increased due to the start-up of a new polyethylene (PE) plant by Borealis AB. This work investigates the opportunity to cover the current ethylene import (i.e. 200 000 tonnes/year) by the introduction of a biorefinery plant (reducing fossil fuel dependence and greenhouse gas (GHG) emissions from the cluster). High material and energy efficiency is of utmost importance to achieve economic competitiveness. Hence, heat integration is essential. A simulation model for a biorefinery is established in Aspen Plus based on literature review and personal contacts with experts. A process integration study is conducted using pinch analysis of simulation results. The aim is to investigate the integration consequences (e.g. potential energy savings and economical aspects) of combining a stand-alone lignocellulosic ethanol and a stand-alone ethanol dehydration plant into a biorefinery producing ethylene from lignocellulosic feedstock via the fermentation route. Several process configurations of the biorefinery are investigated, e.g. the integration of the biorefinery with the existing cluster based on results obtained from a total site analysis (TSA) (Hackl, et al., 2010).

In the lignocellulosic ethanol production spruce (749 MW) is converted to ethanol (337 MW) and a lignin-rich co-product (370 MW), which can be utilised as fuel in a combined heat and power (CHP) plant supplying steam (for hot utility and direct injection into process streams) and electricity. The stand-alone ethanol plant results in excess solid residues (86 MW) and electricity (24 MW_{el}). In the ethylene production, ethanol (337 MW) is converted to ethylene (307 MW). The stand-alone ethylene plant requires external fuel (16 MW) to cover hot utility demand. Moreover, electricity (4 MW_{el}) and steam for direct injection (25 MW) must be produced externally. The results indicate that energy savings (40% and 28% reduction of minimum hot and cold utility respectively) can be achieved by integrating the two stand-alone processes into a biorefinery. Moreover, the integration opportunity to eliminate external fuel, steam and electricity requirements by firing of excess solid residues arises. It is shown that the minimum hot utility demand can be further reduced by 59% by introducing a MVR in the biorefinery (Bio-MVR), which corresponds to a 75% reduction compared with the two stand-alone processes. The results show that the excess solid residues of the biorefinery can eliminate the external fuel requirement by flue gas integration or deliver VHP (41 bar) steam to the existing cluster. The lowest ethylene production cost (1.0 €/kg ethylene) is obtained for the Bio-MVR.

Key words: heat integration, process integration, pinch analysis, chemical cluster, biorefinery, bioethylene, lignocellulosic ethanol, fermentation route, Aspen Plus

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Preface

This study investigates the opportunity to substitute current ethylene import, originating from fossil resources, of the chemical cluster located in Stenungsund with a biorefinery producing ethylene from lignocellulosic feedstock.

This Master's thesis has been carried out at the Department of Energy and Environment, Division of Heat and Power Technology, Chalmers University of Technology, Sweden.

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Notations

Abbreviations

BG/FG	Background/foreground
BOD_7	Biological oxygen demand
C5	Pentose
C6	Hexose
CC	Composite curve
CE	Chemical engineering
CHP	Combined heat and power
COD	Chemical oxygen demand
COP	Coefficient of performance
CW	Cooling water
DM	Dry matter
ELECNRTL	Electrolyte Non-Random Two Liquids
ETBE	Ethyl tert-butyl ether
EtOH	Ethanol
FEHX	Feed-effluent heat exchanger
GCC	Grand composite curve
GHG	Greenhouse gas
HEX	Heat exchange
HHV	High heating values
HMF	5-hydroxymethylfurfural
HP	High pressure steam 20 bar (absolute pressure)
LP	Low pressure steam 4 bar (absolute pressure)
MP	Medium pressure steam 13 bar (absolute pressure)
MVR	Mechanical vapor recompression
NPV	Net present value
NREL	National Renewable Energy Laboratory
NRTL	Non-Random Two Liquids
PE	Polyethylene
SHCF	Separate hydrolysis and co-fermentation
SHF	Separate hydrolysis and fermentation
SSCF	Simultaneous saccharification and co-fermentation
SSF	Simultaneous saccharification and fermentation

TSA	Total site analysis
VHP	Very high pressure steam 41 bar (absolute pressure)
WIS	Water insoluble solids
WWT	Waste water treatment

Symbols

C_E	Equipment cost for capacity Q
W_{el}	Electrical work
$Q_{\text{C,min}}$	Minimum cold utility demand
$Q_{\text{C,Refrig}}$	Refrigeration utility demand
Q_{DH}	District heating potential
$Q_{\text{H,furnace}}$	Hot utility demand covered by furnace
$Q_{\text{H,LP steam}}$	LP steam utility demand
$Q_{\text{H,min}}$	Minimum hot utility demand
$Q_{\text{H,utility}}$	Hot utility demand
Q_{REC}	Maximum heat recovery through internal heat exchange
$Q_{\text{H,VHP steam}}$	Very high pressure steam utility demand
T_{pinch}	Pinch temperature
ΔT_{min}	Minimum temperature difference
€	Euro

1 Introduction

Depleting crude oil reservoirs, climate change due to greenhouse gas (GHG) emissions, a growing population with an increased energy and material demand have driven the interest in finding sustainable alternatives to the fossil feedstock dependent markets forward. One potential alternative is the biorefinery concept, which converts biomass to e.g. fuels, energy, and value-added chemicals. This implies that renewable feedstock is used for products that are traditionally produced from fossil raw material, thereby reducing fossil fuel dependence and GHG emissions. The biorefinery concept will play an important role in achieving a sustainable future society, where energy and material are less fossil fuel dependent.

In Stenungsund, Sweden, a chemical cluster consisting of five sites producing a variety of different products is situated, see Figure 1.1. One of the sites, Borealis AB, produces polyethylene (PE) (700 ktonnes annually (Borealis AB, 2010)) for mainly wire and cable and pipe applications. In 2010 Borealis AB invested in a new high pressure polyethylene (PE) plant which increased the annual production of PE and therefore also the ethylene consumption.

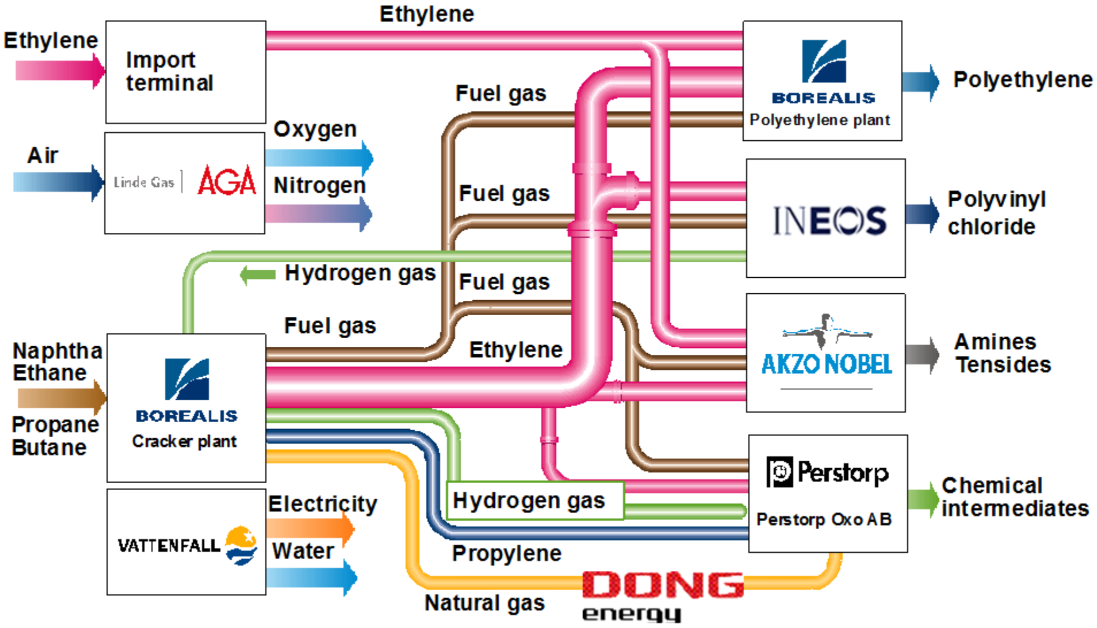

Figure 1.1 Material flows in the chemical cluster in Stenungsund (Borealis AB, 2007).

The current ethylene demand of the cluster is supplied by import (approximately 1/3 of the total ethylene demand) and a steam cracker (approximately 2/3 of the total ethylene demand). The steam cracker converts naphtha, ethane, propane and other raw materials to e.g. ethylene and propylene, see Table 1.1. The introduction of a biorefinery, producing bioethylene from renewable raw material, is one opportunity to cover the increased ethylene demand and consequently reducing the fossil feedstock dependence of the chemical cluster.

Table 1.1 Annual raw material consumption (left) and annual production (right) of the steam cracker in Stenungsund (Borealis AB, 2007).

Raw material consumption	ktonne	Production	ktonne
Naphta	360	**Ethylene**	622
Ethane	358	**Propylene**	200
Propane	246	**Others**	488
Buthane	368	**Ethyl tert-butyl ether (ETBE)**	28
Ethanol	12		

Ethylene can be produced via several alternative routes from biomass. One route is hydrolysis of biomass into monomeric sugars which are further converted to ethanol by fermentation. Ethylene is thereafter produced through catalytic dehydration of ethanol. An alternative route is gasification of biomass producing syngas. From syngas, methanol is generated which is further converted to olefins (mainly ethylene and propylene). A full-scale (production capacity of 200 000 tonnes annually) polyethylene production site from sugarcane based feedstock was started up in Brazil 2010 by Braskem (Braskem, 2010). The technology is expected to reach Europe when ethanol production from lignocellulosic feedstock is economically competitive.

To enable competition with well-established petroleum based processes it is of utter importance to achieve high energy and material efficiency for the biorefinery. To increase the thermal efficiency heat integration is essential. Available process heat sources are then used to cover heat sinks, reducing the demand of external utilities. Heat integration can be conducted internally in processes by heat exchanging of streams having excess of heat with streams having heat deficits. Heat integration can also be conducted between industries in chemical clusters by e.g. heat exchanging and implementation of common utility systems. When implementing process integration between neighbouring sites, it is also important to identify opportunities for exchanging materials, taking advantage of already existing infrastructure.

1.1 Objective

The aim of the thesis, *Process integration study of a biorefinery producing ethylene from lignocellulosic feedstock for a chemical cluster*, is to establish a simulation model for a biorefinery producing ethylene from lignocellulosic feedstock via the fermentation route. The bioethylene production is assumed to cover the current ethylene import of the chemical cluster, i.e. 200 000 tonnes annually. The simulation model is based on process design of a biorefinery configuration gathered from an extensive literature study and personal contact with experts.

The second objective is to investigate the heat integration potential of a stand-alone lignocellulosic ethanol production plant and a stand-alone catalytic ethanol dehydration plant producing ethylene. The consequences (e.g. potential energy savings and economical aspects) of combining a lignocellulosic ethanol production plant and an ethylene production plant into an integrated biorefinery producing ethylene from lignocellulosic feedstock are investigated. Moreover, the aim of the thesis is to investigate the effects of integrating the proposed biorefinery (ethylene production from lignocellulosic feedstock) with the existing industrial cluster in Stenungsund, through exchange of steam with the chemical cluster at suitable pressure levels. Different process configurations of the combined biorefinery are compared. Effects investigated from an energy perspective are e.g. heat integration potential and consequently minimum hot and cold utility demand, co-product (e.g. lignin-rich solid residue from the ethanol production plant) utilisation to reduce/cover the hot utility demand, and electricity production. The process integration is performed using pinch analysis. Relevant process information, i.e. heat sources and sinks in the biorefinery are identified by Aspen Plus simulations of the processes. Results from a total site analysis (TSA) are used concerning heat integration opportunities with the chemical cluster (Hackl, et al., 2010).

Additionally, the economical effects of producing ethylene from lignocellulosic feedstock in a biorefinery are investigated and compared with the case of purchasing ethanol to a stand-alone ethylene production plant.

2 Background

Ethylene production from lignocellulosic feedstock basically consists of two separate processes: ethanol production from lignocellulosic raw material (i.e. stand-alone lignocellulosic ethanol production) and catalytic dehydration of ethanol forming ethylene (i.e. stand-alone ethanol dehydration to ethylene production). The combination of these two processes is referred to as the biorefinery in this report.

2.1 Stand-alone lignocellulosic ethanol production

2.1.1 Renewable raw material

The conversion of carbohydrates into ethanol is a well-known process. Ethanol has traditionally been produced from sugar-based (e.g. sugar cane and sugar beet) or starch-based (e.g. corn and wheat) materials. However, in order to meet increasing future demands and to avoid direct competition with food production, the development of ethanol production processes using lignocellulosic feedstock is of utter importance to reach a sustainable society. Figure 2.1 shows an overview of required process steps for ethanol production from different raw materials.

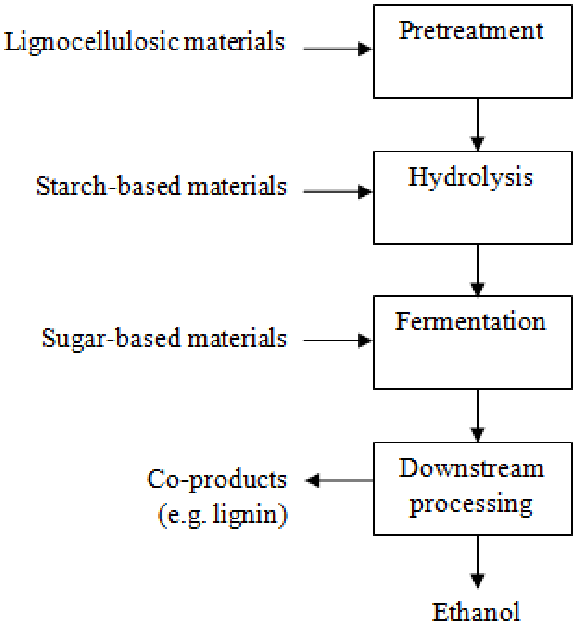

Figure 2.1 Overview of required process steps for bioethanol production for different feedstocks.

As can be seen in Figure 2.1 it is far easier to achieve fermentable monomeric sugars from sugar- and starch-based materials compared to lignocellulosic materials. When producing ethanol from sugar-based raw material the sugars (in the form of sucrose) are fermentable without any pretreatment or hydrolysis. Using starch-based material hydrolysis is required before fermentation is possible. Ethanol production from lignocellulosic raw material requires both pretreatment and hydrolysis prior to fermentation. Examples of lignocellulosic materials are softwood (e.g. spruce), hardwood (e.g. salix), and agricultural residues (e.g. corn stover). Lignocellulosic materials are explained in more detail in Section 2.1.1.1.

In order to achieve an economically competitive ethanol production the raw material cost must be kept low. Together with the enzyme cost, the cost of biomass is the largest contributor to the total ethanol production cost (Gregg, et al., 1998). The cost for lignocellulosic material is comparatively low which makes it attractive as ethanol production feedstock. In several regions in the world the availability of lignocellulosic biomass is considered to be sustainable in large quantities (Zhu, et al., 2010). As a consequence of the significant impact of raw material cost on the total ethanol production cost, complete and efficient utilisation of the raw material is crucial (Eriksson, et al., 2010). The fermentable sugars from lignocellulosic feedstock are comparatively harder to derive, i.e. a pretreatment step is required. In order to attract industrial interest the cost for deriving fermentable sugars from lignocellulosics needs to be reduced. When evaluating the bioethanol production cost the overall ethanol yield is the most important parameter (von Sivers, et al., 1996). In order to improve the ethanol production economics valuable co-products such as lignin can be utilised (Zhu, et al., 2010; Sassner, et al., 2008). This is especially true when lignin-rich raw materials are used. Lignin can be utilised as solid fuel in heat and power generation and/or sold as product, e.g. pellets.

2.1.1.1 Lignocellulosic feedstock

Lignocellulosic materials consist mainly of cellulose, hemicellulose, and lignin in different proportions, see Table 2.1. Cellulose is made up of glucan, a crystalline, linear polysaccharide of linked glucose units. Hemicellulose is an amorphous, highly branched heterogeneous polysaccharide which consists of glucan, mannan, galactan, xylan, and arabinan. In other words, hemicellulose consists of units of hexoses (glucose, mannose, and galactose) and pentoses (xylose and arabinose). Lignin is a highly complex three-dimensional polymer mainly made up of propylphenol derivatives.

Table 2.1 Composition (% dry basis) of three different lignocellulosic materials. (Sassner, et al., 2008)

	Spruce	**Salix**	**Corn stover**
Glucan	44.0	42.5	40.0
Mannan	13.0	3.0	-
Galactan	2.3	2.5	2.0
Xylan	6.0	15.0	21.0
Arabinan	2.0	1.5	5.0
Lignin	27.5	26.0	23.0
Acetate	1.3	3.0	1.6
Ash	1.6	2.0	3.5
Others	2.3	4.5	3.9
Hexose (C6) fraction	59.3	48	42
Pentose (C5) fraction	8	16.5	26

Mannan dominates the hemicellulose fraction in softwood, while in hardwood and agricultural residues the hemicellulose is mainly made up of xylan. As a result softwood has the largest hexose (C6) fraction (59.3%) and the lowest pentose (C5) fraction (8%) of the three lignocellulosic materials, see Table 2.1. A comparatively lower fraction of the xylose units are acetylated in softwood. The lignin content of softwood is generally higher. Additionally lignocellulosics consist of ash. Softwood has a relatively low ash content (<2%), see Table 2.1. This implies that solid residue from softwood may have comparatively better fuel properties (Sassner, 2007). “Others” in Table 2.1 are mainly extractives.

2.1.2 Stand-alone lignocellulosic ethanol production configuration

Ethanol production from lignocellulosic feedstock includes several process steps. In every process step there are several possible alternatives and a good combination is required to obtain a cost-effective production. In a future lignocellulosic ethanol refinery in Sweden, softwood and particularly spruce are considered to be the main feedstock alternative (Sassner, 2007). Hence, the process configuration of the stand-alone lignocellulosic ethanol production plant assumed in this study is based on spruce as main feedstock. However, if commercialising ethanol production from lignocellulosic feedstock the process must be flexible and universal, i.e. it must be feedstock versatile and not only effective for one specific species (Zhu, et al., 2010).

Figure 2.2 illustrates an overview of assumed stand-alone lignocellulosic ethanol production configuration investigated in the study. The assumed process configuration is based on a literature review. When handling softwood the raw material must first be debarked and sized. After sizing the wood chips are pretreated to derive the fermentable hemicellulose sugars and to make cellulose more accessible for hydrolysis. A two-step dilute acid steam explosion pretreatment is assumed, as a result of mainly handling softwood feedstock. Direct injection with MP (13 bar) steam (mainly deriving hemicellulose sugars) and HP (20 bar) steam (mainly making cellulose accessible for hydrolysis) are assumed in the first and second pretreatment step respectively (Wingren, et al., 2004). In order to obtain good properties of the solid residue (i.e. lignin) sulphuric acid is used. An acid concentration of 0.5 wt% and 1 wt% (based on the water content in feedstock) are assumed in the first and second pretreatment step respectively (Söderström, et al., 2005). After the first pretreatment step the slurry is separated into one liquid and one solid fraction in order to reduce hemicellulose sugar degradation. The filter cake is washed in order to achieve high hemicellulose sugar recovery. The solid fraction is sent to the second pretreatment step. The pretreatment step is further explained in Section 2.1.3. The liquid fraction is mixed with the resulting slurry from the second pretreatment step and flashed down to atmospheric pressure. The slurry is diluted to 11.2% water insoluble solids (WIS) concentration (Aden, et al., 2002).

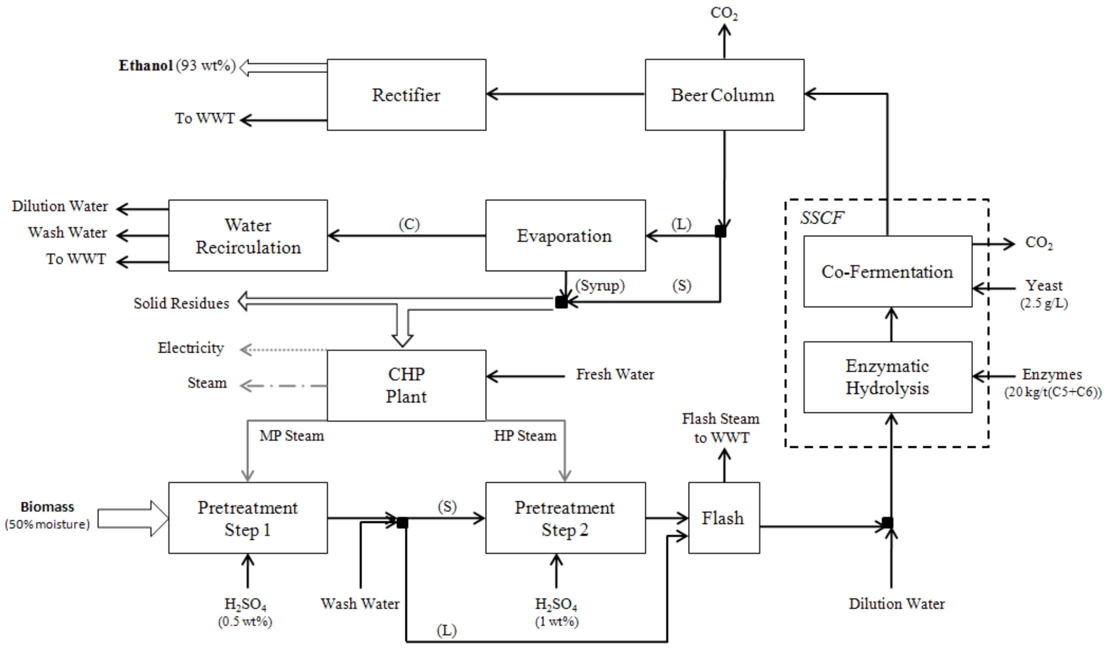

Figure 2.2 Stand-alone lignocellulosic ethanol production configuration. SSCF – Simultaneous Saccharification and Co-Fermentation, (S) – Solid Fraction, (L) – Liquid Fraction, (C) – Condensate.

In the subsequent hydrolysis (or saccharification) step, cellulose is hydrolysed, i.e. glucan is converted to glucose, for more details see Section 2.1.4. After pretreatment and hydrolysis, cellulose and hemicellulose have been converted into their respective sugars. The hexose sugars are converted to ethanol by the addition of yeast in a fermentation step. The hydrolysis and fermentation can occur either simultaneously (SSF) or separately (SHF). If pentose sugar fermentation to ethanol is also occurring it is referred to as simultaneous saccharification and co-fermentation (SSCF) or separate hydrolysis and co-fermentation (SHCF). The cellulose hydrolysis is assumed to be catalysed by enzymes and a futuristic perspective is chosen, thus the ability to ferment both hexoses and pentoses is presumed (i.e. SSCF configuration). The cellulases and yeast are assumed to be adapted, i.e. no detoxification step is necessary. Additionally, enzymes (with a load of 20 kg/t(C5+C6) (Fornell, 2010) and yeast (with addition to a concentration of 2.5 g/L (Sassner, et al., 2008) are assumed to be purchased. For more detailed information see Section 2.1.5.

After fermentation ethanol is purified to 93 wt% in several purification steps. The purification is basically conducted in two steps; one stripper referred to as the beer column and one distillation column referred to as the rectifier. The fermentation slurry enters the beer column where unconverted sugars and solids are separated from the ethanol-water mixture. Additionally, a large fraction of remaining CO$_2$ is removed in order to enhance the ethanol-water separation in the subsequent purification column (i.e. the rectifier). For further description see Section 2.1.6.

The resulting bottom product in the beer column is separated into a solid fraction (i.e. lignin and unconverted wood) and a liquid fraction, see Figure 2.2. The solubilised non-volatile compounds in the liquid fraction of the beer column stillage are assumed to be concentrated in a counter-currently arranged five-effect evaporation unit. The resulting evaporation condensate is suitable as recirculation water reducing fresh water demand (i.e. wash and dilution water), the remainder is sent to WWT. For more details see Sections 2.1.7 and 2.1.8, respectively. The lignin-rich solid fraction of the beer column stillage is mixed with the concentrated evaporation syrup and utilised as fuel in a Combined Heat and Power (CHP) plant supplying steam (for direct steam injection and as hot utility) and electricity to the process. Possible excess solid residues can be sold as product, e.g pellets. For more details see Section 2.1.9.

Wastewater generated in the lignocellulosic ethanol production is sent to a wastewater treatment facility, see Section 2.1.10. However, this is not taken into consideration in the study.

2.1.3 Pretreatment

The fermentable sugars can be derived from cellulose and hemicellulose through hydrolysis. However, cellulose, hemicellulose, and lignin are associated in a complex matrix. The hydrolysis of hemicellulose is relatively easy whereas cellulose is highly insoluble (Hamelinck, et al., 2005). In order to achieve an efficient hydrolysis of cellulose the matrix must be modified. This is particularly true for softwood due to its high lignin content and more rigid structure (Zhu, et al., 2010). Softwood-lignin is believed to be more branched and non-linear than hardwood-lignin (Gellerstedt, et al., 2008). Due to the properties concerning lignin and its association to cellulose and hemicellulose, softwood is more recalcitrant to enzymatic and chemical degradation (Galbe, et al., 2002; Zhu, et al., 2010). To overcome the recalcitrance and enhance the cellulose hydrolysis it is necessary to pretreat the feedstock. The hydrolysis yield can be increased from less than 20% to over 90% if the biomass is pretreated prior to the hydrolysis step (Hamelinck, et al., 2005). First the feedstock is mechanically pretreated, i.e. debarked if woody biomass, cleaned if necessary, and sized. Smaller size results in larger surface area, which is advantageous in the subsequent process step. However the size is a trade-off with energy usage. The size-reduced feedstock is then further treated to solubilise hemicellulose and remove lignin in order to make cellulose accessible for hydrolysis (Galbe, et al., 2002; Zhu, et al., 2010). During pretreatment hemicellulose is hydrolysed into its respective monomeric or oligomeric sugar, i.e. mannose is derived from mannan etc. Furthermore a fraction of cellulose is converted to glucose during pretreatment, even though the main conversion to monomeric glucose occurs in a separate hydrolysis step, see Section 2.1.4. The derived sugars may be degraded during pretreatment. The degree of degradation is dependent on the pretreatment conditions. Higher severity results in higher degree of degradation (Galbe, et al., 2002). Hexoses are degraded to 5-hydroxymethylfurfural (HMF), and if further degradation occurs to levulinic and formic acid. Pentose degradation products are for example furfural and formic acid. An overview of possible degradation products of lignocellulosics is shown in Figure 2.3.

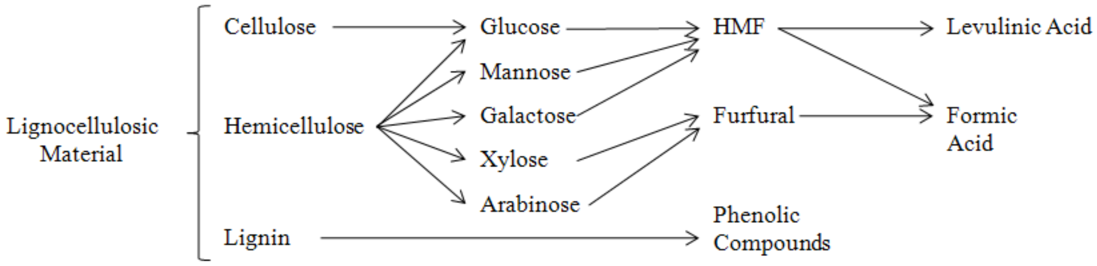

Figure 2.3 Possible degradation products of lignocellulosic material formed during pretreatment. HMF – 5-hydroxymethylfurfural.

The degradation products may act as inhibitors in the subsequent hydrolysis (Tengborg, et al., 2001) and fermentation (Larsson, et al., 1999) steps (Hamelinck, et al., 2005). To increase the hydrolysis yield of cellulose relatively high severity is required (Wingren, et al., 2004). This fact in combination with the fact that the optimum sugar recovery of hemicellulose is obtained at lower severity creates a problem in the pretreatment decision (Tengborg, et al., 1998; Söderström, et al., 2002). The choice of pretreatment significantly affects the utilisation of carbohydrates in the raw material. Accordingly, it plays an important role in achieving a good overall ethanol yield. There are several pretreatment alternatives available. One factor to consider when choosing pretreatment method is its efficiency on various feedstocks. To enable successful commercialisation the biorefinery needs to be independent of feedstock, i.e. it must be flexible and effective on numerous types of feedstock. Another factor to consider is the degree of chemical recovery needed and how the choice of pretreatment affects the downstream waste water treatment. The properties of the resulting solid residue, i.e. lignin, are also significantly affected by the choice of pretreatment (Zhu, et al., 2010). In the following sections acid-catalysed hydrolysis (pretreatment) and steam explosion are explained. A selection of alternative pretreatment methods are described in Appendix A.

2.1.3.1 Acid-catalysed hydrolysis (pretreatment)

Pretreatment of lignocellulosic materials can be performed with the presence of an acid catalyst. The acid can be either concentrated or diluted. Common acids used are sulphuric (H_2SO_4), sulphurous (SO_2), hydrochloric (HCl), phosphorous (H_3PO_3), and nitric acid (HNO_3). The most commonly used is pretreatment with dilute sulphuric acid. The pretreatment method obtains relatively high hemicellulose sugar yield (75-90% xylose yield) (Hamelinck, et al., 2005). However, the cellulose conversion has only been proven to work successfully on hardwood and agricultural residues (Zhu, et al., 2010). When softwood is pretreated by dilute acid the subsequent hydrolysis step only achieves a cellulose conversion of approximately 40% (Zhu, et al., 2010). The relatively severe conditions results in hemicellulose sugar degradation.

Using corrosive acids requires appropriate material. This is especially true when using concentrated acids. Sulphuric acid induces more corrosion compared to SO_2 (Galbe, et al., 2002). However, the utilization of SO_2 as catalyst has some issues concerning safety and health (Wingren, 2005). Furthermore, it is believed that SO_2 binds to lignin, forming ligno-sulphonates (Macki, et al., 1985). This may cause problems during solid residue combustion. Concentrated acids also need to be recovered after hydrolysis (von

Sivers, et al., 1995). This is not required to the same extent when using dilute sulphuric acid, due to the low purchase cost, to obtain an economically efficient process. However, the hydrolysate pH must be neutralised prior the fermentation step in both cases (Sun, et al., 2002). This results in the requirement of substantial amounts of alkaline chemicals (e.g. lime) and a resulting solid residue (e.g. gypsum) requiring deposition (Hamelinck, et al., 2005; Zhu, et al., 2010).

2.1.3.2 Steam explosion

One of the most investigated pretreatment methods for lignocellulosic feedstock is steam explosion, also often referred to as steam pretreatment (Galbe, et al., 2002). The size-reduced feedstock is treated with saturated high-pressure steam (6-28 bar, 160-260°C) (Sassner, 2007). The steam condenses and the wood structure “explodes” with a sudden pressure release causing the condensed moisture to evaporate (Carvalheiro, et al., 2008; Sun, et al., 2002). The method obtains a high yield of solubilised hemicellulose, while lignin remains in the solid fraction (Carvalheiro, et al., 2008). It can be performed with and without the addition of acid catalyst.

If no acid catalyst is added it is referred to as autohydrolysis. The absence of acid catalyst results in a requirement of high severity in order to solubilise the hemicellulose. As discussed earlier this may increase the formation of degradation products, which results in a decreased overall hemicellulose sugar recovery and possibly inhibition in the downstream hydrolysis and fermentation steps (Sassner, 2007).

Dilute-acid steam explosion is a combination of dilute-acid pretreatment and steam explosion (Zhu, et al., 2010). It is considered to be the pretreatment method with the highest potential, particularly for woody raw material (Galbe, et al., 2002). With the addition of an acid catalyst the yield of hemicellulosic sugars is increased, furthermore the cellulose hydrolysis in the following step is enhanced (Eklund, et al., 1995; Wingren, et al., 2004). The increase of hemicellulose recovery is due to the reduced severity needed resulting in a lower degree of hemicellulose degradation (Wingren, et al., 2004; Eklund, et al., 1995; Sassner, 2007). The lower amount of inhibitors formed may improve the cellulose hydrolysis yield (Sassner, 2007).

The size-reduced feedstock is first impregnated with dilute-acid and then treated with steam. Dilute-acid steam pretreatment has similar drawbacks to dilute-acid pretreatment, e.g. the need for pH-neutralisation resulting in solid residue requiring deposition. The most extensively used acids are sulphuric acid and gaseous SO_2. Impregnation of SO_2 and H_2SO_4 using spruce as feedstock results in the overall fermentable sugar yield of approximately 66% and 65% respectively (Tengborg, et al., 1998).

To increase the carbohydrate utilization in the raw material the pretreatment can be divided into two separate steps, i.e. a two-step dilute acid steam pretreatment (Söderström, et al., 2003; Nguyen, et al., 2000). This is favorable since the optimum conditions for sugar recovery for hemicellulose and cellulose differs (Galbe, et al., 2002; Stenberg, et al., 1998b). The first step is conducted at low severity solubilising and hydrolysing the hemicellulose. In order to avoid formation of degradation compounds the liquid and solid fraction are separated. 95% of the hemicellulosic sugars can be recovered in the liquid fraction if the filter cake is washed (Sassner, 2007; Aden, et al., 2002). The liquid fraction bypasses the second pretreatment step and also the hydrolysis step if operating the hydrolysis and fermentation steps separately, see Section 2.1.5. The solid fraction is sent to the second pretreatment step conducted at high severity making the cellulose more accessible for the subsequent hydrolysis. The overall sugar yield increases from 65-66% to approximately 75-80% dividing the pretreatment of spruce into two separate steps (Söderström, et al., 2003; Nguyen, et al., 2000).

The most favorable conditions for maximising the sugar recovery using SO_2 as acid catalyst are an acid concentration of 3% and 190°C in the first step and 220°C in the second step. Using H_2SO_4 the corresponding conditions are an acid concentration of 0.5% and 180°C in the first step and an acid concentration of 1% and 210°C in the second pretreatment step. (Söderström, et al., 2005)

The advantages of a two-step dilute acid steam pretreatment are its enhanced carbohydrate utilisation and high ethanol yield. If applying enzymatic hydrolysis, see Section 2.1.4.1, the method also results in lower enzyme consumption (Galbe, et al., 2002). On the other hand, the capital cost increases, requiring two separate pretreatment reactors, and the pretreatment configuration results in comparatively higher energy demand (Zhu, et al., 2010).

2.1.4 Hydrolysis

As mentioned in Section 2.1.3, the fermentable sugars in cellulose and hemicellulose can be derived through hydrolysis. When handling lignocellulosic feedstock the hydrolysis of hemicellulose is performed in the pretreatment step. The cellulose hydrolysis occurs in the subsequent step referred to as the hydrolysis, or saccharification, step. In cellulose hydrolysis, cellulose is broken down to its respective sugar (i.e. glucose) according to reaction (2.1) (Hamelinck, et al., 2005):

$$(C_6H_{10}O_5)_n + nH_2O \rightarrow nC_6H_{12}O_6 \tag{2.1}$$

The hydrolysis yield can exceed 90% if the feedstock is pretreated (Hamelinck, et al., 2005). The hydrolysis can be catalysed by acid (dilute or concentrated) or by enzymes. Acid hydrolysis is conducted under similar circumstances as dilute- or concentrated acid pretreatment respectively, see Section 2.1.3.1. The dilute acid hydrolysis process is the first technology used for commercial ethanol production from cellulosic biomass (Galbe, et al., 2002; Hamelinck, et al., 2005).

2.1.4.1 Enzymatic hydrolysis

The cellulose conversion to glucose by cellulase enzymes results in a very specific reaction and is conducted at low severity (pH 4.0-5.0, temperature 45-50°C), thus providing high yields and low sugar decomposition. The potential of the process is very high, and it is considered as the most promising hydrolysis method in ethanol production from lignocellulosic feedstock (Hamelinck, et al., 2005).

The conversion of glucose by enzymes from native cellulose is extremely slow, hence pretreatment making the cellulose accessible to enzymes is essential. The enzymatic hydrolysis efficiency decreases if biomass possesses characteristics as high crystallinity, high cellulose polymerization degree, and high lignin content. Conversely the efficiency is improved with large internal surface area. Cellulose hydrolysis by enzymes is compatible with most pretreatment methods, except for pure mechanical methods. Chips pretreated with steam explosion can reach conversions greater than 90% in the enzymatic hydrolysis step (Grous, et al., 1986).

Sugar degradation products formed in the preceding pretreatment may inhibit the enzymatic hydrolysis process. Furthermore, cellulase enzymes are inhibited by intermediate and end products formed during hydrolysis, i.e. cellobiose and glucose (Hamelinck, et al., 2005; Sun, et al., 2002). This effect can be reduced if performing the enzymatic hydrolysis at low dry matter content (Galbe, et al., 2002). Other solutions to reduce the end-product inhibition are increasing the enzyme concentration (e.g. through enzyme recovery and recycling), removing the end-product (e.g. through ultrafiltration) or by allowing the hydrolysis and fermentation to occur in the same reactor. The latter method is referred to as simultaneous saccharification and fermentation (SSF), for more details see Section 2.1.5. (Hamelinck, et al., 2005; Sun, et al., 2002)

Advantages of the enzymatic hydrolysis method are its high overall sugar yields and its comparatively (to acid hydrolysis) lower equipment and maintenance costs. The process is performed at low temperatures. The method does not require a subsequent neutralisation step, accordingly no solid waste is (Hamelinck, et al., 2005).

2.1.5 Fermentation

Several microorganisms, e.g. bacteria, yeast, and fungi, have the ability to ferment carbohydrates to ethanol. The most promising microorganisms in fermenting lignocellulosics are the yeast *Saccharomyces cerevisiae* (ordinary baker's yeast), and the bacteria *Zymomonas mobilis*. The latter results in higher glucose to ethanol yield (Galbe, et al., 2002). On the other hand, S. cerevisiae is tolerant to inhibitory compounds and robust, i.e. very suitable for fermentation of lignocellulosics (Galbe, et al., 2002; Olsson, et al., 1993). Moreover, it has the ability to ferment mannose and after modification, also galactose (Galbe, et al., 2002). This is especially beneficial when deriving sugars from softwood, see Table 2.1 in Section 2.1.1.1.

Lignocellulosic materials also consist of pentoses, i.e. xylose and arabinose. At present, the conversion of pentoses to ethanol is relatively difficult. Microorganisms can be adapted to increase the ability to ferment xylose and arabinose (Hamelinck, et al., 2005; Galbe, et al., 2002). Progress has been achieved when S. cerevisiae, Z. mobilis, and the bacteria Escherichia coli have been genetically engineered (Galbe, et al., 2002; Hamelinck, et al., 2005).

The pentose and hexose sugar conversions to ethanol occur according to the following reactions respectively (Hamelinck, et al., 2005):

$$3C_5H_{10}O_5 \rightarrow 5C_2H_5OH + 5CO_2 \tag{2.2}$$

$$C_6H_{12}O_6 \rightarrow 2C_2H_5OH + 2CO_2 \tag{2.3}$$

The enabling of pentose conversion would significantly increase the carbohydrate utilisation of the raw material, and thus increase the ethanol efficiency and economy. This would have particular impact for lignocellulosics with high proportion of pentoses, i.e. agricultural residues and hardwood. The enabling of pentose fermentation utilising softwood, would have comparatively less impact on the overall ethanol efficiency. Nevertheless, it would not be without significance. Table 2.2 shows the theoretical ethanol yield from hexoses and pentoses for spruce, salix, and corn stover (with the feedstock composition presented in Table 2.1) respectively.

Table 2.2 Theoretical ethanol yield (kg ethanol/tonne dry feedstock) (Sassner, et al., 2008)

	Spruce	**Salix**	**Corn stover**
From hexoses	336	272	238
From pentoses	47	95	151

The cellulose hydrolysis and the hexose sugar fermentation to ethanol can be conducted separately, in different reactors, or simultaneously, in the same reactor. The first is referred to as separate hydrolysis and fermentation (SHF) and the latter to simultaneous saccharification and fermentation (SSF). If also pentose fermentation is occurring the corresponding processes are referred to as separate hydrolysis and co-fermentation (SHCF) and simultaneous saccharification and co-fermentation (SSCF). The main advantage to perform hydrolysis and fermentation separately is that the two processes can be conducted under its respective optimal condition. Optimally, the enzymatic hydrolysis is conducted at temperatures of 45-50°C, while fermentation is carried out at 30°C (Galbe, et al., 2002). If hydrolysis and fermentation occurs simultaneously the temperature is usually around 35°C (Galbe, et al., 2002). If thermo-tolerant yeast can be developed the SSF performance is expected to be enhanced. As mentioned in Section 2.1.4.1, the intermediate and end-products (i.e. cellobiose and fermentable sugars respectively) inhibit the cellulases in the cellulose hydrolysis process. This is the main drawback of SHF. Conversely, in the SSF configuration, glucose and other fermentable sugars are immediately consumed by the yeast, i.e. end-product inhibition is prevented. On the other hand, ethanol also inhibits cellulose saccharification however not to the same extent. Another advantage with SSF is its lower capital cost followed by the requirement of only one reactor. Conducting hydrolysis and fermentation simultaneously (i.e. SSF) yeast is incorporated with the solid lignin-rich residue, leading to problems in recovering and recycling of yeast. (Galbe, et al., 2002)

2.1.6 Product purification

The fermentation broth consists of a wide variety of substances, both solids and liquids. The ethanol dehydration to ethylene process requires an ethanol purity of 95 vol% (Kochar, et al., 1981). Ethanol is generally concentrated in two steps. In the first step the solids and non-volatile substances are separated from the ethanol-water mixture in a stripper. This separation unit is referred to as the beer column. The beer column is followed by the rectification column, where ethanol purity approaches the ethanol-water azeotrope (around 95 wt%). (Hamelinck, et al., 2005)

The energy consumption in the distillation step exponentially decreases with an increasing ethanol concentration in the distillation feed (Galbe, et al., 2007; Wingren, et al., 2008). As the distillation step is one of the most energy consuming process units in the ethanol production, it has a major impact on the overall process energy demand. Therefore, obtaining a high ethanol concentration after fermentation is of great significance. Utilising lignocellulosic feedstock an ethanol concentration of approximately 4 wt% is desired (Sassner, 2007).

The ethanol concentration can be further increased to 99.5-99.9 wt% (Cardona-Alzate, et al., 2006; Hamelinck, et al., 2005). This is achieved through distillation performed with an entrainer, drying with desiccants, using pervaporation, or membrane techniques.

2.1.7 Evaporation

Beer column bottom product is sent to a solid-liquid separator. The liquid fraction is sent to an evaporation unit to enable utilisation of the dissolved, non-volatile substances as fuel. This implies that it is concentrated to sufficiently high dry matter (DM) content at the expense of thermal energy. The resulting evaporation syrup is mixed with the solid fraction (from solid-liquid separator) prior to combustion. The resulting evaporate condensate is relatively free from non-volatile substances which makes it suitable for water recycling, for more details see Section 2.1.8 (Larsson, et al., 1997).

The evaporation process is relatively energy demanding. In order to reduce the energy consumption it can be performed in multiple effects. It can be arranged as forward-feed, counter-current, or as a combination of the two.

2.1.8 Recirculation of process streams

The ethanol production process from lignocellulosic material requires large quantities of water in several process steps. In large-scale production internal recirculation of process streams is necessary to decrease the fresh water consumption. Consequently also the amount of wastewater is reduced. When recirculating process streams, energy consumption is also decreased due to the reduced need for preheat of wash water. A downside with recirculation is the accumulation of potential inhibitors in the hydrolysis and fermentation (Larsson, et al., 1997; Stenberg, et al., 1998a). These compounds originate from the raw material or are formed in the pretreatment step.

The selection of recirculation streams affects the flow through the various process steps, hence also the energy consumption in the distillation and evaporation (Alkasrawi, et al., 2002). The properties of the recycling stream affects the ethanol yield, consequently it is of utmost importance to evaluate its respective suitability. Non-volatile substances inhibit fermentation significantly, while hydrolysis is moderately affected. Volatile substances do not inhibit the fermentation (Larsson, et al., 1997). Therefore it is desirable to avoid recirculation of process streams containing non-volatile substances. It has been shown that 60% of the fresh water can be replaced by distillation stillage without negatively affecting the hydrolysis or fermentation. If recirculating the stream before distillation the corresponding amount is 40%. Recirculation of higher proportions will cause inhibition in the fermentation, however not in the hydrolysis. The use of customised yeast or the investment of a detoxification step could increase the recirculation proportion. (Alkasrawi, et al., 2002)

An effective alternative to reduce the inhibitory substances in the hydrolysis and fermentation when recirculation process streams is evaporation, see Section 2.1.7. At the expense of thermal energy possible inhibitors are removed. The concentrated evaporation syrup, i.e. non-volatiles, can be utilised as fuel in a combined heat and power (CHP) plant, see Section 2.1.9. Additionally the chemical (COD) and biological (BOD_7) oxygen demands of the distillation stillage are reduced by 90%, leading to a cost reduction of the wastewater treatment of the evaporation condensate fraction that is not recirculated. (Larsson, et al., 1997)

2.1.9 Combined Heat and Power (CHP) plant

The solid residue (i.e. mainly lignin) from beer column and concentrated evaporation syrup are suitable as combustion fuel. Additionally, bark from the debarking unit can used be as fuel. Available fuel can be utilised in a combined heat and power (CHP) plant supplying steam and electricity to the process. Steam extraction possibilities are available at several pressure levels.

2.1.10 Wastewater treatment (WWT)

The ethanol production process involves large water flows, as a result a water purification step is necessary. It is mainly the resulting flash-vapor streams from the pretreatment, the rectifier stillage, and possibly a fraction of the evaporation condensate that require treatment. The wastewater treatment (WWT) is usually performed in one anaerobic and one aerobic step. The feed streams are cooled to the operating temperature of the digesters. In the anaerobic digestion 50% of the chemical oxygen demand (COD) is consumed producing methane (Sassner, et al., 2008). The biogas can be used as fuel in the steam generation unit. In the succeeding aerobic step the greater part of the remaining COD is removed. The treated water can be considered as clean. The wastewater treatment results in the formation of sludge, mainly in the second aerobic step. This requires additional treatment. (Sassner, et al., 2008)

2.2 Stand-alone ethanol dehydration to ethylene production

2.2.1 Stand-alone ethanol dehydration to ethylene production configuration

In 2010 Braskem started a full-scale ethanol dehydration plant in Brazil (Braskem, 2010). The ethanol dehydration process basically consists of a reactor and several purification steps. The Braskem patent mainly focuses on the reactor, which is adiabatic. The reactor feed is diluted with steam to a large extent. The patent reveals limited information and the heat exchanger network is specified. Halcon SD developed a process in the 1960’s (Kochar, et al., 1981) that is used by the process plant supplier Chematur International AB (Chematur AB). Research has been performed and published on the process, i.e. some process data is available (Chematur AB; Kochar, et al., 1981)

Figure 2.4 illustrates an overview of assumed stand-alone ethanol dehydration to ethylene production configuration investigated in the study. The assumed process configuration is based on a literature review. The assumed process configuration is based on background information presented in Chapter 2.2. Ethanol (93 wt%) is assumed to be purchased. Accordingly, for a stand-alone ethanol dehydration to ethylene plant, the incoming ethanol feed is in liquid phase and thus requires vaporisation prior to entering the reactor. A multi-bed adiabatic reactor system consisting of four reactors in series with a SynDol catalyst bed in each reactor is assumed. The feed to each reactor is heated to 450°C in a furnace. Studies have shown that adiabatic reactors show good performance at 11.4 bar (Kochar, et al., 1981). The Braskem ethanol dehydration plant operates its adiabatic reactor at a pressure of 11.93 bar (Valladares Barrocas, et al., 2007). The reactors in the thesis are assumed to operate at 11.4 bar. Superheated steam (11.4 bar) is directly injected to the reactor feed at a 1:1 weight proportion in order to achieve high conversion and selectivity. As reactor dimensions are not considered, the space velocity is assumed to be 0.5 on a water free basis (Kochar, et al., 1981). For more detailed information regarding the reactor design see Section 2.2.2.

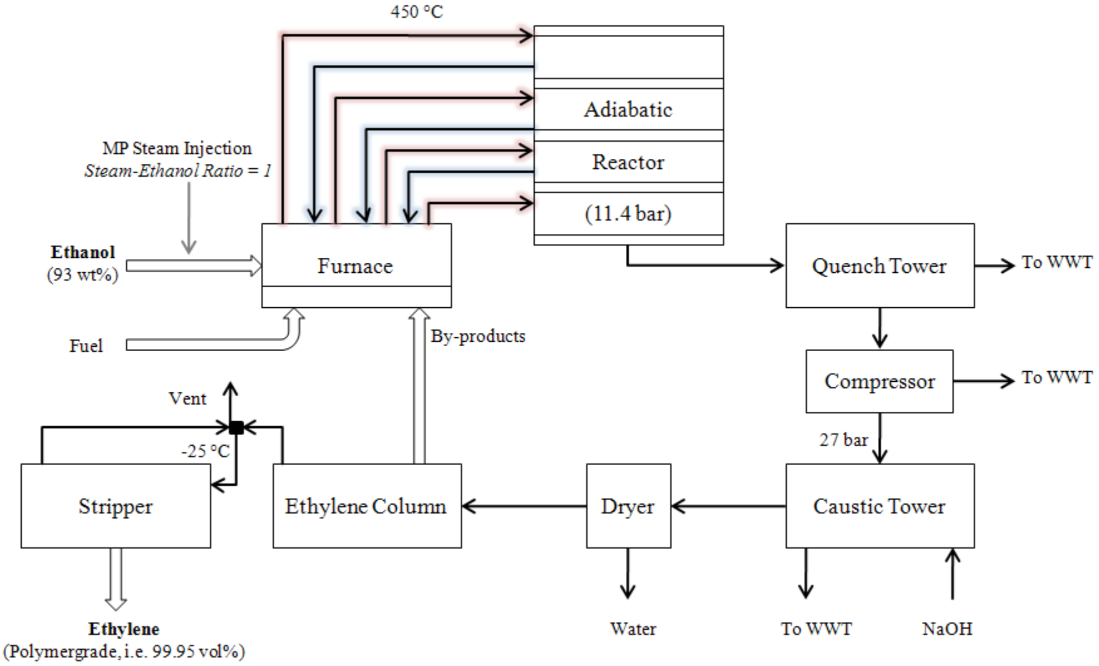

Figure 2.4 Stand-alone ethanol dehydration to ethylene production configuration.

The reactor effluent is cooled with spraying water in the quench tower, consequently water present in the gas is condensed. For more details see Section 2.2.3. It is assumed that there is access to a refrigeration medium allowing a condenser temperature of -25°C in the ethylene column. The operating pressure of the column is therefore set to 24.5 bar. In order to achieve desired operating conditions in the ethylene column, the pressure is increased to 27 bar in a three-stage compressor with a pressure ratio of 3 between inlet and outlet of each stage, for more details see Section 2.2.4.

After purifying ethylene from CO_2 (by absorption in the caustic tower with NaOH) the remaining water is removed in a dryer (i.e. a molecular sieve), for more detailed information see Section 2.2.5 and Section 2.2.6 respectively. The bottom products from the ethylene column (containing heavier by-products) can be used as fuel in the furnace reducing the need for external fuel. The bottom product from the stripper satisfies the product specifications for polymer grade ethylene (i.e. 99.95 vol%

ethylene), see Table 2.3. For further information about the ethylene column and stripper see Section 2.2.7.

2.2.2 Reactor

The reactor is the most important unit in the ethanol dehydration to ethylene process. It is where the conversion of ethanol to ethylene occurs.

2.2.2.1 Catalytic reaction

Ethylene from ethanol dehydration is a catalytic endothermic reaction. Chematur uses a SynDol, i.e. aluminum-oxide, catalyst developed by Halcon SD (Kochar, et al., 1981; Chematur AB). Ethylene (C_2H_4) formation is predominant in temperature regions of 320°C – 500°C, while in temperature regions of 150°C – 300°C the formation of diethyleter ($C_4H_{10}O$) is predominant, see reactions (2.4) and (2.5) respectively (Morschbaker, 2009; Kochar, et al., 1981; Valladares Barrocas, et al., 1980). Consequently, the operating conditions in the reactor are of utmost importance to achieve high selectivity towards ethylene.

$$C_2H_5OH \xrightarrow{cat} C_2H_4 + H_2O \tag{2.4}$$

$$2C_2H_5OH \xrightarrow{cat} C_4H_{10}O + H_2O \tag{2.5}$$

Ethylene can also be formed with diethyleter as an intermediate, see reaction (2.6). This makes the contact time with the catalyst an important parameter in order to achieve the desired product, i.e. ethylene (Valladares Barrocas, et al., 1980).

$$2C_2H_5OH \xrightarrow{cat} C_4H_{10}O + H_2O \xrightarrow{cat} C_2H_4 + H_2O \tag{2.6}$$

At temperatures above 500°C the formation of acetaldehyde, see reaction (2.7), increases (Kochar, et al., 1981). As a result the ethylene selectivity is reduced.

$$C_2H_5OH \xrightarrow{cat} C_2H_4O + H_2 \tag{2.7}$$

Additional reactions occurring during ethanol dehydration are the formation of by-products, such as propene (C_3H_6), buthylene (C_4H_8), ethane (C_2H_6), carbon monoxide (CO) and carbon dioxide (CO_2). High ethanol conversion (up to 99.9%) and high selectivity towards ethylene (94.5-99%) can be achieved operating at the right reactor conditions (Valladares Barrocas, et al., 1980; Kochar, et al., 1981).

2.2.2.2 Adiabatic versus isothermal reactors

As mentioned in Section 2.2.2.1, the ethanol dehydration reaction is endothermic and the product formation is highly temperature dependent. Therefore the operating temperature is required to be kept in a certain range in order to govern the selectivity towards ethylene. This can be achieved with either adiabatic or isothermal reactors.

Isothermal reactors operate with a circulating heating fluid outside the reactor supplying heat and maintaining the temperature in the reactor. Commercial heating fluids have a maximum working temperature of approximately 370°C, due to thermal decomposition (Kochar, et al., 1981). As a concequence the reactor is limited to relatively low operating temperatures, resulting in reduced ethanol conversion and ethylene selectivity (Morschbaker, 2009; Kochar, et al., 1981). To provide sufficient heat to the reactor, i.e. maintain the temperature, the area is increased by introducing a tube-package. The large number of tubes will increase the capital cost for the reactor (Valladares Barrocas, et al., 1980).

Operating with adiabatic reactors, the heating fluid outside the tubes is avoided. This will enable operating temperatures above 370°C. Thus the reactor inlet temperature can reach temperature regions of 450°C – 500°C (Kochar, et al., 1981; Morschbaker, 2009). The reactor can consist of one reactor or several in series or in parallel. The process used by Chematur International AB uses four tubular adiabatic reactors connected in series. Since the reaction is endothermic the effluent from each reactor requires reheating before entering the subsequent reactor. If the temperature is kept within an appropriate range, high ethanol conversion and high ethylene selectivity will be obtained. Additionally, higher selectivity towards ethylene results in lower production of by-products which require removal downstream in the process in several purification steps. The capital cost for adiabatic reactors is comparatively lower than for isothermal reactors (Kochar, et al., 1981).

2.2.2.3 Reactors operating conditions

The operating conditions of the reactor have a significant effect on obtained conversion and selectivity. The effects of changes of temperature, pressure, steam dilution of feed, and space velocity have been investigated (Kochar, et al., 1981). As already mentioned in Section 2.2.2.1, operating temperature has a significant effect on the ethylene yield. Adequate operating temperature (isothermal reactor) and inlet temperature (adiabatic reactor) to maintain high conversion and selectivity in/throughout the reactor is important. Ethanol conversion and ethylene selectivity decreases with increasing pressure. The effect is stronger in lower temperature regions (Kochar, et al., 1981). Figure 2.5 illustrates the effect of temperature and pressure on ethylene yield operating with a Syndol catalyst and at a fixed space velocity of 0.8.

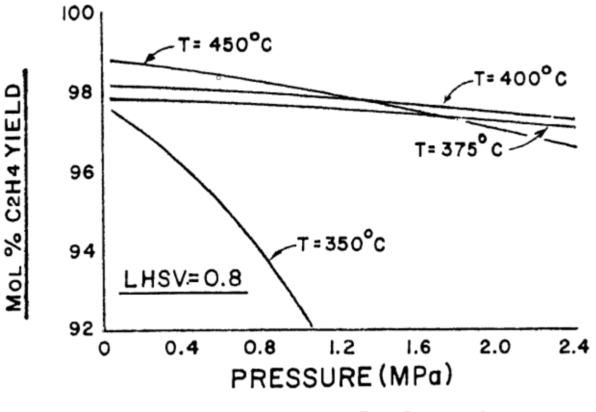

Figure 2.5 Temperature [°C] and pressure [MPa] effect on ethylene yield operating with a Syndol Catalyst at a fixed space velocity of 0.8. (Kochar, et al., 1981)

It has been shown that steam addition to reactor feed has a positive effect on conversion and selectivity in temperature regions above 375°C (Kochar, et al., 1981). Steam acts as a heat carrier. In an adiabatic reactor steam injection reduces the temperature gradient. As a result the amount of catalyst required is reduced and the formation of by-products (such as diethyleter) is reduced. Additionally a lower frequency of catalyst regeneration is required due to less coke formation and the catalyst lifetime increases (Morschbaker, 2009; Valladares Barrocas, et al., 1980). However, the addition of steam results in higher heating demand if operating with several adiabatic reactors (in e.g. series) when reheating the effluent of the reactors.

The contact time with the catalyst has a significant effect on the selectivity towards ethylene. The selectivity towards ethylene is decreased with increasing space velocity, see reaction (2.6).

2.2.2.4 Furnace

A furnace provides sufficient heat to the reactor(s) to enable desired operating temperature.

2.2.3 Quench tower

In the quench tower, water present in the reactor effluent stream is condensed by cooling the entering gas with spray water from the top of the tower. The liquid, in the bottom of the tower contains condensed water, impurities, and unconverted ethanol (Winter, et al., 1976). A fraction of the bottom product is cooled and recirculated back as spray-water, while the remainder is sent to the wastewater treatment.

2.2.4 Compressor

The gas stream leaving the quench tower mainly consists of ethylene. In order to enable sufficient pressure through downstream units the gas is compressed in a multi-stage compressor. Between each compressor stage an intercooler and a knock-out drum is placed, removing some of the remaining water. Literature states outlet pressures from the last compressor between 20-29 bar (Kochar, et al., 1981; Huang, 2010). The outlet pressure is set to obtain desirable operating temperature in the downstream ethylene column condenser.

2.2.5 Caustic tower

In the caustic tower CO_2 is absorbed by washing the gas with sodium hydroxide (NaOH) in a packed column. The final ethylene product needs to fulfill the product specification of maximum 10 vol-ppm CO_2 in order to enable polymerisation (Kochar, et al., 1981). On top of the caustic tower a water wash is placed spraying water on the gas. As a result the sodium hydroxide is washed out.

2.2.6 Dryer

The remaining water is removed in a dryer. The incoming gas is first cooled prior entering a molecular sieve. The gas leaving the dryer contains zero or close to zero moles of water.

2.2.7 Ethylene column and stripper

After the dryer, heavier impurities are removed in a cryogenic distillation column. The ethylene column, also referred to as the C_2-splitter, essentially separates ethane from ethylene. The light key component is ethylene and the heavy key component is ethane. The operating temperature for the column is restricted by available cooling medium.

The bottom product consists of heavier carbohydrates, ethanol, diethyleter, and acetaldehyde, which e.g. can be used as fuel. The condenser serves as a joint condenser for both ethylene column and stripper (Chematur AB). In the stripper carbon monoxide (CO), methane (CH_4), and hydrogen (H_2) are separated from ethylene. To minimise ethylene losses the top product of the stripper is sent to the joint condenser. In the condenser the light by-products separated in the stripper is vented to air while the condensed phase (containing mainly ethylene) is recirculated to ethylene column and stripper.

The final ethylene product has to meet certain purity specifications prior to polymerisation, i.e. it must be of polymer grade (which means having a purity of 99.85 – 99.95 vol% ethylene (Kochar, et al., 1981). Acceptable impurity levels are shown in Table 2.3. This requirement must be achieved in order to obtain desirable product qualities and also because the PE-catalyst is oxygen sensitive.

Table 2.3 Polymer grade ethylene (Kochar, et al., 1981).

Component	**Composition**
Ethylene (vol%)	99.95
Carbon Monoxide (vol ppm)	5
Carbon Dioxide (vol ppm)	10
Ethane (vol%)	0.05

2.3 Biorefinery - Ethylene production from lignocellulosic feedstock

The heat integration potential of a stand-alone lignocellulosic ethanol production via fermentation route plant and a stand-alone ethylene production through catalytic dehydration of ethanol plant is investigated in the thesis. Figure 2.6 shows an overview of the main material and energy flows in the two separate systems.

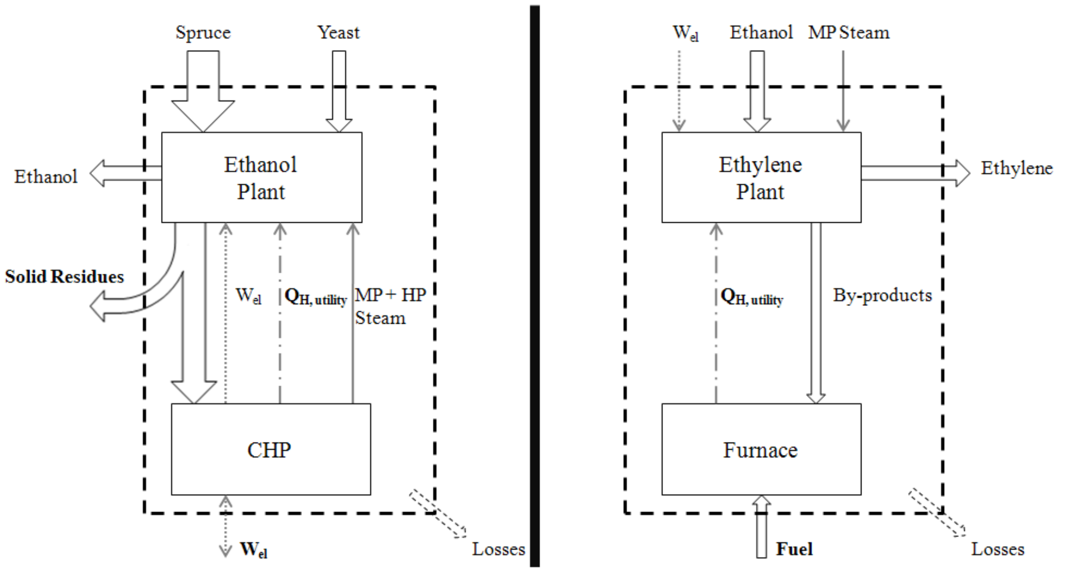

Figure 2.6 Overview of material (black and solid grey arrows for material and steam for direct injection respectively) and energy (dotted and dashed grey arrows for electricity and hot utility respectively) streams in the stand-alone lignocellulosic ethanol production plant (left) and the stand-alone catalytic ethanol dehydration to ethylene production plant (right).

The integration effects (e.g. energy savings by internal heat exchange (HEX), minimum hot and cold utility demand, possible excess solid residues and/or external fuel purchase, and net electricity production/demand) of combining the two separate systems into a biorefinery producing ethylene from lignocellulosic raw material are investigated in the thesis. Figure 2.7 shows an overview of main material and energy flows in the biorefinery.

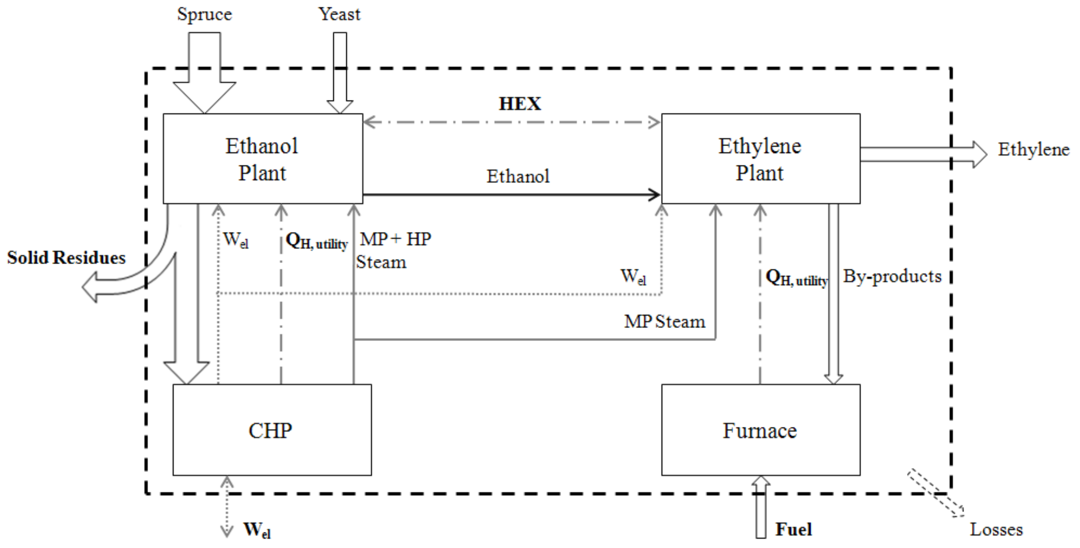

Figure 2.7 Overview of material (black and solid grey arrows for material and steam for direct injection respectively) and energy (dotted and dashed grey arrows for electricity and heat exchange or hot utility respectively) streams in the combined biorefinery, i.e. ethylene production from lignocellulosic feedstock via the fermentation route.

2.4 Chemical cluster

The biorefinery is assumed to be located in conjunction with the largest chemical cluster in Sweden. A Total Site Analysis (TSA) study of the cluster has shown that the cluster, after site wide energy efficiency measures, has an overall hot utility deficit of 62 MW (Hackl, et al., 2010). The hot utility deficit can be covered with externally generated VHP (41 bar) steam. The possibility to integrate the biorefinery with the cluster is investigated in the thesis.

As can be seen in Figure 2.8 one opportunity to integrate the biorefinery with the chemical cluster is to increase the capacity of the CHP plant. The integration opportunity is investigated by estimating if the amount of excess solid residues (after utilisation for covering direct steam injection- and hot utility demand of the biorefinery) can produce adequate VHP steam to cover the hot utility deficit in the chemical cluster (i.e. 62 MW). In Figure 2.8 it can also be seen that ethylene from the ethylene plant can be directly transported to the chemical cluster (e.g. to the polymerisation plant) if locating the biorefinery in Stenungsund.

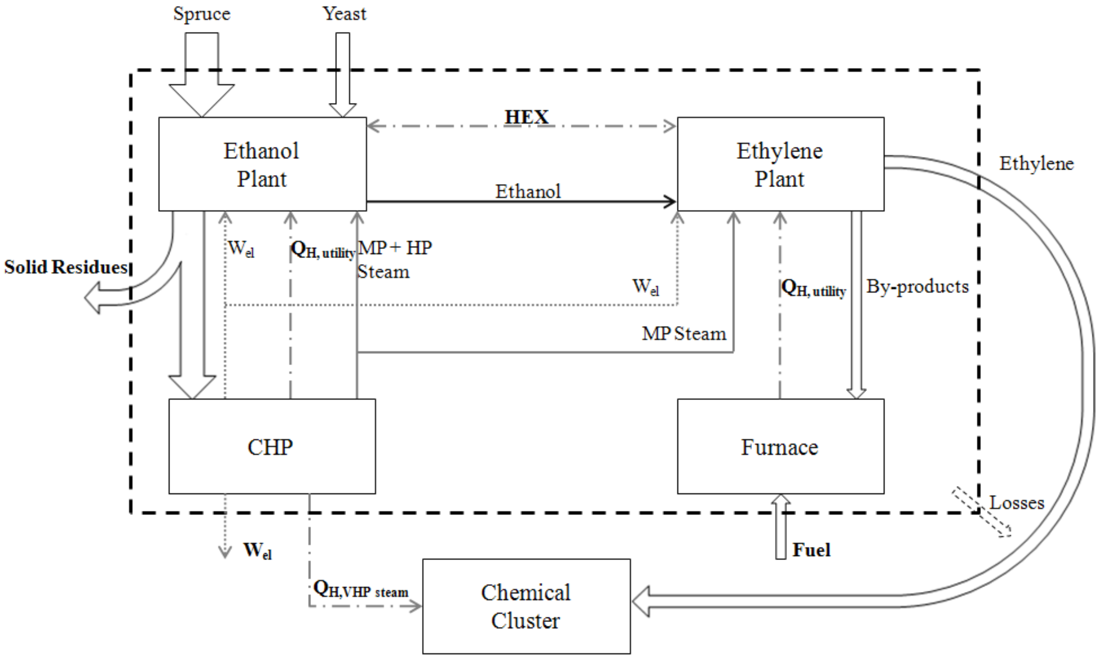

Figure 2.8 Overview of main material (black and solid grey arrows for material and steam for direct injection respectively) and energy (dotted and dashed grey arrows for electricity and heat exchange or utility respectively) streams when integrating the biorefinery with the chemical cluster.

3 Methodology

A literature study was conducted in order to establish a simulation model for a stand-alone ethanol from lignocellulosic feedstock (via fermentation route) production plant and a stand-alone ethanol dehydration to ethylene plant. The study of the two stand-alone processes is based on the production assumption of 200 000 tonnes ethylene annually. Material- and energy balances for the two separate processes are solved in the commercial flowsheeting software Aspen Plus from Aspen Technology. From simulation results obtained a process integration study is conducted based on pinch analysis. The heat integration potential of a stand-alone ethanol production plant and a stand-alone ethylene production plant are investigated. The energy saving potential of integrating the two stand-alone processes is investigated in a background/foreground analysis. Furthermore the effects (e.g. minimum hot and cold utility demand, possible excess solid residues and/or external fuel purchase, and net electricity production/demand) of integrating the two processes into a biorefinery producing ethylene from lignocellulosic feedstock are also investigated. Several biorefinery configurations are investigated; e.g. the integration opportunity for the biorefinery (i.e. ethylene production from lignocellulosic feedstock) to deliver VHP steam, by increasing the CHP plant capacity, to the chemical cluster.

3.1 Stand-alone lignocellulosic ethanol production simulations in Aspen Plus

The NRTL property method with Henry components is used in the ethanol production simulations recommended by guidelines in Aspen Plus. The NRTL property method is recommended for e.g. liquid phase reactions and azeotropic alcohol separation. The property method uses Henry's law for vapor-liquid binary interactions.

3.1.1 Components

The composition for spruce in Table 2.1 is used as feedstock composition in the simulations, see Section 2.1.1.1. Some of the materials included in the process are water insoluble and are only present in solid state and do not participate in liquid-liquid or vapor-liquid equilibriums. To enable handling of solid material in the system two substreams are used: one vapor-liquid stream (MIXED) and one solid stream (CISOLID).

Some of the materials involved in the ethanol production do not exist in the conventional databanks in Aspen Plus. In order to obtain the required physical properties of the materials to enable mass- and energy balance calculations data are taken from a NREL database for biofuel component (Wooley, et al., 1996). Examples of materials including in the legacy databank are cellulose, xylan, and lignin. HMF and soluble lignin are not included in the database and are added as user defined components. Examples of required specified data are chemical formula, boiling point, and coefficients to the Extended Antoine vapor pressure equation and the Ideal gas heat capacity equation. For more details see Appendix B.

The hexosans glucan, mannan, and galactan are assumed to have the same properties as cellulose (Wooley, et al., 1996; Aden, et al., 2002). The pentosans xylan and arabinan are assumed to have the same properties, hence arabinan is modeled as xylan (Wooley, et al., 1996; Aden, et al., 2002). Wood also consists of extractives. The extractives are assumed to have the composition of “Others” in Table 2.1 (see Section 2.1.1.1) and are modeled as one volatile (α-pinene) and one non-volatile (oleic acid) component (Sassner, 2007). Ash is assumed to consist of CaO (Sassner, 2007). Initially all wood components, with the exception of extractives, are in solid state. The moisture content of wood is assumed to be 50% (Wingren, et al., 2003).

3.1.2 Pretreatment

A two step dilute acid steam pretreatment is modeled. In the first step wood is impregnated with dilute sulphuric acid, a concentration of 0.5 wt% based on moisture content in wood is used (Söderström, et al., 2005). The acid-impregnated wood is steam pretreated with saturated MP (13 bar) steam in order to obtain the required conditions in the first pretreatment reactor, i.e. 190°C (Wingren, et al., 2004). In the first pretreatment reactor mainly hemicellulose is hydrolysed. The first pretreatment reactor is modeled as a stoichiometric reactor (RStoic). The reactions that are assumed to occur in the first pretreatment reactor are presented in Table C1 in Appendix C.

In order to reduce the steam consumption in the second pretreatment step the pressure of the pretreatment slurry is retained (Monavari, et al., 2009). Thus, the subsequent solid-liquid separation and washing steps are performed under pressure. The filter cake is washed with recirculated evaporator condensate. The washed solid phase is sent to the second pretreatment step. The filtrate is flashed to atmospheric pressure before being sent to the SSCF step. The flash vapor is sent to wastewater treatment. The separator is assumed to be a press in which the resulting solid cake consists of 55 wt% solids with 99.5% insoluble solid recovery (Aden, et al., 2002). A wash water to feed ratio of 0.58 is assumed to remove 95% of the solubilised hemicellulose sugars from the solid cake (Aden, et al., 2002).

In the second pretreatment step the slurry is impregnated with dilute sulphuric acid, 1 wt% based on moisture content of the wood (Söderström, et al., 2005). Higher severity is required to make cellulose accessible for enzymatic hydrolysis, hence the slurry is treated with saturated HP (20 bar) steam to reach 210°C (Söderström, et al., 2005). The second pretreatment reactor is modeled as a stoichiometric reactor (RStoic). The reactions that are assumed to occur in the second pretreatment reactor are presented in Table C2 in Appendix C.

The resulting slurry in the second pretreatment reactor is flash-cooled by pressure reduction in two steps before it is sent to the SSCF step (Wingren, et al., 2004). As a consequence latent heat can be recovered at two levels, 4 bar and 1 bar respectively. Figure 3.1 shows the pretreatment simulation flowsheet.

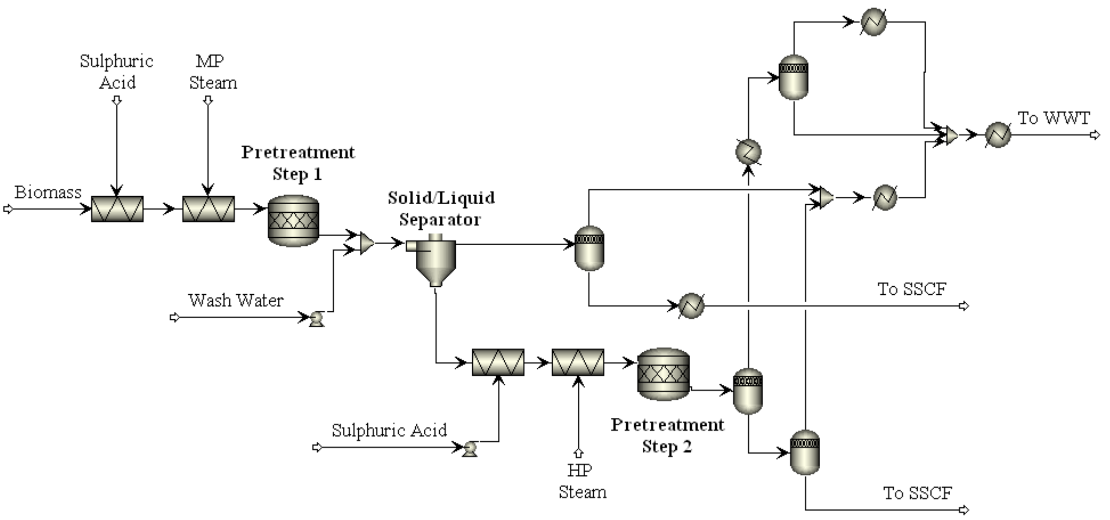

Figure 3.1 Flowsheet for the pretreatment steps in the ethanol production. MP – saturated 13 bar steam, HP – saturated 20 bar steam.

3.1.3 Simultaneous Saccharification and Co-Fermentation (SSCF)

The cellulose hydrolysis and fermentation of both hexoses (C6) and pentoses (C5) are assumed to occur simultaneously (i.e. SSCF). However, the pentose conversion to ethanol is comparatively lower. The filtrate from the solid-liquid separation after the first pretreatment is mixed with the resulting slurry from the second pretreatment. The mixture is diluted with recycled evaporator condensate to a water insoluble solids (WIS) concentration of 11.2% (Aden, et al., 2002). Purchased enzymes (20 kg/t(C5+C6) (Fornell, 2010)) and yeast (2.5 g/L (Sassner, et al., 2008)) are added, they are assumed to have the physical properties of cellulase and zymo respectively in the legacy databank (Wooley, et al., 1996). Cellulases and yeast are assumed to be able to handle the possible inhibitors formed in the pretreatment, hence no detoxication (with e.g. solid lime resulting in a solid disposal of gypsum) is necessary prior to SSCF (Franzén, 2010). The SSCF process is conducted under atmospheric pressure and 35°C (Galbe, et al., 2002). The reactions taking place in the SSCF-reactor are exothermic, hence the unit has a certain cooling demand. In order to make the simulation dynamic and to simplify process configuration changes etc, the hydrolysis and fermentation are divided into two separate reactors in the simulation. Both unit steps are modeled as stoichiometric reactors (RStoic). A 94 wt% conversion of glucan to glucose is assumed during hydrolysis (Wingren, et al., 2008). The sugar conversion reactions that are assumed to occur during SSCF are presented in Table C3 in Appendix C.

During fermentation carbon dioxide (CO_2) is formed. In reality the CO_2 is vented from the fermentation reactor. However, in the simulation the major part of CO_2 is separated in a gas-liquid separator, i.e. a flash. Figure 3.2 shows the SSCF simulation flowsheet.

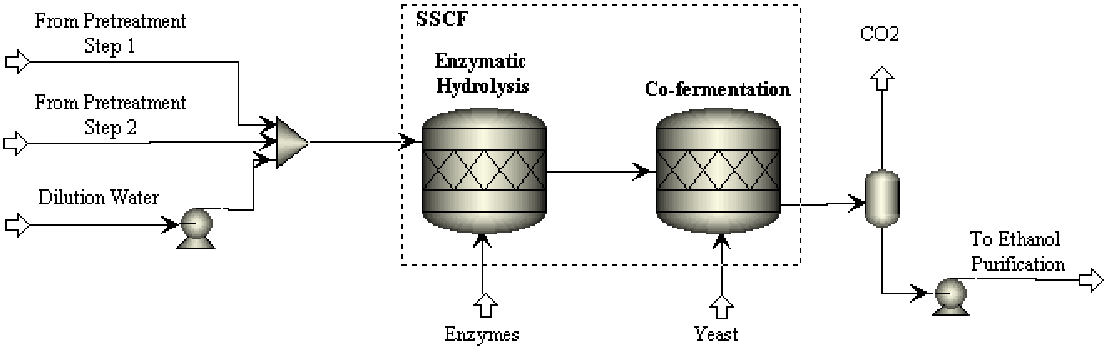

Figure 3.2 Flowsheet for the simultaneous saccharification and co-fermentation (SSCF) unit.

3.1.4 Product purification

The fermentation broth is preheated to 100°C before entering the beer column in stage 2. The beer column is simulated with RadFrac Equilibrium model and strongly non-ideal liquid convergence. The column has 35 trays and operates at a pressure of 1.89 bar (National Renewable Energy Labratory, 2004). The beer column is in reality a stripper. However, in order to enhance the separation most of the remaining CO_2 needs to be removed. Therefore the beer column is run with a partial condenser in the simulation, venting CO_2 (Aden, et al., 2002). A vapor side product stream is extracted on stage 3 and entering the rectifier. The mass recovery of ethanol in the vapor side product stream is set to 99.5% (Sassner, et al., 2008; Aden, et al., 2002). The condenser temperature is specified to 60°C (Aden, et al., 2002). The distillate rate and vapor side stream rate are varied in order to obtain the two specifications. Due to the presence of solids the Murphree efficiency is set to 50% between stage 3 and 34, and 75% on stage 2 (Sassner, 2007). The beer column stillage is sent to a solid-liquid separation prior evaporation and combustion. The separator is assumed to result in a 55 wt% solid cake with 99.5% recovery of insoluble solids (Aden, et al., 2002).

The rectifier is simulated with RadFrac Equilibrium model and strongly non-ideal liquid convergence. The column has 25 trays and operates at 1.7 bar (National Renewable Energy Labratory, 2004). The feed from the beer column enters at stage 23. The Murphree efficiency is set to 75% (Sassner, 2007). For the stand-alone lignocellulosic ethanol production the rectifier is run with a total condenser. The purity of the distillate is specified to 93 wt% ethanol and ethanol mass recovery is specified to 99.5% (Sassner, et al., 2008; Aden, et al., 2002). The ethanol purity is a trade-off with energy demand in the reboiler. The separation of the binary system ethanol and water reaches an azeotrope at around 96% ethanol in vapor phase. However, also other substances are present in the rectifier when producing ethanol from lignocellulosic material which will affect the separation and achievable ethanol purity. The reflux ratio and the distillate rate are varied in order to obtain the two specifications. To enable estimation of the dimensions of the two columns, tray sizing is performed. The simulation flowsheet of the ethanol purification steps are illustrated in Figure 3.3.

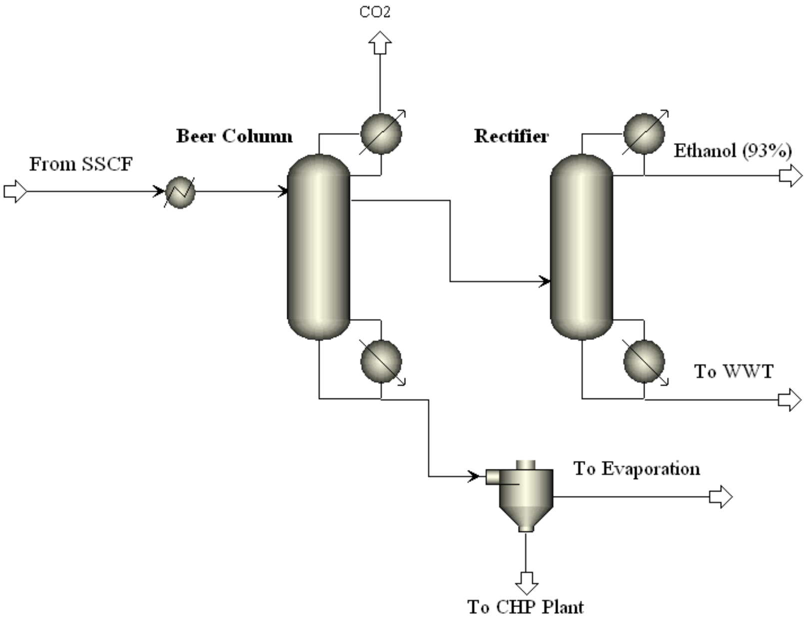

Figure 3.3 Flowsheet of the ethanol purification simulation.

3.1.5 Evaporation

The evaporation unit has two major functions: it concentrates the dissolved combustible compounds and it removes inhibitory compounds from the recirculation water. The liquid fraction of the beer column stillage is sent to a five-effect counter-currently arranged evaporation system. The stillage pressure is gradually reduced in flashes before it enters the last effect, i.e. effect 5. The pressure levels in the flashes are set to match the operating pressure levels in the evaporator effects, thus the latent heat in the vapor streams can be recovered.

No evaporator built-in equipment models are available in Aspen Plus. Hence, the evaporator effects are modeled as one heat exchanger (HeatX) and one flash. The overall heat transfer coefficient is set to Aspen default (850 W/m^2K) in all effects. No boiling point elevation is accounted for. In order to minimise the total heat transfer area of the evaporator train the temperature difference in the effects should be similar. This is achieved by choosing proper pressure levels in the effects. If the temperature difference is too low, there is a risk for very large heat transfer areas. Conversely, if the temperature difference is too large, there is a risk for dryout. Heating medium for the first effect is LP (4 bar) steam. The pressure in the last effect is set to obtain suitable temperature level to condensate the vapor stream with cold utility. The operating pressures for the effects are reported in Table 3.1.

Table 3.1 Operating pressures for the effects in the evaporation system.

Effect	Pressure	Temp
1	1.4	114
2	0.93	99
3	0.6	86
4	0.35	73
5	0.22	62

The steam supply is set to achieve 40% moisture in the resulting evaporation syrup. The evaporate condensate is assumed have adequate quality for recycling. Figure 3.4 shows the flowsheet of the evaporation train simulation.

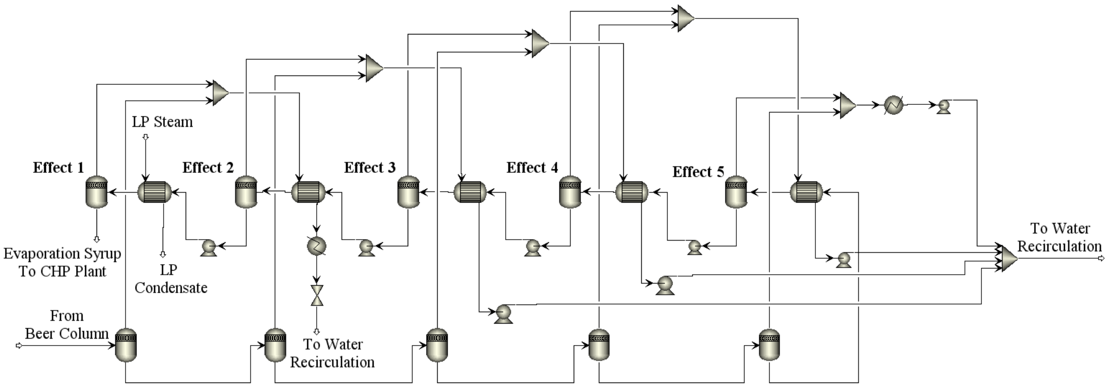

Figure 3.4 Flowsheet of the evaporation train simulation.

3.1.6 Combined Heat and Power (CHP) plant

The concentrated evaporation syrup and the solid fraction of the beer column stillage are fed to the steam boiler as fuel. Bark from the debarking unit is also available as solid fuel. The amount of solid fuel fed to the CHP plant is set to cover steam for direct injection and hot utility demand of the process. The steam boiler is modeled as a stoichiometric reactor (RStoic). The combustion is assumed to be performed at atmospheric pressure and the flue gas temperature is assumed to be 870°C (National Renewable Energy Labratory, 2004). The supplied air is preheated to 205°C (National Renewable Energy Labratory, 2004) and is assumed to be in 20% excess. The reactions assumed to occur are presented in Table C4 in Appendix C.

Cooling of the flue gases to 278°C (National Renewable Energy Labratory, 2004) and 99% of heat of reaction from combustion is used for steam production. The steam boiler is assumed to produce 540°C, 120 bar steam. Further flue gas cooling to 155°C is used in heat integration.

Boiler feedwater make-up and condensate return are preheated to 177°C (National Renewable Energy Labratory, 2004). The steam generation is divided into three sections: economiser (water is heated to saturation), evaporator (evaporation of the saturated water), and superheater (superheating to 540°C). The steam production is modeled with heat exchanging (HeatX) between flue gases and steam. The superheated steam is expanded to 4 bar in a turbine. An isentropic efficiency of 0.9 and an electrical efficiency of 0.97 are assumed. Steam required for direct injection in first and second pretreatment steps in the ethanol production are extracted at 13 bar and 20 bar respectively. Direct injection steam for the pretreatment steps are desuperheated with condensate, for which flow rates are designed to produce a specific amount of saturated steam at its respective pressure.

Accordingly, hot utility steam can be supplied at 20, 13, and 4 bar to the process. The possibility of varying the amount of electricity produced and heat delivered is enabled by a letdown system by-passing the turbine. Produced steam as hot utility (e.g. LP (4 bar) steam) is condensed in order to supply the required amount of heat to the process. The condensate is returned to the steam boiler. The feedwater make-up flow rate is designed to produce the maximum amount of steam with the heat available from the steam boiler. That is, the feedwater compensates for the extracted direct injection steam in the turbine and for the condensate required for desuperheating. Figure 3.5 illustrates the flowsheet of the Combined Heat and Power (CHP) plant simulation.

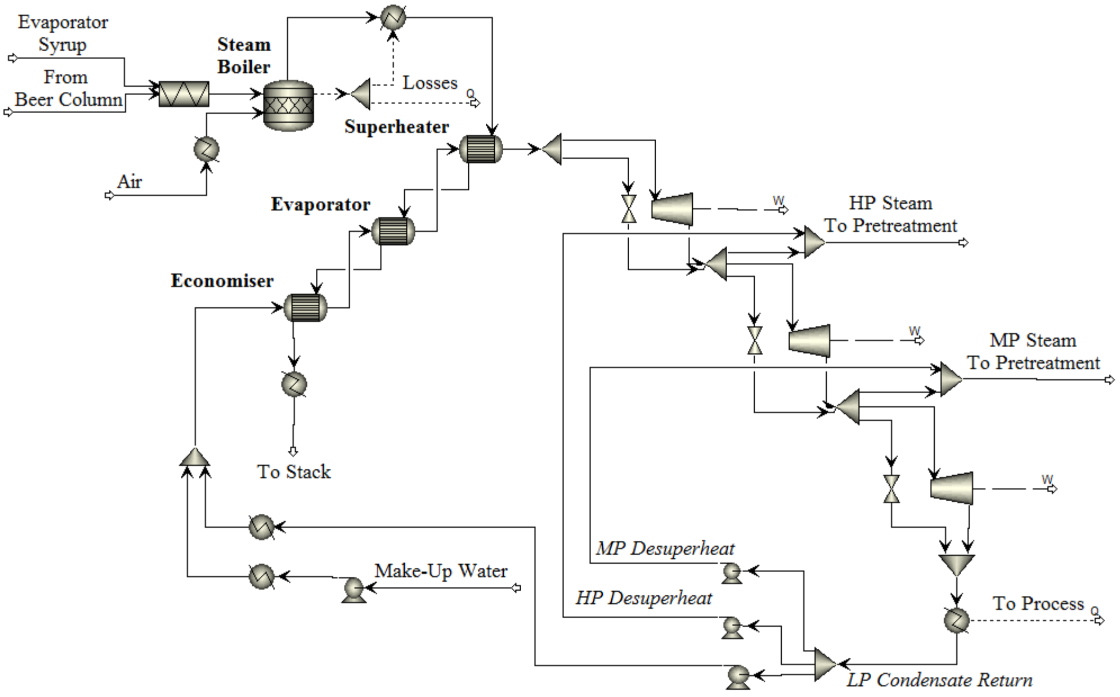

Figure 3.5 Flowsheet of the Combined Heat and Power (CHP) plant simulation.

3.2 Stand-alone ethanol dehydration to ethylene production simulations in Aspen Plus

The Peng-Robinson property method is used in the ethanol dehydration simulations recommended by guidelines in Aspen Plus. The Peng-Robinson property method is recommended when handling light hydrocarbons in e.g. an ethylene plant. The separation units in the ethanol dehydration process are considered similar to those in a traditional ethylene production process with naphtha as feedstock. Therefore the Peng-Robinson property method is chosen for all non-electrolyte systems in the process.

3.2.1 Components

The physical properties for relevant components are acquired from the conventional database in Aspen Plus. No solid substances are present in the ethanol dehydration process, thus no solid substream (CISOLID) is used. In the simulation only a mixed substream (MIXED), handling liquid and vapor, is present.

3.2.2 Adiabatic reactor

Ethanol (93 wt%) is delivered to the ethylene plant in liquid phase. The pressure is increased to reactor operating conditions (i.e. 11.4 bar) and vaporised. Superheated steam (11.4 bar) is direct injected into the ethanol feed. The temperature is increased to its specified value (i.e. 450°C) before entering the ethylene reactors.

The reactor is assumed to consist of four tubular adiabatic reactors with a catalyst bed in each connected in series, i.e. similar to the design proposed by Chematur International AB. The reactor is modeled with two different types of reactor models: one stoichiometric reactor to obtain the selectivity for the different reactions (i.e. to retrieve the right mass fraction of each component) and one kinetic reactor to achieve a desired temperature profile in each reactor (i.e. to determine the amount of energy needed to be supplied to the reactors). This is performed due to difficulties modeling both aspects in one reactor without defining the kinetics for all reactions occurring in the reactor.

The total ethanol conversion is assumed to be approximately 99.5%. A stoichiometric reactor (RStoic) is used to model the reactions, for more details see Table D1 in Appendix D. The ethanol conversion to each product is varied in order to obtain selectivities within limits reported in the literature, see Section 2.2.2 (Kochar, et al., 1981; Chematur AB; Valladares Barrocas, et al., 1980). As a result the mass fractions for each compound out from the last reactor are obtained.

The tubular kinetic reactor (RPlug) model is used to estimate the temperature drop caused by the endothermic reaction and thereby also the amount of energy required to reheat the effluent from each reactor to the desired inlet temperature, i.e. 450°C. Reaction kinetics for ethanol dehydration to ethylene over an aluminum-oxide catalyst (Stauffer, et al., 1962) is implemented in the reactor using Power-Law kinetic expression. The catalyst mass is varied to obtain an outlet temperature above 375°C from each reactor bed and to achieve a selectivity towards ethylene out from the last reactor corresponding to the result obtained in the simulation with the stoichiometric reactor, i.e. 98.8% see Table D1 in Appendix D. Only kinetics for the dehydration of ethanol to ethylene reaction are used. However, the energy demand in the reactor is assumed to correspond to the energy demand of the ethanol dehydration reaction due to the high selectivity.

The hot effluent from the last reactor is cooled to 84°C. Figure 3.6 represents the flowsheet of the adiabatic catalytic reactors.

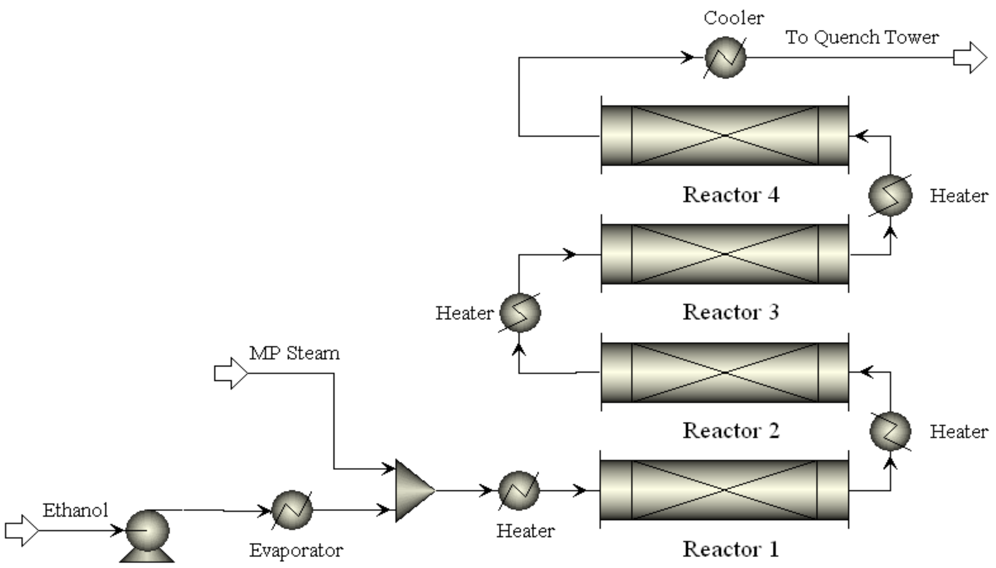

Figure 3.6 Flowsheet of ethanol dehydration to ethylene reactor unit.

3.2.3 Quench tower

The quench tower is simulated with RadFrac equilibrium model. The tower is assumed to have 14 stages and the operating pressure is set to atmospheric pressure. At the top of the tower water (20°C) is sprayed, causing water in the gas to condense. A fraction of the bottom product is cooled to 20°C and recirculated as spray-water. The water recirculation mass flow is designed to obtain a mole fraction of ethylene in the top product of 0.91. The quench tower flowsheet is illustrated in Figure 3.7.

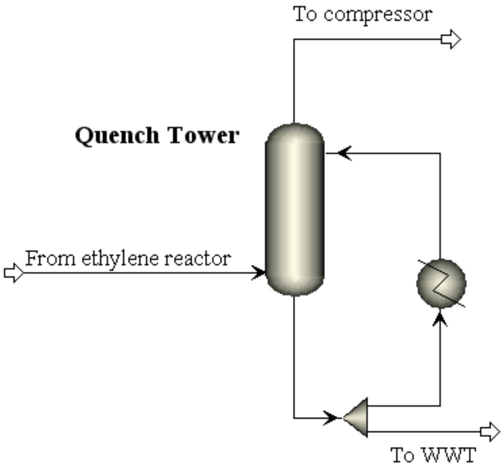

Figure 3.7 Flowsheet of the quench tower simulation.

3.2.4 Compressor

The pressure is increased to 27 bar in a three-stage compressor (isentropic efficiency 72%) each having a pressure ratio of 3, see Figure 3.8. Between each compressor an intercooler cools the gas down to 38°C and condensed water is removed in a knock-out drum, modeled as a flash in Aspen Plus, before entering the subsequent stage.

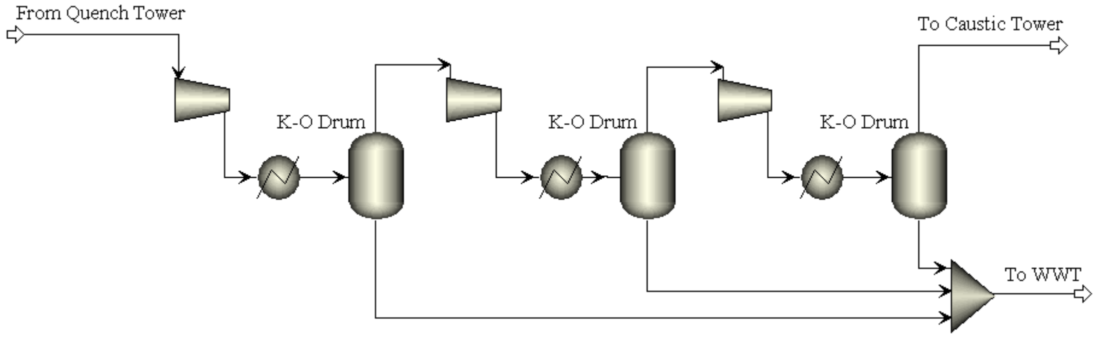

Figure 3.8 Multi-stage compressor flowsheet.

3.2.5 Caustic tower

In the caustic tower sodium hydroxide (50 wt% NaOH) is used to absorb CO_2. In order to obtain plausible results the ELECNRTL property method is used recommended by Aspen Plus guidelines. The ELECNRTL property method is recommended for systems handling versatile electrolyte properties, e.g. in the case of absorption with NaOH in water solution.

The caustic tower is simulated as two separate parts: one modeling the absorption of CO_2 and one modeling the water wash. The reaction between NaOH and CO_2 is simulated in two different steps. First a conventional property package (ECLSCR) models the NaOH dissolution in water. Then the absorption reaction between hydroxide ions (OH^-) and CO_2 is modeled with kinetics obtained from Aspen Plus amine property package. In order to facilitate convergence for the simulation true components are applied and NaOH-recirculation is not included. The absorption tower is modeled as a packed RadFrac kinetic column in order to implement the required kinetics. The tower is assumed to have 8 sections (where each section is 0.6 meter) packed with 25 mm raschig rings. The gas is fed at the bottom of the tower, and NaOH is added at the top. The tower dimensions and NaOH mass flow are varied in order to absorb enough CO_2 to obtain polymer grade ethylene. The dimensions are also varied to avoid flooding and loading in the column.

The water wash is modeled with a RadFrac equilibrium column with 2 stages. The flowsheet of the caustic tower is shown in Figure 3.9.

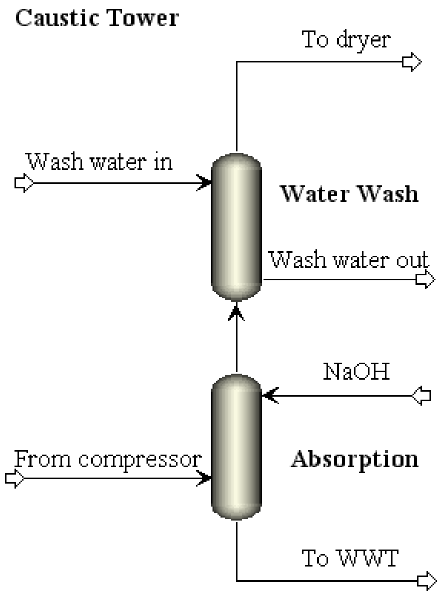

Figure 3.9 Flowsheet of the caustic tower simulation.

3.2.6 Dryer

The remaining water is removed in a dryer, i.e. a molecular sieve. The stream is cooled to 15°C before entering the dryer. The dryer is modeled with a separation unit splitting water from the incoming stream, see Figure 3.10. Regeneration of the dryer is not taken into consideration.

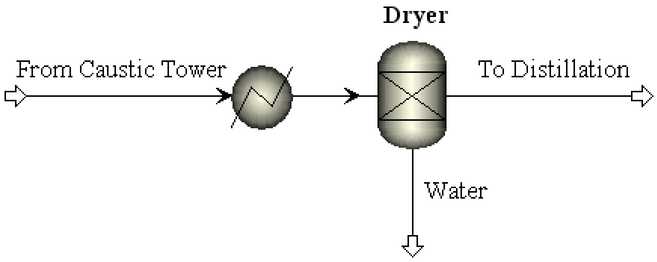

Figure 3.10 Flowsheet of the dryer simulation.

3.2.7 Ethylene column and stripper

After drying the stream is cooled to saturation before entering the ethylene column (also referred to as the C2 splitter). The ethylene column is modeled as a RadFrac equilibrium column with cryogenic algebra calculations (due to the low condenser temperature, -25°C) and with partial condenser. The Murphree efficiency is set to 75%. The column has 84 stages and a pressure drop of 2.5 bar through the column is assumed. The column is specified to have 99.1% mass recovery of ethylene and maximum 0.041 mol% ethane in the distillate. The column specifications are obtained by varying the reflux ratio and bottoms rate.

The stripper is modeled as a RadFrac equilibrium column with a Murphree efficiency of 75%. The stripper has 20 stages and a pressure drop of 2.5 bar through the column is assumed. The top product is sent to the joint partial condenser where light by-products are vented and condensed ethylene sent to the stripper and ethylene column, see Figure 3.11. The stripper is designed to have maximum 5 ppm CO in the bottom product by varying the reboiler duty. That is, polymergrade ethylene is obtained in the bottom product of the stripper.

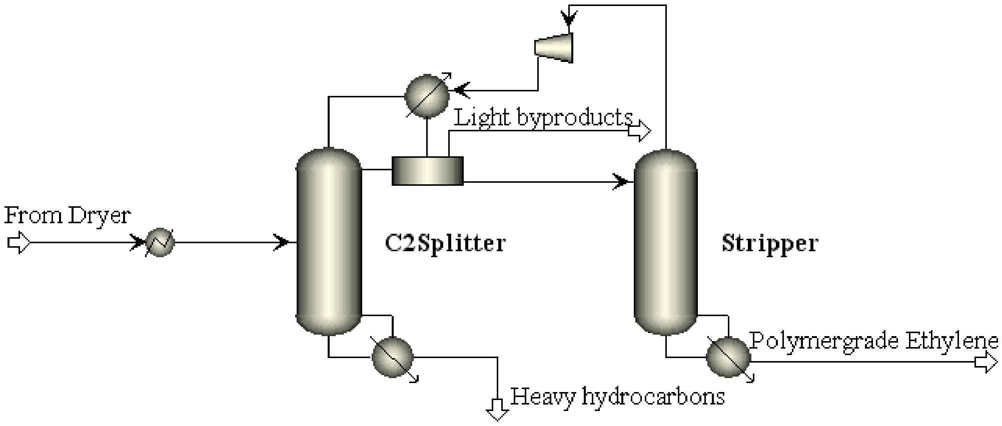

Figure 3.11 Ethylene column (or C2 splitter) and stripper flowsheet.

3.3 Biorefinery - Ethylene production from lignocellulosic feedstock simulations in Aspen Plus

Most process steps in the biorefinery, i.e. ethylene production from lignocellulosic feedstock, are relatively unaffected by the integration of the two plants (i.e. stand-alone ethanol production and stand-alone ethylene production plant). The three major differences are: the change from total to partial condenser on the rectifier column (delivering ethanol in gas phase instead of in liquid phase to the ethylene production plant), the pressure increase of ethanol feed to the ethylene reactor, and the steam extraction requirements at different pressure levels in the CHP plant.

3.3.1 Configuration of rectifier column

When integrating the stand-alone lignocellulosic ethanol production and the stand-alone ethanol dehydration to ethylene production plant into a biorefinery producing ethylene from lignocellulosic feedstock, ethanol is assumed to be delivered directly from the rectifier column in gas phase to the ethylene production plant. Hence, the rectifier condenser is run with a partial condenser and not a total condenser as in the case when studying the stand-alone lignocellulosic ethanol production plant producing liquid ethanol.

3.3.2 Configuration of ethanol dehydration to ethylene reactor

In the biorefinery, ethanol production is assumed to be in direct connection with the ethylene plant. As a consequence ethanol is directly delivered from the rectifier column (in vapor phase) to the ethylene plant. The ethanol (93 wt%) feed is compressed (assumed isentropic efficiency of 72%) to reactor operating conditions (i.e. 11.4 bar). Superheated steam (11.4 bar) is direct injected into the ethanol feed. The temperature is increased to its specified value (i.e. 450°C) before entering the ethylene reactors. Figure 3.12 illustrates the configuration assumed for the stand-alone ethylene production (i.e. purchasing ethanol in liquid phase) and for the biorefinery (i.e. ethanol directly delivered from rectifier column in gas phase).

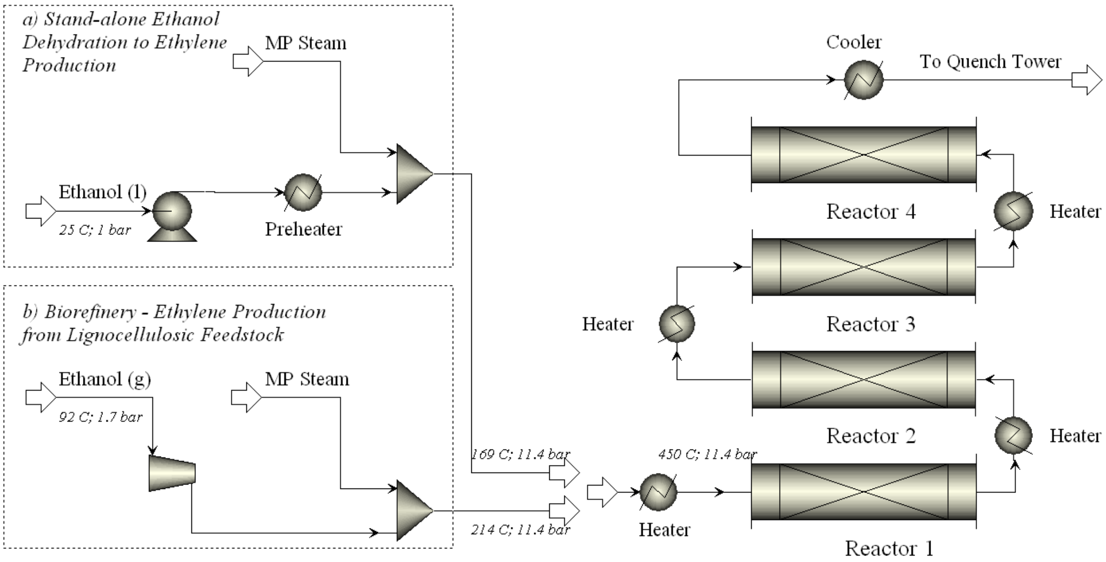

Figure 3.12 Configuration of ethanol dehydration to ethylene reactor unit for a) the stand-alone ethanol dehydration to ethylene (i.e. ethanol feed in liquid phase) and for b) the biorefinery – ethylene production from lignocellulosic feedstock (i.e. ethanol is directly delivered in gas phase from rectifier column).

3.3.3 Configuration of CHP plant

The integration of ethanol- and ethylene production plants into a biorefinery, producing ethylene from lignocellulosic feedstock, affects the steam extraction requirements in the CHP plant. When considering the two processes separately the CHP plant produces sufficient amounts of steam to cover the demand of saturated steam for direct injection in the two pretreatment steps (13 and 20 bar respectively) and hot utility demand of the ethanol production process, see Figure 2.6 for an overview of material- and energy flows in a stand-alone lignocellulosic ethanol plant. Hence, the CHP plant has the opportunity to deliver hot utility steam at 20, 13, and 4 bar respectively. Additionally, the CHP plant has the opportunity to deliver electricity to the stand-alone lignocellulosic ethanol plant.

Superheated steam for direct injection in the ethylene reactor feed and hot utility demand in stand-alone ethylene production process is produced by external fuel, see Figure 2.6 for an overview of material- and energy flows in the stand-alone ethylene production plant. Additionally, the electricity demand of the ethylene plant is required to be produced externally.

When integrating the two processes the solid fuel load (i.e. the combined lignin-rich solid residue and concentrated evaporation syrup) is set to cover the steam demand for direct injection (i.e. saturated steam to pretreatment steps and superheated steam to ethylene reactor feed) and hot utility demand (excluding ethylene reactor furnace fuel demand) of the biorefinery, see Figure 2.7 for an overview of material- and energy flows in the biorefinery. Steam extraction possibilities and hot utility pressure levels are available at 20, 13, and 4 bar respectively in the CHP plant. Hence, superheated steam (11.4 bar) for direct injection in the ethylene reactor feed is extracted at 13 bar. Additionally, the CHP plant has the opportunity to deliver electricity to the biorefinery.

When investigating the effects of integrating the biorefinery with the chemical cluster, i.e. producing VHP steam in the CHP plant, an additional steam extraction possibility at 41 bar is required. Hence, hot utility steam can be supplied at 41, 20, 13, and 4 bar to the process(es). The extracted VHP steam is desuperheated to some extent. Figure 3.13 illustrates the flowsheet of the Combined Heat and Power (CHP) plant simulation with steam extraction requirements for the biorefinery integrated with the chemical cluster. Note that in Figure 3.13 hot utility steam is only extracted and delivered to the process(es) at 4 bar. Hot utility steam can additionally be extracted at 41, 20, and 13 bar, however it is not shown in Figure 3.13.

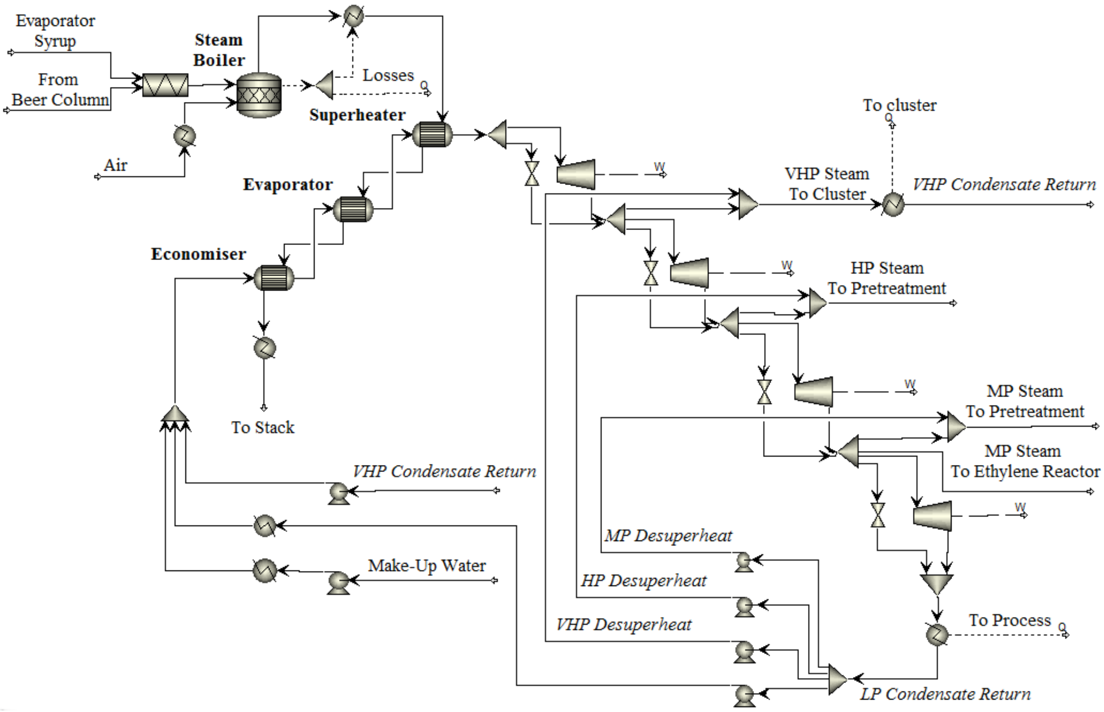

Figure 3.13 Simulation flowsheet of CHP plant with steam extraction requirements for the biorefinery integrated with the chemical cluster.

3.4 Pinch technology

Pinch technology is a systematic energy analysis methodology introduced in the 70's to investigate and analyse the heating and cooling demands of industrial processes. The methodology is based on basic thermodynamic principles, i.e. first and second laws of thermodynamics. Pinch technology investigates and analyses the heat integration potential of processes, i.e. it allows the user to establish targets for the maximum amount of process heat that can be recovered and re-used within a process, as well as the minimum amounts of hot and cool utility that must be supplied to the process. The methodology also provides systematic guidelines for designing heat exchanger networks (to internally recover maximum amount of heat) and investigating utility options (Kemp, 2007).

In a process integration study using pinch analysis thermal data is extracted from the process in order to identify heating and cooling demands of relevant streams. The streams are defined as either hot (require cooling) or cold (require heating). The total energy excess or deficit in different temperature ranges of hot and cold streams respectively can be graphically illustrated in composite curves (CC) where temperature is on the y-axis and enthalpy is on the x-axis, see Figure 3.14.

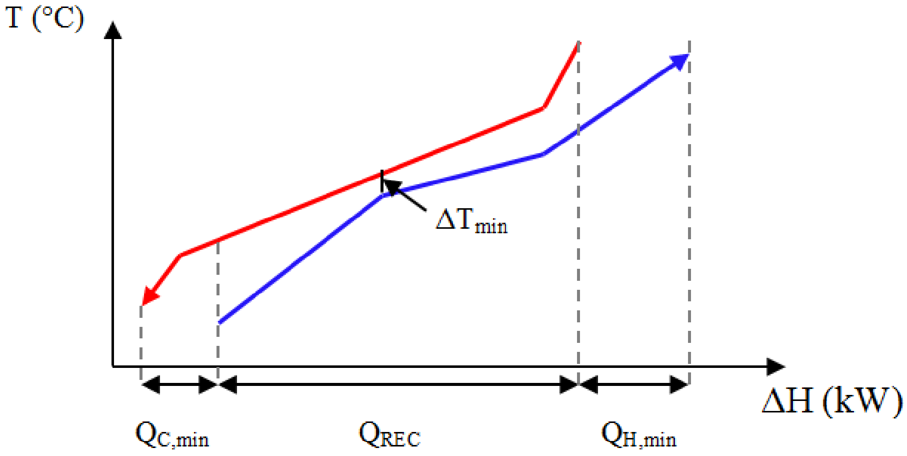

Figure 3.14 Example of hot and cold composite curves (CC), where red streams represents hot streams (require cooling) and blue streams represents cold streams (require heating).

The minimum external hot ($Q_{H,min}$) and cold ($Q_{C,min}$) utility demands of the process, for a specified minimum temperature difference (ΔT_{min}) for heat exchanging, can be identified from the composite curves. Consequently the heat integration potential (Q_{REC}), i.e. the maximum heat recovery through internal heat exchange, can be identified from the composite curves. The point where ΔT_{min} occurs is referred to as the pinch.

The pinch temperature (T_{Pinch}), $Q_{H,min}$, and $Q_{C,min}$ for a specific ΔT_{min} can also be identified if constructing a Grand Composite Curve (GCC), see Figure 3.15. The streams are then handled in interval temperatures (i.e. half ΔT_{min} is subtracted from the real temperatures of a hot stream and conversely half ΔT_{min} is added to the real temperatures of a cold streams) in order to enable minimum approach temperature difference of zero. In each temperature interval the total heat excess or deficit is identified. In a GCC interval temperature is on the Y-axis and enthalpy is on the X-axis. As seen in Figure 3.15 the process has a heat deficit requiring external heating above the pinch and an excess of heat requiring external cooling below the pinch. From the GCC T_{Pinch}, Q_{Hmin}, and Q_{Cmin} of the process can be identified for a given ΔT_{min}.

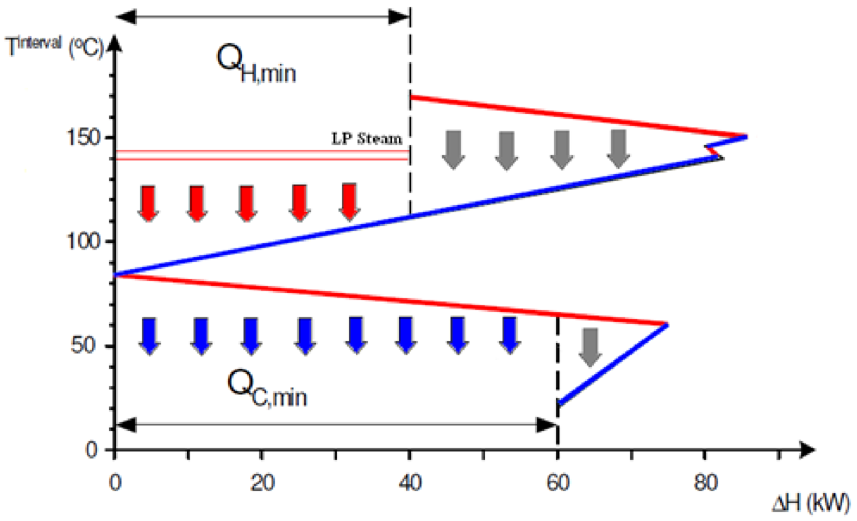

Figure 3.15 Example of Grand Composite Curve (GCC). (Harvey, 2009)

The “pockets” (grey arrows in Figure 3.15) in the GCC represents temperature regions where no external utility is required. Here process streams with excess of heat can be integrated with streams with deficit of heat. In order to obtain minimum external hot- and cold utility consumption for the process it is important to follow the three golden rules of pinch technology:

- Do not cool with external coolers above the pinch
- Do not heat with external heaters below the pinch
- Do not transfer heat through the pinch.

Violating any of these rules will result in an increase of energy consumption. Results from pinch analysis can be used to design a heat exchanger network recovering maximum amount of heat by internal heat exchange.

From the GCC, the utility level(s) required for the process can also be decided. Generally utility levels close to pinch are preferable due to lower cost. The utility can also be divided into several levels if necessary, e.g. having both LP and MP steam levels covering hot utility demand. Condensing steam, which is the most common hot utility, is represented in the GCC as a horizontal line. Examples of cold utility are cooling water (CW) and district heating networks. Cooling water is also represented in the GCC as a horizontal line, due to constraints in temperature rise for discharge.

In order to construct a GCC and determine the minimum hot and cold utility demand for the investigated process the Excel add-in Pro Pi is used. Thermal data are extracted from simulation results. A global minimum temperature difference of 10°C is assumed in the heat integration study.

3.5 Economic evaluation

A rough economic evaluation is performed of the stand-alone lignocellulosic ethanol production, stand-alone ethanol dehydration to ethylene production, and the biorefinery. Capital and operating costs of the two stand-alone processes and the biorefinery are estimated. Additionally, revenues are included to estimate the production costs of ethanol and ethylene respectively through discounted cash flow analysis. The production cost of ethanol and ethylene are estimated by determining the equipment capital cost and operating (fixed and variable) costs of the two stand-alone production plants and the biorefinery. Costs for the lignocellulosic ethanol production are estimated using equipment cost correlations in the literature (Hamelinck, et al., 2005; Aden, et al., 2002; Harvey, 2009) and simulation results. Costs for the ethanol dehydration plant are based on correlations found in the literature (Jones, et al., 2010). The economic evaluation is based on the assumption of 8542[1] operating hours of the biorefinery annually.

3.5.1 Total capital cost estimation

Equipment costs for lignocellulosic ethanol production are estimated according to the capacity power law expression in equation (3.1) (Harvey, 2009).

$$C_E = C_B \left(\frac{Q}{Q_B}\right)^M \qquad (3.1)$$

C_E - Equipment cost for capacity Q
C_B - Base equipment cost for capacity Q_B
M - Scaling factor

Where C_B, Q_B, and M are obtained from the literature (Hamelinck, et al., 2005; Aden, et al., 2002; Harvey, 2009) and Q is obtained from simulation results for each equipment unit respectively. In order to obtain the total capital cost for lignocellulosic ethanol production, an installation factor (accounting for designing, engineering, construction, etc) for each equipment unit (Hamelinck, et al., 2005; Aden, et al., 2002; Harvey, 2009) is multiplied with the corresponding equipment cost. In order to up-date old data obtained from literature in the equipment cost estimation to year 2010 Chemical Engineering (CE) Index is used. Capital costs for storage- and wastewater treatment facility, or pellets production are not included in the estimated total capital cost for lignocellulosic ethanol production. Heat exchangers not included in major unit operations (e.g. distillation reboilers, evaporation boiler, etc) are not accounted for in the capital cost estimation.

Total capital costs for ethanol dehydration to ethylene production are estimated from a power law expression based on plant capacity and data are obtained from the literature (Jones, et al., 2010). The CE Index is used to update literature data to year 2010. An average of a low and high investment scenario and a capacity of 200 000 tonne/year of ethylene are assumed.

Total capital cost for the biorefinery producing ethylene from lignocellulosic feedstock are estimated as the combined costs for the ethanol and ethylene production with corresponding equipment requirements.

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[1] Based on ethylene production rate of biorefinery simulation (i.e. 23.415 tonne/h) and production requirement of 200 000 tonnes ethylene annually.

3.5.2 Operating costs estimation

Operating costs in the economical evaluation consist of fixed (maintenance, administration and insurance, and labour) and variable (e.g. raw material, other required chemicals, and utilities) costs. Annual maintenance costs are assumed to be 4% of total capital cost, and administration and insurance are assumed to be 2% of total capital cost. Lignocellulosic ethanol production is assumed to be operated with 2 shifts, with 10 operators and 1 foreman in each shift (Aden, et al., 2002). The ethanol dehydration to ethylene plant is assumed to be operated with 2 shifts, with 4.7 operators and 1 foreman in each shift (Winter, et al., 1976).

The electricity demand of the stand-alone lignocellulosic ethanol production is scaled from literature data (Hamelinck, et al., 2005). Units such as chipping and debarking, agitators in reactors, and auxiliaries (e.g. the cooling system) are included in the electrical consumption. If sufficient amounts of electricity and steam (both for direct injection and hot utility) are not produced in the CHP plant, they are included as variable operating costs. Other variable operating costs for the lignocellulosic ethanol production (i.e. raw material, enzymes, yeast, other required chemicals, and process water) are estimated from simulation results.

The variable operating costs for catalyst and chemicals in the ethanol dehydration production are assumed to be 6.9 €/tonne ethylene of annual plant capacity after up-dating to year 2010 by price index (Kochar, et al., 1981; Statistiska Centralbyrån). Other variable operating costs for the ethanol dehydration production (i.e. raw material[2], steam, electricity, and fuel) are estimated from simulation results. The cost for providing the stand-alone ethylene plant with cooling water (i.e. the minimum cold utility demand which is not covered by a separate refrigeration system) is estimated as the amount of electricity required to maintain the cooling water flow (i.e. 0.025 $MW_{el}/MW_{heat\ cooled\ with\ CW}$ (Hackl, et al., 2009)) and is therefore included in the total electricity demand of the stand-alone ethylene production. Costs for the separate refrigeration system are not included in the operating costs estimation of the stand-alone ethylene production.

Variable operating costs for the biorefinery producing ethylene from lignocellulosic feedstock include: raw material (i.e. spruce), enzymes, yeast, other required chemicals for the ethanol production, process water, catalyst and chemicals for the ethylene production, and fuel. Additionally, if the CHP plant (firing excess solid residues) cannot produce sufficient amounts of electricity and steam (both for direct injection and hot utility) to cover the demand of the biorefinery, they require purchase and are hence included as variable costs. The cost for providing the biorefinery with cooling water is assumed to be included in the electricity demand of the biorefinery. However, costs for the separate refrigeration system are not accounted for in the operating costs estimation of the biorefinery.

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[2] Assuming ethanol purchase from European producers (i.e. non-softwood feedstock)

3.5.3 Production cost estimation

Sources of revenues are: produced ethylene and co-products such as excess solid residues, electricity, and VHP steam delivered to the chemical cluster. Selling prices for co-products are assumed to be market selling prices. Production cost of ethylene is estimated through discount cash flow analysis. The method used is similar to the method used by National Renewable Energy Laboratory (NREL) (Aden, et al., 2002), i.e the ethylene production cost is obtained when the net present value (NPV) is zero over the lifetime of the plant. Construction time of the biorefinery is assumed to be 2 years. First year of production the biorefinery is assumed to run at 70% of its capacity, second year 90%, and then full production is assumed for a lifetime of 20 years (Aden, et al., 2002). A discount cash flow rate of return of 10% (Aden, et al., 2002) is assumed. No tax on profit is accounted for in this thesis.

4 Results and Discussion

4.1 Simulation results

4.1.1 Stand-alone lignocellulosic ethanol production

Figure 4.1 presents material balance results obtained from the Aspen Plus simulation model of the stand-alone lignocellulosic ethanol production (i.e. the process configuration described in Section 2.1.2). In Figure 4.1 the main energy flows are also represented (e.g. biomass input, direct steam injection requirements in pretreatment, ethanol output, etc).

The load of the lignin-rich solid residues (i.e. combined slurry of the solid fraction from the beer column and the concentrated evaporation syrup) to the CHP plant is set to cover the minimum hot utility demand (112 MW) of the stand-alone lignocellulosic ethanol production obtained in the heat integration study (see Section 4.2.1). The resulting amount of excess solid residues after covering the minimum hot utility and steam for direct injection in the pretreatment steps is estimated at 86 MW, and the co-generated electricity is estimated at 56 MW_{el}, see Figure 4.1.

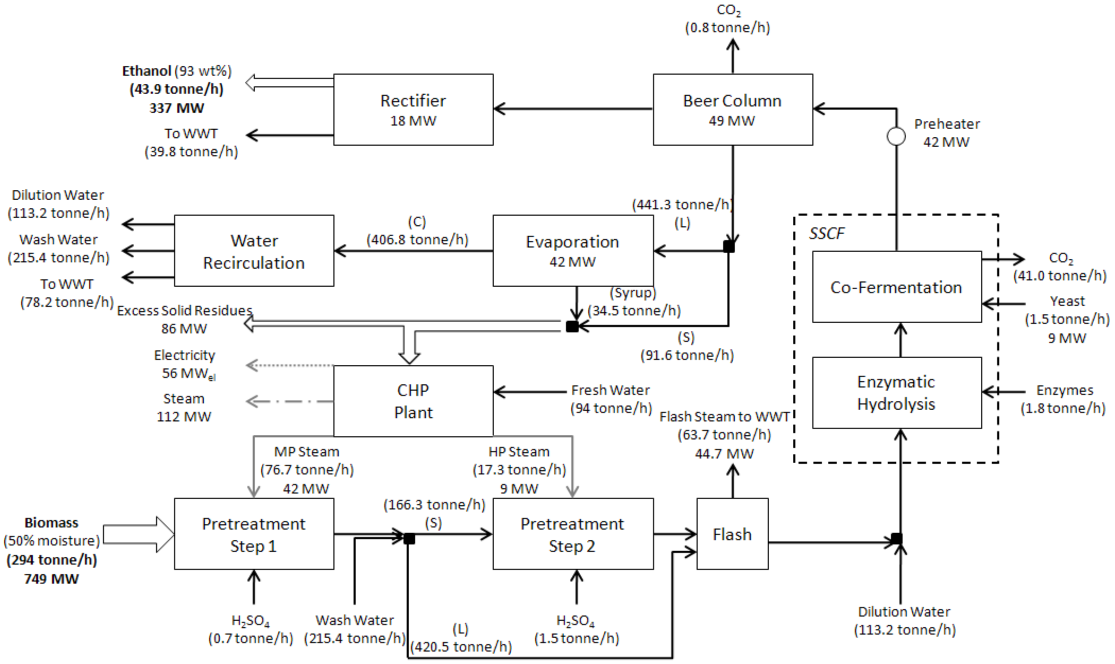

Figure 4.1 Material and main energy balance results for the stand-alone lignocellulosic ethanol production simulation. Energy flows are estimated in Aspen Plus based on High Heating Values (HHV). SSCF – Simultaneous Saccharification and Co-Fermentation, (S) – Solid Fraction, (L) – Liquid Fraction, (C) – Condensate.

In Figure 4.1 the most energy demanding process steps in the stand-alone lignocellulosic ethanol production are represented, which are also summarised in Table 4.1.

Table 4.1 Most energy demanding unit operations in the ethanol production.

Unit Operation	MW	Unit Operation	MW
Pretreatment 1 (MP)	42.1	**Beer column reboiler**	48.8
Pretreatment 2 (HP)	9.1	**Rectifier reboiler**	17.9
Preheater beer column	41.8	**Evaporation**	41.8

Table 4.2 presents key results obtained from simulation of the stand-alone lignocellulosic ethanol production plant. The stand-alone ethanol production plant produces 43.9 tonne ethanol (93 wt%) per hour, which corresponds to a yield of 277.6 kg ethanol per tonne dry wood. As discussed in Section 2.1.5, the theoretical amount of ethanol that can be derived from assumed feedstock composition is 383 kg/tonne dry wood (i.e. 336 kg/tonne dry wood and 47 kg/tonne dry wood from hexoses and pentoses respectively). Hence, the obtained overall ethanol yield (of theoretical) is 72.5%. As mentioned in Section 2.1.6, the ethanol concentration in the beer column feed greatly affects the energy demand of the column (higher ethanol feed concentration results in lower reboiler duty). The obtained ethanol feed concentration to beer column (6.7 wt%) is considered relatively high when handling lignocellulosic feedstock. After combining the solid fraction of the beer column stillage and the concentrated evaporation syrup, a moisture content of 41.8 wt% is obtained.

Table 4.2 Simulation results for the stand-alone ethanol production plant.

Produced ethanol (93%)	43875	kg/h
Ethanol yield (kg ethanol / tonne dry wood)	277.6	kg/tonne
Overall ethanol yield (of theoretical)	72.5	%
Ethanol concentration before beer column	6.7	wt%
Ethanol concentration to rectifier	49.0	wt%
Moisture content of solid residues to CHP plant	41.8	wt%

4.1.2 Stand-alone ethanol dehydration to ethylene production

Figure 4.2 presents material balance results from the Aspen Plus simulation model of the stand-alone ethanol dehydration to ethylene production (i.e. the process configuration described in Section 2.2.1). In Figure 4.2 the main energy flows are also represented (e.g. ethanol input, direct steam injection requirements to reactor feed, ethylene output, etc). It should be noted that the MP steam required for direct injection into ethylene reactor feed need to be produced externally. The required amount of external fuel to the furnace (after firing of by-products) is dependent on the results obtained from the heat integration study (see Section 4.2.2).

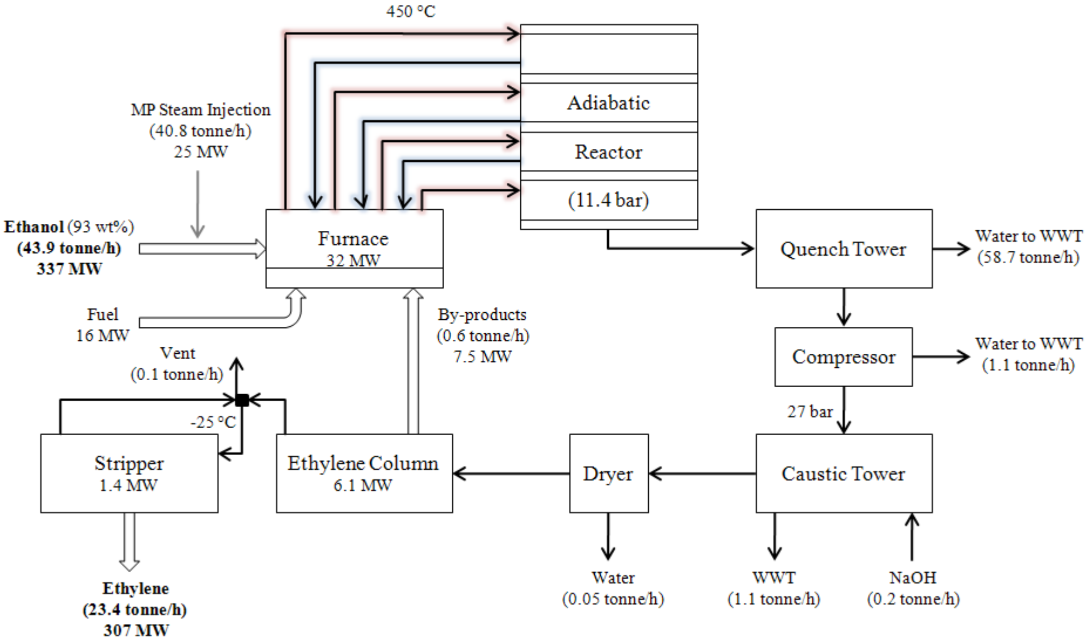

Figure 4.2 Material and main energy balance results for the stand-alone ethanol dehydration to ethylene production simulation. Energy flows are estimated in Aspen Plus based on High Heating Values (HHV).

In Figure 4.2 the most energy demanding process steps in the stand-alone ethanol dehydration to ethylene production are represented, which are also summarised in Table 4.3.

Table 4.3 Most energy demanding unit operations in the stand-alone ethylene production.

Unit Operation	**MW**
Furnace	31.6
Ethylene Column	6.1
Stripper	1.4

Table 4.4 presents key results obtained from simulation of the stand-alone ethanol dehydration to ethylene production plant. The stand-alone ethylene production plant produces 23.4 tonne ethylene (99.95 vol%) per hour (i.e. 200 000 tonne ethylene annually), which correspond to a yield of 0.57 kg ethylene per kg ethanol. It should be noted that the electricity demand for the stand-alone ethanol dehydration to ethylene production (i.e. 4.4 MW_{el}) must be produced externally.

Table 4.4 Simulation results for the stand-alone ethanol dehydration to ethylene production plant.

Produced ethylene (99.95 vol%)	23415.0	kg/h
Ethylene / ethanol yield	0.57	kg/kg
Electricity demand	4.4	MW_{el}

4.2 Heat integration results

Streams with excess or deficit of heat in the ethanol and ethylene production processes are identified. Pinch analysis is conducted of relevant simulation data and a GCC is constructed using a global minimum temperature difference (ΔT_{min}) of 10°C. From the GCC heat integration potential, minimum hot ($Q_{H,min}$) and cold ($Q_{C,min}$) utility demand of the processes are identified. From obtained GCCs required utility levels can be identified.

Steam required for direct injection, i.e. steam to pretreatment steps (42.1 MW and 9.1 MW respectively) and ethylene reactor feed (25.1 MW), are not included in the pinch analysis. This is due to the fact that the respective unit steps cannot be heat integrated by general heat exchanging but direct steam injection is required, i.e. steam is mixed with the process streams. Hence the energy demand for pretreatment and ethylene reactor feed dilution is not included in the resulting $Q_{H,min}$ from the obtained GCCs, i.e $Q_{H,min}$ only refers to the hot utility demand of the processes.

The resulting solid residues from the ethanol production are utilised in the CHP plant to supply steam at various levels to the process. The solid fuel load to the CHP plant is varied in order to cover the steam requirements; $Q_{H,min}$ identified with pinch technology and steam required for direct injection. If considering steam delivery to the chemical cluster an additional 62 MW VHP steam (41 bar) must be produced in the CHP plant. The combined stream of the solid fraction from the beer column stillage and the concentrated evaporation syrup (369.9 MW[3]) is available as solid fuel for steam generation in the CHP plant. In addition, bark from the debarking unit is available as fuel. The resulting heavier by-products from the ethylene column (7.5 MW[4]) in the ethylene production are used to reduce the need of external fuel in the reactor furnace.

Electricity is produced as a co-product in the CHP plant. The electricity production is dependent on the required steam production and is estimated in Aspen Plus. The electricity demand for the ethanol process is 32.1 MW_{el}[5]. Units such as chipping and debarking, agitators in reactors, and auxiliaries (including the cooling system) are included in the electrical consumption. The electricity demand for the stand-alone ethanol dehydration to ethylene production process is 4.4 MW_{el}, of which 3.4 MW_{el} is gathered from simulation results and 1.0 MW_{el}[6] corresponds the electrical consumption to provide the stand-alone ethylene process with cooling water. The electricity demand for the biorefinery is 37.9 MW_{el}, taking the introduction of a compressor (for pressure increase of gaseous ethanol) and the reduction of total cooling water consumption (i.e. assuming that the electricity consumption to provide the biorefinery with cooling water (CW) is included in the electricity demand of the ethanol plant) into account.

4.2.1 Stand-alone lignocellulosic ethanol production

Relevant streams in the ethanol production process, i.e. streams with excess or deficit of heat, are identified (see Appendix E). In order to investigate the heat integration

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[3] Based on HHV of 10.6 MJ/kg obtained from Aspen Plus

[4] Based on HHV of 43.83 MJ/kg (Schnelle, et al., 2002)

[5] Scaled from literature data (Hamelinck, et al., 2005), softwood HHV of 18.3 GJ/tonne dry wood obtained from Aspen Plus

[6] Based on the estimation of 0.025 $MW_{el}/MW_{heat\ cooled\ with\ cw}$ (Hackl, et al., 2009)

potential of the stand-alone lignocellulosic ethanol production, a GCC is constructed, see Figure 4.3. The pinch temperature is 95.9°C using a global minimum temperature difference of 10°C. As can be seen in Figure 4.3 the minimum hot utility ($Q_{H,min}$ of 112.2 MW) demand of the ethanol production process can be covered with LP (4 bar) steam. Minimum cold utility ($Q_{C,min}$ of 147.6 MW) demand is also identified in Figure 4.3.

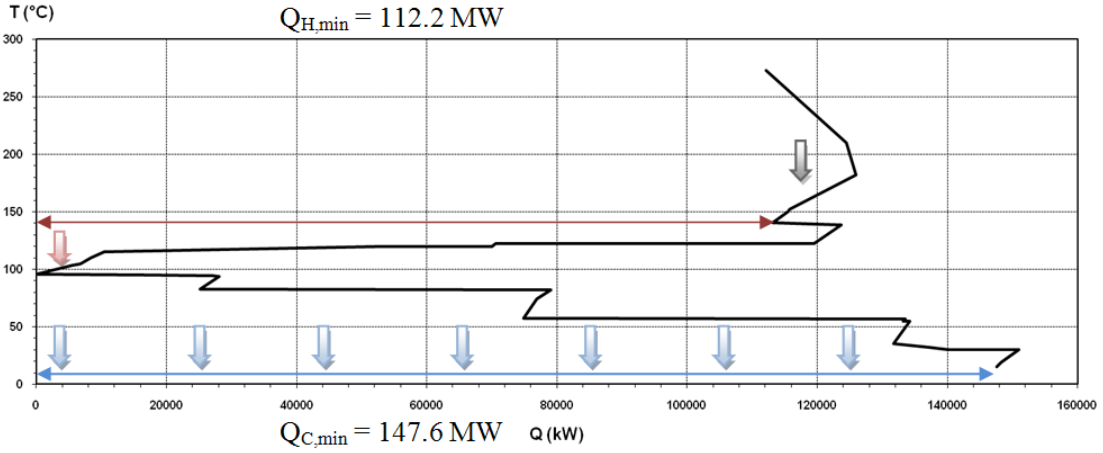

Figure 4.3 GCC for the stand-alone lignocellulosic ethanol production.

The solid fuel load to the CHP plant is set to cover the steam demand of the ethanol production process. It should be noted that steam required for direct injection in the pretreatment steps (42.1 MW MP steam and 9.1 MW HP steam respectively) is not included in $Q_{H,min}$. However, the additional steam production has an impact on the amount of solid residues utilised in the CHP plant, hence also the electricity production. The resulting amount of excess solid residues after covering the minimum hot utility (i.e. LP steam of 112.2 MW) and steam for direct injection in the pretreatment steps is estimated at 86.3 MW. The resulting electricity production in the turbines is estimated at 56.5 MW_{el}, hence after covering the ethanol plant electricity demand (32.1 MW_{el}) the stand-alone ethanol production plant has a net electricity excess of 24.3 MW_{el}. Table 4.5 presents key results obtained for the stand-alone lignocellulosic ethanol production (Stand-alone EtOH).

Table 4.5 Key results obtained for the stand-alone lignocellulosic ethanol production (Stand-alone EtOH).

	$Q_{H,min}$ [MW]	**$Q_{C,min}$ [MW]**	**Excess Solid Residues [MW]**	**Net Electricity [MW_{el}]**	**Net Fuel [MW]**
Stand-alone EtOH	112.2	147.6	86.3	24.3	0

4.2.2 Stand-alone ethanol dehydration to ethylene production

Relevant streams in the ethanol dehydration to ethylene process are identified (see Appendix F) to investigate the heat integration potential of the stand-alone ethylene plant. Figure 4.4 illustrates the obtained GCC. The pinch temperature for the stand-alone ethylene plant is 174°C assuming a global minimum temperature difference of 10°C. From Figure 4.4 the minimum hot utility demand ($Q_{H,min}$ of 18.7 MW) is determined for the stand-alone ethylene production process. From Figure 4.4 it can be seen that the required minimum hot utility demand of the ethylene production must be supplied at relatively high temperatures (due to high operating temperatures in the adiabatic reactors). According to pinch analysis all heat deficits, except for ethylene reactors, can be covered internally in the process through heat integration. The minimum hot utility demand for ethylene production (i.e. utility demand for the adiabatic reactors) is covered by a separate furnace, which after firing by-products from the ethylene column as fuel has an external fuel requirement of 15.9 MW (assuming a furnace efficiency of 80%).

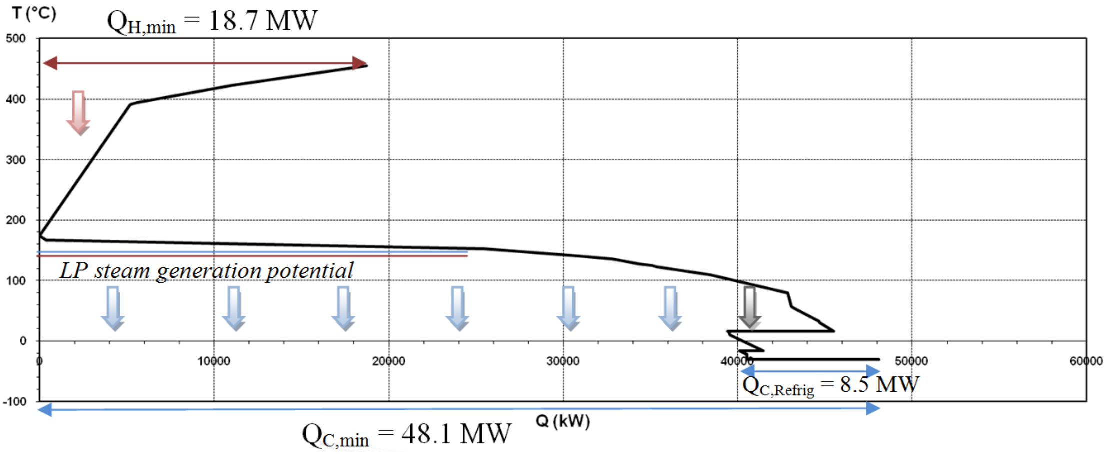

Figure 4.4 GCC for the stand-alone ethanol dehydration to ethylene production.

The total furnace duty obtained from simulations is 31.6 MW, see Section 4.1.2. Pinch analysis indicates that there is a potential to reduce the furnace load by heat integration ($Q_{H,min}$ of 18.7 MW). Identifying individual streams it can be recognised that there is a potential to preheat reactor feed (169°C) with reactor effluent (428°C) without committing any pinch violations in a feed-effluent heat exchanger (FEHX). Implementation of FEHX reduces the furnace load by 12.9 MW (i.e. to 18.7 MW). In Figure 4.4 it can be seen that the stand-alone ethylene production has a potential to produce LP steam (25.6 MW) from waste heat available in reactor effluent (after FEHX).

It should be noted that required steam for direct injection to ethylene reactor feed (25.1 MW MP steam) is not included in $Q_{H,min}$, and must be produced externally. Additionally, the electricity demand for the ethylene production must be produced externally (4.4 MW_{el}).

The minimum cold utility demand ($Q_{C,min}$ of 48.1 MW) can also be identified from Figure 4.4. Cold utility demand can be covered with cooling water to a large extent, however the low operating temperature of the ethylene column (-25°C) requires a separate refrigeration system ($Q_{C,Refrig}$ of 8.5 MW). Table 4.6 presents key results obtained for the stand-alone ethanol dehydration to ethylene production (Stand-alone Ethylene).

Table 4.6 Key results for the stand-alone ethylene production (Stand-alone Ethylene).

	$Q_{H,min}$ [MW]	$Q_{C,min}$ [MW]	Excess Solid Residues [MW]	Net Electricity [MW_{el}]	Net Fuel [MW]
Stand-alone Ethylene	18.7	48.1	-	-4.4	-15.9

4.2.3 Background/foreground analysis of the stand-alone lignocellulosic ethanol production and the stand-alone ethanol dehydration to ethylene production

A background/foreground (BG/FG) analysis is conducted of the stand-alone lignocellulosic ethanol (see Appendix E) and the stand-alone ethanol dehydration to ethylene production (see Appendix F) in order to investigate the heat integration potential, see Figure 4.5.

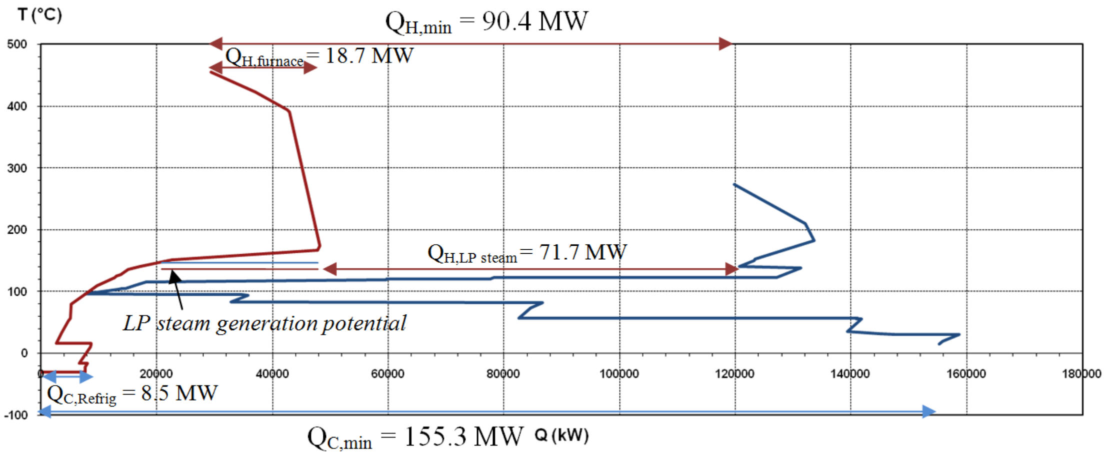

Figure 4.5 Background/foreground analysis of the stand-alone lignocellulosic ethanol (blue) and the stand-alone ethanol dehydration to ethylene (red) production.

The background/foreground analysis indicates that an integration of the two stand-alone processes can result in a minimum hot and cold utility demand of 90.4 MW and 155.3 MW respectively (pinch temperature 95.9 °C). As discussed in Section 4.2.1 and Section 4.2.2 the minimum hot utility demand of the ethanol production plant can be covered with LP steam and the minimum hot utility demand (18.7 MW) of the ethylene reactors is covered by a separate furnace.

Results from the background/foreground analysis indicate that heat integration of the two stand-alone processes does not affect the hot utility demand of the ethylene reactors. Hence, the ethylene reactors has a hot utility demand of 18.7 MW ($Q_{H,furnace}$). As can be seen in Figure 4.5, waste heat in the ethylene production plant has the potential to generate LP steam which can be used to reduce the hot utility demand of the ethanol production plant. Internal heat integration between the stand-alone ethanol and the stand-alone ethylene production plants can additionally reduce the hot utility demand of the ethanol production plant. The results indicate that the CHP plant has a LP steam production requirement of 71.7 MW to cover the remaining minimum hot utility demand ($Q_{H,LP\ steam}$) of the ethanol production plant. The background/foreground analysis indicates that excess of heat in the ethanol production can only be recovered in the ethylene production to a small extent. Hence, the main energy saving opportunity is the recovery of waste heat in the stand-alone ethylene production plant to cover heat deficits in the stand-alone lignocellulosic ethanol production. Note that the heat integration of the two stand-alone processes has an unchanged requirement of a separate refrigeration system of 8.5 MW ($Q_{C,Refrig}$), see Figure 4.5.

In Figure 4.6 the minimum hot and cold utility demand obtained for the separated stand-alone ethanol and stand-alone ethylene production plants are compared with the results obtained when investigating the heat integration potential of the two stand-alone processes using a background/foreground analysis. The results indicate that there is an energy saving potential of 40.5 MW for hot and cold utility demand respectively when heat integrating the two stand-alone processes (compared with the two stand-alone processes). The energy saving potential corresponds to a reduction of minimum hot and cold utility demand of 31% and 21% respectively.

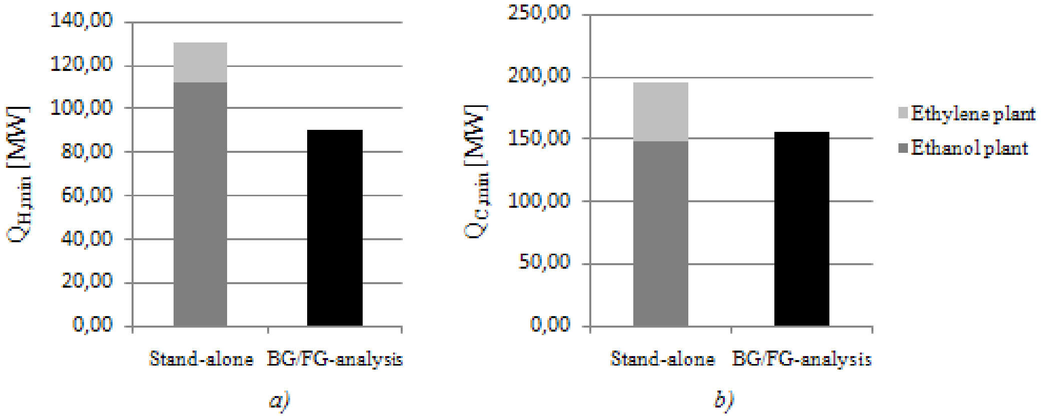

Figure 4.6 a) Minimum hot utility demand for the separated stand-alone ethanol and stand-alone ethylene production plants and the results obtained with background/foreground analysis. b) Minimum cold utility demand for the separated stand-alone ethanol and stand-alone ethylene production plants and the results obtained with background/foreground analysis.

4.2.4 Biorefinery - Ethylene production from lignocellulosic feedstock

Relevant stream data is extracted from simulation results (see Appendix G) in order to conduct a GCC for the biorefinery, see Figure 4.7. The pinch temperature of the biorefinery is 95.9 °C, using a global minimum temperature difference of 10°C. The minimum hot and cold utility demands ($Q_{H,min}$ of 79.2 MW and $Q_{C,min}$ of 141.1 MW) are determined from pinch analysis. The steam requirements for direct injection (pretreatment steps and ethylene reactor feed respectively) are unaffected by the integration.

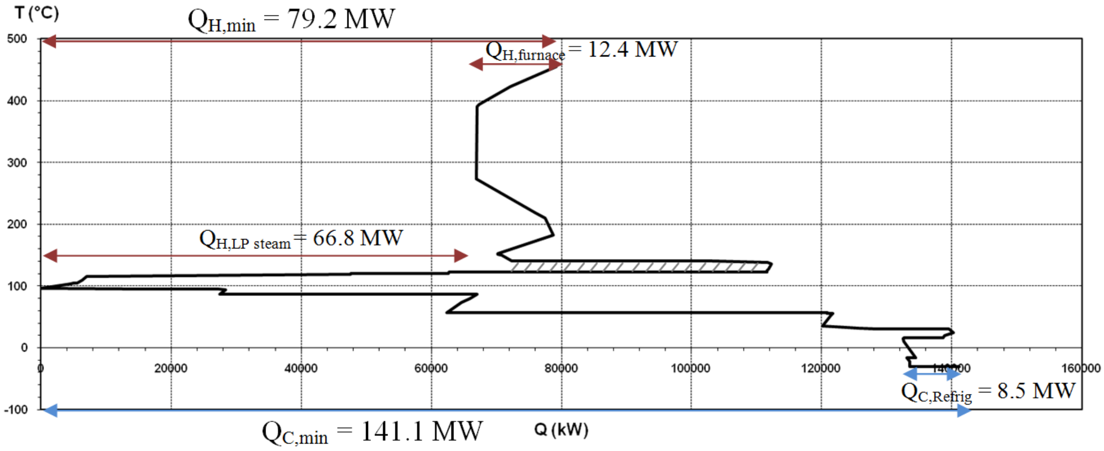

Figure 4.7 GCC for biorefinery producing ethylene from lignocellulosic feedstock.

As described in Chapter 3.3, the pressure increase of the ethylene reactor feed is achieved by compression when stand-alone ethanol and ethylene production are integrated into a biorefinery (due to the fact that ethanol is delivered in gas phase). As a result ethanol is delivered to the ethylene plant at a higher temperature reducing the FEHX load from 12.9 MW to 10.6 MW and the furnace load from 18.7 MW to 12.4 MW (which after utilisation of by-products has an external fuel requirement of 7.9 MW, assuming a furnace efficiency of 80%). As a consequence of the FEHX load reduction the LP steam generation potential is increased to 27.8 MW. However when ethanol is delivered directly to the ethylene plant the pressure is increased with a compressor instead of a pump, which increases the electricity demand of the biorefinery by 2.4 MW$_{el}$. Additionally, the electricity consumption for providing the biorefinery with sufficient amount of cooling water is taken in into consideration (i.e. it is assumed to be included in the electricity demand estimation of the ethanol plant). The total electricity demand for the biorefinery is then 37.9 MW$_{el}$.

Accordingly, the hot utility demand for the ethylene reactors is covered by external fuel ($Q_{H,furnace}$ of 12.4 MW) in a separate furnace and the remaining hot utility demand of the biorefinery can be covered with LP steam ($Q_{H,LP\ steam}$ of 66.8 MW), see Figure 4.7. The integration opportunity to produce LP steam from waste heat (i.e. from ethylene reactor effluent) and deliver it to the ethanol process can be identified in the pocket at 146°C in Figure 4.7. It should be noted that in the temperature interval of the pocket in Figure 4.7 other streams are also included (e.g. flash steam after pretreatment steps in the ethanol production). Note that the heat integration of the two stand-alone processes into a biorefinery producing ethylene from lignocellulosic feedstock has an unchanged requirement of a separate refrigeration system of 8.5 MW ($Q_{C,Refrig}$), see Figure 4.7.

Utility steam and steam for direct injection (i.e. pretreatment steps and ethylene reactor feed respectively) requirements are covered by the CHP plant utilising lignin-rich residues. After producing necessary steam to the process the biorefinery results in 123.1 MW of excess solid residues. Additionally 45.9 MW$_{el}$ are co-generated in the CHP plant, which results in a net electricity production of 8.0 MW$_{el}$ after covering the electricity demand of the biorefinery (i.e. 37.9 MW$_{el}$). Table 4.7 presents key results obtained for the biorefinery producing ethylene from lignocellulosic feedstock.

Table 4.7 Key results obtained for the biorefinery producing ethylene from lignocellulosic feedstock.

	$Q_{H,min}$ [MW]	$Q_{C,min}$ [MW]	Excess Solid Residues [MW]	Net Electricity [MW_{el}]	Net Fuel [MW]
Biorefinery	79.2	141.1	123.1	8.0	-7.9

As discussed in Section 4.2.3, an energy saving potential of 40.5 MW can be achieved by integration of the stand-alone ethanol and the stand-alone ethylene production plants. As can be seen in Figure 4.8 the minimum hot utility demand can be further decreased when integrating the two stand-alone processes into a biorefinery producing ethylene from lignocellulosic feedstock (i.e. ethanol is directly delivered to the ethylene reactors in gas phase). Hence, the energy saving potential is additionally increased by 11.2 MW. The results indicate that the minimum hot utility demand can be reduced by 40% through integration of the two stand-alone processes into a biorefinery (compared with the two stand-alone processes), see Figure 4.8. The reduction is mainly due to the integration opportunity to produce LP steam from waste heat available in the ethylene production plant and deliver it to the ethanol plant, see pocket in Figure 4.7.

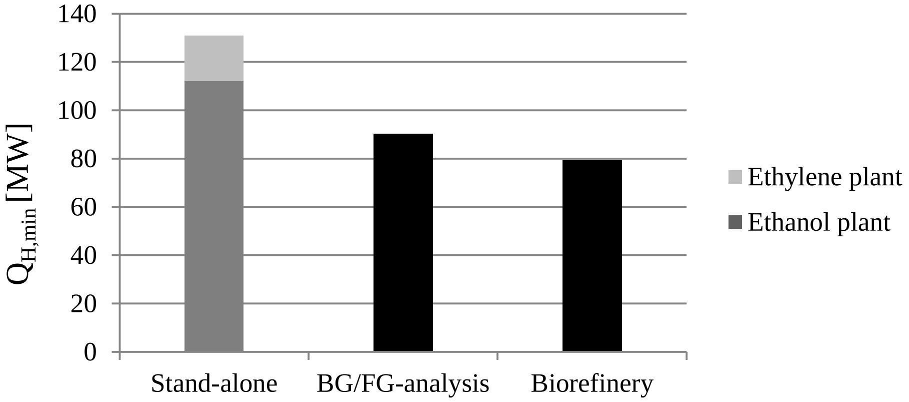

Figure 4.8 Minimum hot utility demands for the stand-alone ethanol and the stand-alone ethylene production plants (left bar), the background/foreground analysis (middle bar), and for the integrated biorefinery (right bar) respectively.

As discussed in Section 4.2.3, the minimum cold utility demand can be reduced by 40.5 MW through integration of the stand-alone ethanol and the stand-alone ethylene production plants. As can be seen in Figure 4.9 the minimum cold utility demand can also be further decreased by 14.1 MW through integrating the two stand-alone processes into a biorefinery producing ethylene from lignocellulosic feedstock. The results indicate that the minimum cold utility demand can be reduced by 28% through integration of the two stand-alone processes into a biorefinery (compared with the two stand-alone processes), see Figure 4.9. The reduction is mainly due to waste heat recovery of the ethylene reactor effluent.

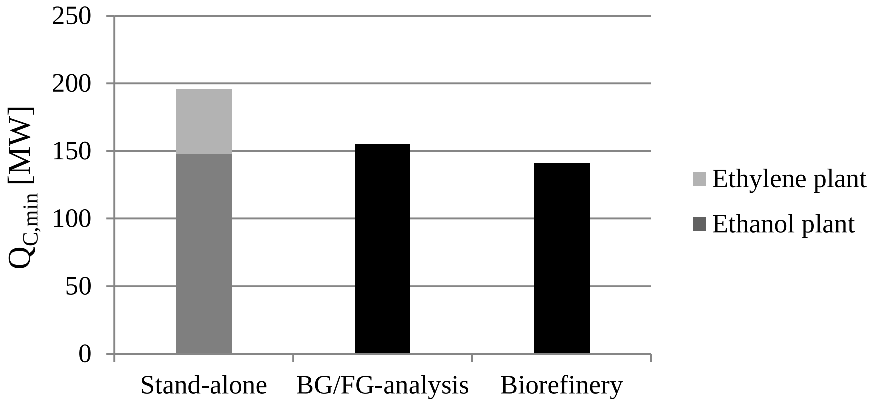

Figure 4.9 Minimum cold utility demands for the stand-alone ethanol and the stand-alone ethylene production plants (left bar), the background/foreground analysis (middle bar), and for the integrated biorefinery (right bar) respectively.

4.2.5 Alternative biorefinery configurations

In an attempt to additionally increase the process and heat integration potential, alternative biorefinery configurations are investigated in the thesis. The effects of the different configuration modifications of the biorefinery are investigated (i.e. the change in minimum hot and cold utility demand, the amount of excess solid residues, the net electricity production/demand, and net fuel usage). Note that the biomass feed to the biorefinery is constant at 43.9 tonne/h for all biorefinery configurations in order to have an ethylene production of 200 000 tonnes annually. As a consequence all material flows in the biorefinery are constant (e.g. yeast, sulphuric acid, NaOH, etc). The amount of produced lignin-rich solid residues is therefore also constant, however the utilisation in the CHP plant differs between the different biorefinery configurations (due to different minimum hot utility demand) leading to a variation in excess solid residues. The amount of by-products produced in the ethylene plant is also constant. It is only the utilisation that differs between the different biorefinery configurations: utilised in a separate furnace reducing the external fuel requirement or sold as a product when integrating the ethylene reactors with flue gases, see Section 4.2.5.1.

4.2.5.1 Flue gas integration with ethylene reactors

According to the biorefinery configuration investigated in Section 4.2.4, a separate furnace requiring external fuel covers the hot utility demand of the ethylene reactors. An alternative is to cover the remaining heat demand of the ethylene reactors by integration with the CHP plant (i.e. flue gases) eliminating the separate furnace, see Figure 4.10, and thereby also reduce/eliminate the purchase of external fuel.

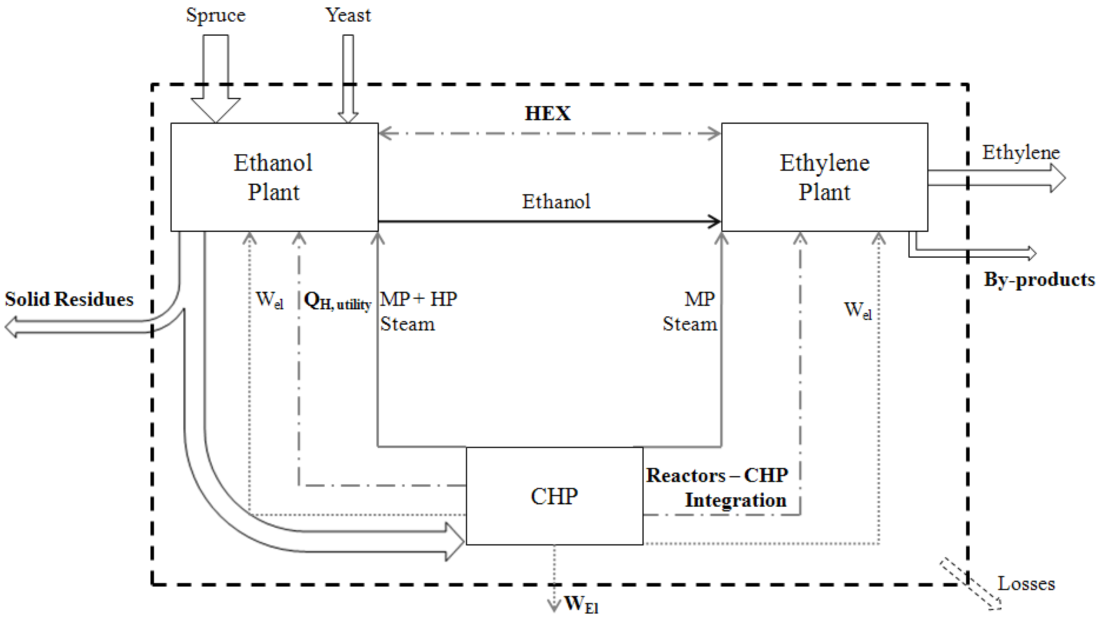

Figure 4.10 Overview of main material and energy streams for the biorefinery with ethylene reactors integrated with flue gases.

4.2.5.2 Introduction of MVR on rectifier distillate

The shape of the GCC in Figure 4.7 indicates that there is a potential to introduce a mechanical vapor recompression (MVR) system. A MVR system is suitable for systems with pinch temperatures above 80°C but below 150 – 200°C (Harvey, 2009). In Figure 4.7 the potential to lift excess heat below the pinch and deliver it above the pinch can be identified. When identifying individual streams the rectifier condenser, operating at 92°C i.e. below the pinch, is suitable to be lifted using a semi-open MVR heat pump. When implementing a MVR system on the rectifier condenser the distillate is compressed to a suitable pressure level to deliver heat to the biorefinery. As a result excess heat below the pinch is lifted to enable delivery above the pinch at the expense of mechanical work. Implementing a MVR system across the pinch reduces both the minimum hot and cold utility demand of the biorefinery (Harvey, 2009). The effects of implementing a MVR system on both the total distillate and on the reflux are investigated, see Figure 4.11.

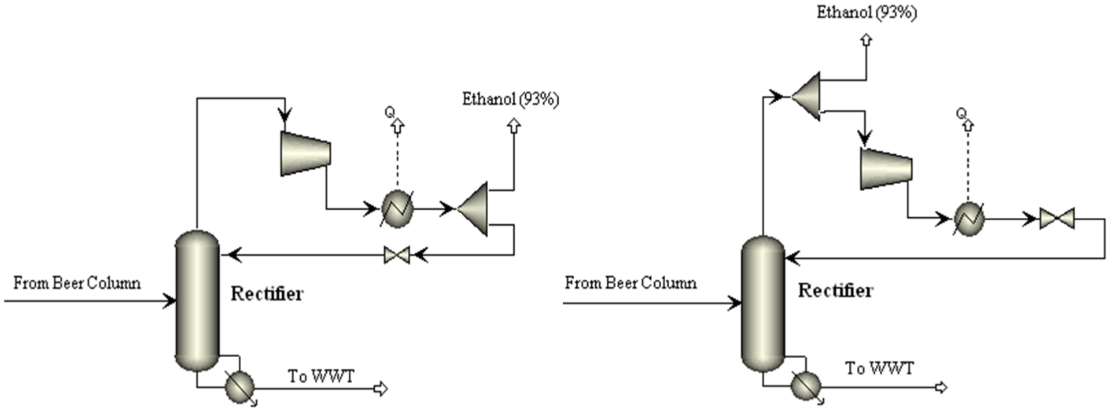

Figure 4.11 MVR configurations when implemented on the total distillate (left) and when heat pumping the reflux (right).

The MVR efficiency can be measured with:

$$COP = \frac{Q_{Delivered}}{W} \tag{4.1}$$

Where COP is the Coefficient of Performance, $Q_{Delivered}$ is useful heat delivered to the process, and W is the required compressor work. $Q_{Delivered}$ and W are taken from simulation results in order to estimate the COP of the MVR.

4.2.5.3 VHP (41 bar) steam delivery to the chemical cluster

As discussed in Section 2.4, results from a TSA study show that the chemical cluster in Stenungsund has a heat deficit of 62 MW after site wide energy efficiency measures which can be covered with VHP (41 bar) steam. The opportunity to produce a sufficient amount of VHP steam (after covering the minimum hot utility demand and steam demand for direct injection of the biorefinery) by utilisation of excess lignin-rich solid residues is investigated in the thesis. The delivery of VHP steam to the chemical cluster will result in an additional income to the biorefinery affecting the ethylene production cost. However, it will occur at the expense of excess solid residues which also provide an income source to the biorefinery. The integration opportunity will contribute by reducing the degree of fossil fuel dependence of the biorefinery, as the hot utility deficit is covered by “green” fuel.

4.2.6 Biorefinery – Flue gas integration with ethylene reactors (Bio-F)

The effects of integrating the dehydration reactors with the flue gases of the CHP plant are investigated (Bio-F). As a result the need of a separate furnace is eliminated and the ethylene by-products can be sold as a product.

Sufficient energy to cover the energy demand in ethylene reactors (12.4 MW) is extracted from the flue gases in the CHP plant. A ΔT_{min} of 20°C is assumed in the heat exchanging between the two gas streams. The extracted flue gas stream and the ethylene reactors requiring hot utility are excluded in the pinch analysis, since no other heat integration opportunity is desired to be investigated. As a consequence the hot utility requirement for the ethylene reactors is excluded in the obtained minimum hot utility demand for the Bio-F. The resulting GCC for the Bio-F is presented in Figure 4.12.

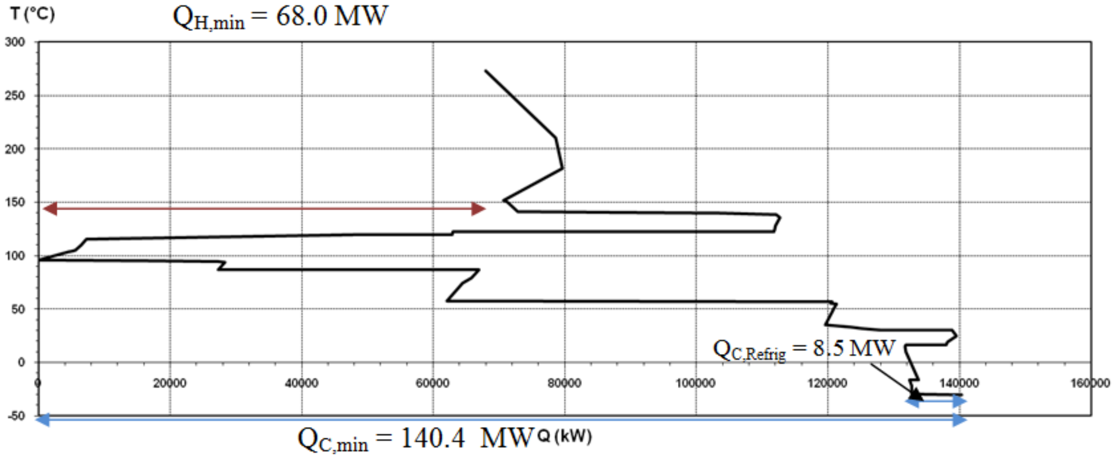

Figure 4.12 GCC for the Bio-F.

The pinch temperature of the biorefinery configuration with flue gas integration with the ethylene reactors (Bio-F) is 95.9 °C, using a global minimum temperature difference of 10°C. As can be seen in Figure 4.12 the Bio-F has a minimum hot and cold utility demand of 68.0 MW and 140.4 MW respectively. It can be seen in Figure 4.12 that the hot utility demand of the Bio-F can be covered with LP steam. The steam production in the CHP plant results in an excess of 105.0 MW lignin-rich solids and an electricity production of 46.4 MW_{el} (i.e. a net electricity production of 8.5 MW_{el}). By-products produced (7.5 MW) in the ethylene plant have the potential to be sold as product. Table 4.8 presents key results obtained for the Bio-F and the Biorefinery (i.e. without any configuration modifications).

Table 4.8 Key results obtained for the Biorefinery and Bio-F.

	$Q_{H,min}$ [MW]	**$Q_{C,min}$ [MW]**	**Excess Solid Residues [MW]**	**Net Electricity [MW_{el}]**	**Net Fuel [MW]**
Biorefinery	79.2	141.1	123.1	8.0	-7.9
Bio-F	68.0	140.4	105.0	8.5	7.5

The results from the Bio-F indicate that it is possible to increase the capacity of the CHP plant to cover the requirements of the dehydration reactors. However, this results in a reduction of the amount of excess solid residues (i.e. reduction by 18 MW, see Table 4.8). The capacity increase of the CHP plant results in an increased air preheating demand. Consequently the LP steam demand of the Bio-F is increased ($Q_{H,LP\ steam,Bio\text{-}F}$ of 68.0 MW) compared with the Biorefinery ($Q_{H,LP\ steam,Biorefinery}$ of 66.8 MW). As a consequence of the increased steam generation, the electricity generation in the turbine is increased by 0.5 MW_{el} in the CHP plant.

In Figure 4.13 the minimum hot utility demands for the two stand-alone processes, the Biorefinery, and the Bio-F are compared. According to Figure 4.13 the minimum hot utility demand for the Bio-F is reduced by 14% (corresponding to a reduction of 11.2 MW) compared with the Biorefinery. However, it should be noted that the hot utility demand of the ethylene reactors are excluded in the pinch analysis (due to integration with flue gases) and that the LP steam demand is in fact increased (due to an increased air preheating demand).

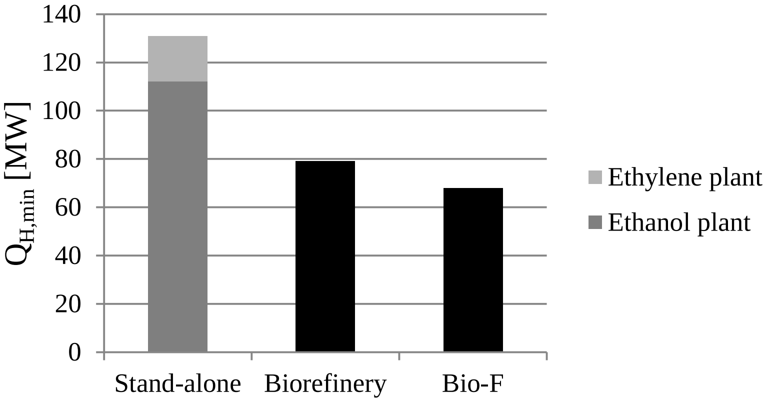

Figure 4.13 Minimum hot utility demands for the stand-alone ethanol and the stand-alone ethylene production plants, the Biorefinery (i.e. without modifications), and for the Bio-F respectively.

In Figure 4.14 the minimum cold utility demands for the two stand-alone processes, the Biorefinery, and the Bio-F are compared. As can be seen in Figure 4.14 the minimum cold utility of the Bio-F is reduced by 0.7 MW in comparison to the Biorefinery (i.e. without modifications). The decrease is due to the increased demand for air preheating (below the pinch) in the CHP plant.

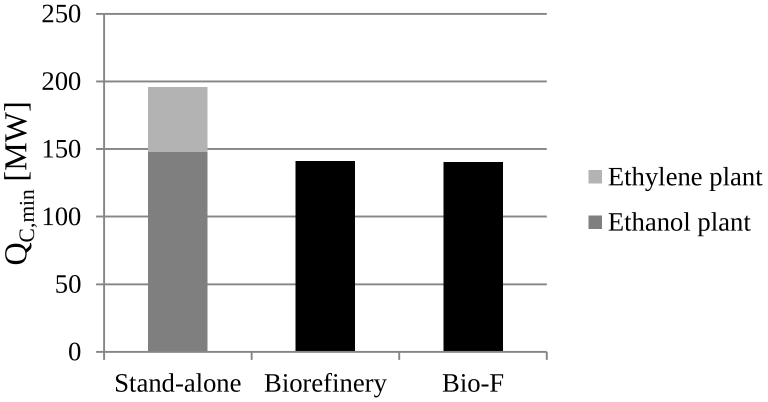

Figure 4.14 Minimum cold utility demands for the stand-alone ethanol and the stand-alone ethylene production plants, the Biorefinery (i.e. without modifications), and for the Bio-F respectively.

4.2.7 Biorefinery – Introduction of MVR on the rectifier distillate (Bio-MVR)

The effects of implementing a MVR heat pump on the rectifier condenser are investigated (Bio-MVR). A MVR system is introduced on both total distillate and reflux of the rectifier, see Section 4.2.5.2. Both MVR-systems obtained a COP of 7.4, which is reasonable (Harvey, 2009). See Appendix H for stream data. The results indicate that when implementing a MVR on the total rectifier distillate, compared with on the reflux, the additional energy savings does not outweigh to the increase in compressor work. Hence, only the results obtained for the biorefinery with a MVR introduced on the rectifier reflux (Bio-MVR) are presented here. Figure 4.15 illustrates the GCC obtained for the Bio-MVR.

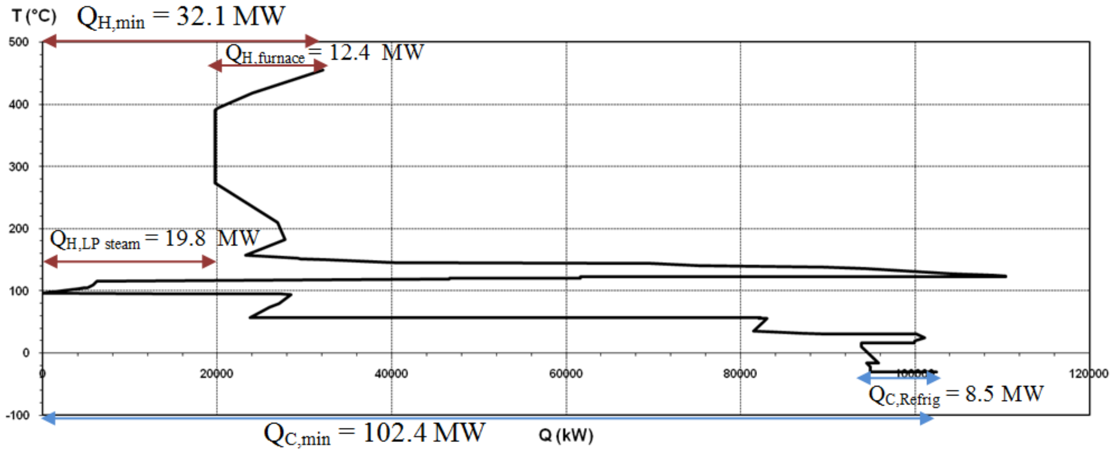

Figure 4.15 GCC for the Bio-MVR

The pinch temperature of the biorefinery configuration with a MVR introduced on the rectifier reflux (Bio-MVR) is 95.9 °C, using a global minimum temperature difference of 10°C. As shown in Figure 4.15 the Bio-MVR has a hot and cold utility demand of 32.1 MW and 102.4 MW respectively. The hot utility demand for the ethylene reactors is covered by external fuel ($Q_{H,furnace}$ of 12.4 MW, which after firing of ethylene by-products has an external fuel demand of 7.9 MW, assuming a furnace efficiency of 80%) in a separate furnace and the remaining hot utility demand of the Bio-MVR can be covered with LP steam ($Q_{H,LP\ steam}$ of 19.8 MW), see Figure 4.15. The low steam production requirement in the CHP plant results in 205.3 MW excess solid residues and 28.2 MW_{el} co-generated electricity, which after covering the electricity demand of the Bio-MVR (i.e. 44.1 MW_{el}) results in a net electricity deficit of 15.8 MW_{el}. Table 4.9 presents key results obtained for the Bio-MVR. Additionally, key results for the Biorefinery (i.e. without configuration modifications) and the Bio-F are included in Table 4.9 for comparison.

Table 4.9 Key results obtained for the Biorefinery, Bio-F, and Bio-MVR.

	$Q_{H,min}$ [MW]	$Q_{C,min}$ [MW]	Excess Solid Residues [MW]	Net Electricity [MW_{el}]	Net Fuel [MW]
Biorefinery	79.2	141.1	123.1	8.0	-7.9
Bio-F	68.0	140.4	105.0	8.5	7.5
Bio-MVR	32.1	102.4	205.3	-15.8	-7.9

As can be seen in Table 4.9 the minimum hot and cold utility demand of the biorefinery can be significantly reduced by the introduction of a MVR on the rectifier reflux, lifting excess heat below the pinch to deliver it above the pinch (i.e. comparing the Biorefinery and the Bio-MVR). As a consequence the amount of excess solid residues are increased (by 82.2 MW) due to a lower LP steam production in the CHP plant. However, as discussed in Section 4.2.5.2 the introduction of a MVR system increases the electricity consumption of the biorefinery. Thus, as the electricity co-generation decreases, the Bio-MVR results in a net electricity demand (i.e. the Bio-MVR requires electricity purchase) while the Biorefinery has a net surplus of electricity.

In Figure 4.16 the minimum hot utility demands for the two stand-alone processes, the Biorefinery, the Bio-F, and the Bio-MVR are compared. According to Figure 4.16 the minimum hot utility demand for the Bio-MVR is reduced by 59% (corresponding to a reduction of 47.0 MW) compared with the Biorefinery.

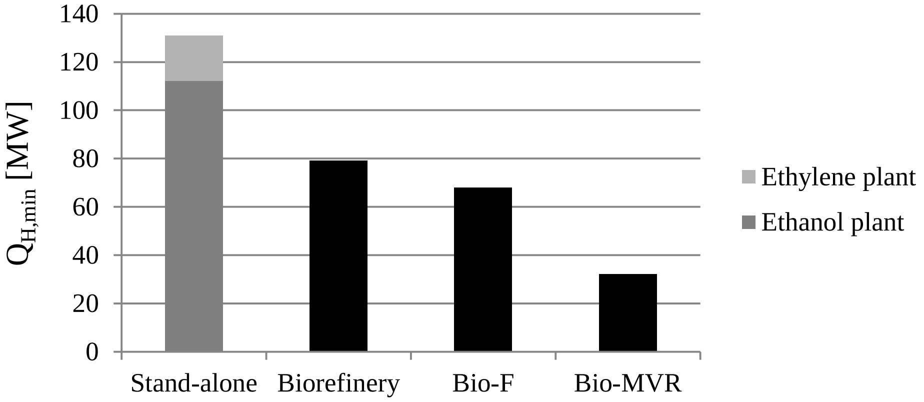

Figure 4.16 Minimum hot utility demands for the stand-alone ethanol and the stand-alone ethylene production plants, the Biorefinery, the Bio-F, and the Bio-MVR respectively.

In Figure 4.17 the minimum cold utility demands for the two stand-alone processes, the Biorefinery, the Bio-F, and the Bio-MVR are compared. According to Figure 4.17 the minimum cold utility demand for the Bio-MVR is reduced by 27% (corresponding to a reduction of 38.7 MW) compared with the Biorefinery.

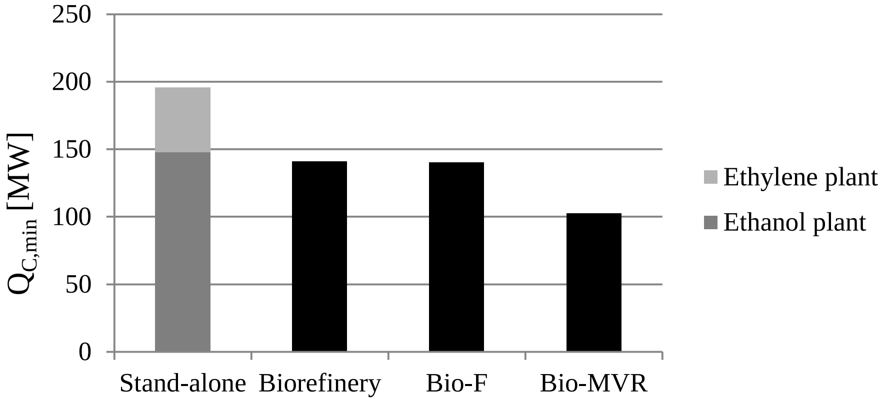

Figure 4.17 Minimum cold utility demands for the stand-alone ethanol and the stand-alone ethylene production plants, the Biorefinery, the Bio-F, and the Bio-MVR respectively.

4.2.8 Biorefinery – VHP (41 bar) steam delivery to the chemical cluster (Bio-VHP)

As mention in Section 4.2.5.3 it is shown that the chemical cluster has a heat deficit of 62 MW, after side wide energy efficiency measures, which can be covered with VHP (41 bar) steam. The opportunity to produce a sufficient amount of VHP steam in the biorefinery (i.e. by increasing the solid residue load to the CHP plant) and deliver it to the chemical cluster is investigated in this case (Bio-VHP).

Pinch analysis show that the pinch temperature of the biorefinery configuration delivering VHP steam to the chemical cluster (Bio-VHP) is 95.9 °C, using a global minimum temperature difference of 10°C. The Bio-VHP has a hot and cold utility demand of 76.0 MW and 137.6 MW respectively. The hot utility demand for the ethylene reactors is covered by external fuel ($Q_{H,furnace}$ of 12.4 MW, which after firing of ethylene by-products has an external fuel demand of 7.9 MW, assuming a furnace efficiency of 80%) in a separate furnace and the remaining hot utility demand of the Bio-VHP can be covered with LP steam ($Q_{H,LP\ steam}$ of 63.7 MW). The production of utility steam, steam for direct injection (i.e. for the pretreatment steps and the ethylene reactor feed), and VHP steam for the chemical cluster in the CHP plant results in 36.1 MW excess solid residues. The Bio-VHP has an electricity production of 55.0 MW_{el} resulting in a net surplus of 17.1 MW_{el}. Table 4.10 presents key results obtained for the Bio-VHP. Additionally, key results for the Biorefinery (i.e. without configuration modifications), the Bio-F, and the Bio-VHP are included in Table 4.9 for comparison.

Table 4.10 Key results obtained for the Biorefinery, the Bio-F, the Bio-MVR, and the Bio-VHP.

	$Q_{H,min}$ [MW]	$Q_{C,min}$ [MW]	Excess Solid Residues [MW]	Net Electricity [MW_{el}]	Net Fuel [MW]
Biorefinery	79.2	141.1	123.1	8.0	-7.9
Bio-F	68.0	140.4	105.0	8.5	7.5
Bio-MVR	32.1	102.4	205.3	-15.8	-7.9
Bio-VHP	76.0	137.6	36.1	17.1	-7.9

The results indicate that the biorefinery can deliver 62 MW of VHP steam to the chemical cluster by increasing the solid residue load to the CHP plant by 87 MW, resulting in 36.1 MW of excess solid residues. Consequently the co-generated electricity is increased (55.0 MW_{el}) resulting in a net electricity production of 17.1 MW_{el}.

In Figure 4.18 the minimum hot utility demands for the two stand-alone processes, the Biorefinery, the Bio-F, the Bio-MVR, and the Bio-VHP are compared. According to Figure 4.18 the minimum hot utility demand for the Bio-VHP is reduced by 4% (corresponding to a reduction of 3.1 MW) compared with the Biorefinery. The reduction in minimum hot utility demand is mainly due consequences followed by the high return temperature (252°C) of the VHP condensate resulting in a higher temperature entering the economiser in the CHP plant.

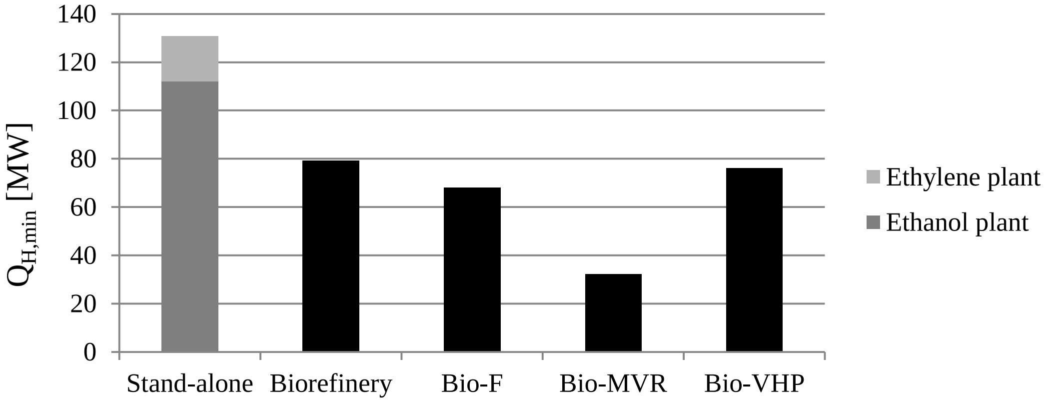

Figure 4.18 Minimum hot utility demands for the stand-alone ethanol and the stand-alone ethylene production plants, the Biorefinery (i.e. without modifications), the Bio-F, the Bio-MVR, and for the Bio-VHP respectively.

In Figure 4.19 the minimum cold utility demands for the two stand-alone processes, the Biorefinery, the Bio-F, the Bio-MVR, and the Bio-VHP are compared. According to Figure 4.19 the minimum cold utility demand for the Bio-VHP is reduced by 3% (corresponding to a reduction of 3.6 MW) compared with the Biorefinery.

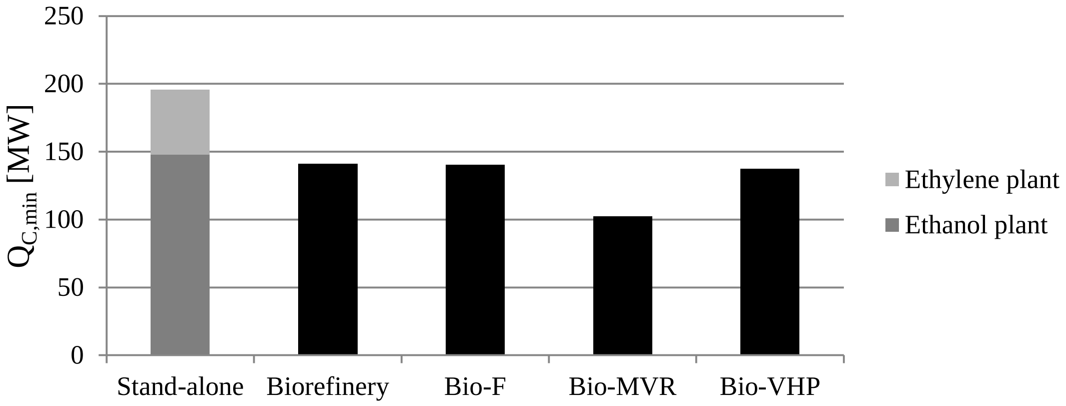

Figure 4.19 Minimum cold utility demands for the stand-alone ethanol and the stand-alone ethylene production plants, the Biorefinery (i.e. without modifications), the Bio-F, the Bio-MVR, and for the Bio-VHP respectively.

4.2.9 Summary of heat integration results

The results show that the stand-alone lignocellulosic ethanol production plant can cover the minimum hot utility demand (112.2 MW) and steam for direct injection in the first and second pretreatment steps (42.1 MW MP steam and 9.1 MW HP steam respectively) by utilisation of lignin-rich solid residues in the CHP plant. The stand-alone ethanol production plant results in 86.3 MW excess solid residues. The net production of co-generated electricity is 24.3 MW_{el} after covering the electricity demand of the process.

The stand-alone ethylene production plant requires purchase of externally produced MP steam (25.1 MW) and electricity (4.4 MW_{el}). Additionally, the stand-alone ethylene production plant requires external fuel to cover the minimum hot utility demand (15.9 MW).

Table 4.11 presents the obtained key results for the two stand-alone processes, the Biorefinery, and the alternative biorefinery configurations (i.e. Bio-F, Bio-MVR, and Bio-VHP) investigated in the thesis.

Table 4.11 Obtained key results for the two stand-alone production plants, the Biorefinery, and the alternative biorefinery configurations investigated.

	$Q_{H, min}$ [MW]	**$Q_{C, min}$ [MW]**	**Excess Solid Residues [MW]**	**Net Electricity [MW_{el}]**	**Net Fuel [MW]**	**Steam to Cluster [MW]**
Stand-alone EtOH	112.2	147.6	86.3	24.3	0	0
Stand-alone Ethylene	18.7	48.1	-	-4.4	-15.9	0
Biorefinery	79.2	141.1	123.1	8.0	-7.9	0
Bio-F	68.0	140.4	105.0	8.5	7.5	0
Bio-MVR	32.1	102.4	205.3	-15.8	-7.9	0
Bio-VHP	76.0	137.6	36.1	17.1	-7.9	62

The results from the background/foreground analysis, see Section 4.2.3, indicate that heat integration of the two stand-alone processes have a potential to reduce the minimum hot and cold utility demand by 31% and 21% respectively. The reduction is mainly due to the waste heat recovery in the stand-alone ethylene production plant. Combining the two stand-alone processes into a biorefinery (delivering ethanol directly to the ethylene production plant in gas phase) the minimum hot and cold utility demand can be further reduced. The results show that the minimum hot and cold utility demand is reduced by 40% and 28% respectively by integrating the two stand-alone processes into a biorefinery. The results also show that the minimum hot and cold utility demand of the biorefinery can be further reduced (i.e. by 59% and 27% respectively) by introducing a MVR on the rectifier reflux. Compared with the two stand-alone processes the MVR implementation corresponds to a minimum hot utility reduction of 75%.

The results indicate that the stand-alone lignocellulosic ethanol production results in sufficient amount of excess solid residues to cover the MP steam requirement in the stand-alone ethylene production plant. Additionally the electricity demand of the stand-alone ethylene production plant can be covered with co-generated electricity produced in the CHP plant. The results show that the resulting lignin-rich solid residues in the ethanol production additionally has the potential to cover the ethylene reactor furnace by flue gas integration or producing 62 MW VHP steam for covering the heat deficit in the chemical cluster. Both integration opportunities result in excess solid residues. Furthermore the ethylene by-products are not utilised in the Bio-F configuration and can thus be sold, introducing an additional revenue source, however this is enabled at the expense of excess solid residues. The introduction of a MVR significantly increases the amount of excess solid residues (due to the reduction in minimum hot utility demand).

All process configurations investigated except for the stand-alone ethylene production and Bio-MVR result in a net electricity production, allowing export to the grid.

4.3 Economic evaluation

4.3.1 Total capital cost estimation

4.3.1.1 Stand-alone lignocellulosic ethanol and stand-alone ethanol dehydration to ethylene production

The total capital costs for the stand-alone lignocellulosic ethanol and the stand-alone ethanol dehydration to ethylene production plants are estimated at 394 million € and 91 million € respectively. The capital cost for the stand-alone lignocellulosic ethanol production is estimated by calculating the capital cost for each equipment individually (see Appendix I and J) as discussed in Section 3.5.1. The total capital cost for the stand-alone ethanol dehydration to ethylene production is estimated with an average total capital cost between 61 and 122 million € gathered from literature (Jones, et al., 2010). The total capital costs for the two stand-alone plants are presented in Table 4.12.

Table 4.12 Total capital cost for the two stand-alone production plants.

	Total capital cost [Million €]
Stand-alone EtOH	393.9
Stand-alone Ethylene	91.1

4.3.1.2 Biorefinery – Ethylene production from lignocellulosic feedstock

The total capital cost for the biorefinery is estimated by calculating the capital cost for each equipment individually (see Appendix I and Appendix J), as discussed in Section 3.5.1. Parameters affecting the biorefinery capital cost between the different configurations are:

- CHP plant size
- MVR system implementation
- Separate furnace

The total capital cost of the ethylene production plant is fixed at 91 million € in all biorefinery capital cost estimations expect in Bio-F. The elimination of the furnace reduces the total capital cost for the ethylene plant by 1 million € (Gavin, et al., 2008). Table 4.13 presents the estimated total capital costs for the different biorefinery configurations.

Table 4.13 Total capital cost estimations for the biorefinery configurations investigated.

	Total Capital Cost [Million €]
Biorefinery	474.7
Bio-F	479.9
Bio-MVR	450.7
Bio-VHP	496.9

Investigating the impact flue gas integration with the ethylene reactors (i.e. eliminating the separate furnace) has on the total capital cost, a comparison between the Biorefinery and Bio-F is conducted. The results indicate that the elimination of the separate furnace, by integrating the ethylene reactors with the CHP plant flue gases, increases the total capital cost of the biorefinery. The integration results in an increased solid fuel load to the CHP plant, increasing the CHP plant size, hence the total capital cost is increased.

The introduction of a MVR results in the addition of one unit (i.e. a compressor). The introduction of a MVR system in the biorefinery significantly reduces the minimum hot utility demand, and consequently reduces the CHP plant size. As seen in Table 4.13 the Bio-MVR results in comparatively lower capital cost.

Investigating the influence VHP steam delivery to the chemical cluster has on the total capital cost, a comparison between the Biorefinery and Bio-VHP is conducted. As expected the CHP plant size increases due to the increased steam production, and thereby the total capital cost of the biorefinery increases.

The results show that the CHP plant size has a great impact on the total capital cost (approximately 20%). As can been seen in Table 4.13 the Bio-VHP and the Bio-MVR obtains the highest and lowest total capital costs respectively.

4.3.2 Annual operating cost estimation

4.3.2.1 Stand-alone lignocellulosic ethanol and stand-alone ethanol dehydration to ethylene production

In the annual operating costs for the stand-alone lignocellulosic ethanol and the stand-alone ethanol dehydration to ethylene production plants all the expenses for the two stand-alone production plants are included, see Section 3.5.2. Table 4.14 presents assumed prices in the estimation. Note that no income is taken into consideration in the annual operating cost estimation, but it is treated in a separate section, see Section 4.3.3. See Appendix K for exchange rates used.

Table 4.14 Assumed prices for raw materials, energy demands, and labour used in the annual operating cost estimation.

	Price		**Reference**
Spruce	121	€/tonnedry	(Karlsson, 2009)
Yeast	18	€/tonne	(Fornell, 2010)
Enzyme	115	€/tonne	(Fornell, 2010)
Sulphuric Acid	35	€/tonne	(ICIS)
Process Water (Fresh water)	1.15	€/tonne	(Spetz, 2011)
Purchase of Ethanol	497	€/tonne	(ICIS)
Steam	41.1	€/MWh	Based on natural gas price[7]
Fuel (Natural Gas)	32.9	€/MWh	(Göteborgs Energi)
Purchased Electricity Price	68.9	€/MWh	(Spetz, 2011)
Shift operator	31.8	€/h	
Supervision	47.7	€/h	

The annual operating costs for the stand-alone lignocellulosic ethanol production and the stand-alone ethanol dehydration to ethylene production plant are estimated at 193 million € and 201 million € respectively, see Table 4.15. It should be noted that the stand-alone ethanol production plant is energy self-sufficient, while the stand-alone ethylene production plant requires purchase of steam, fuel, and electricity. The annual operating costs are estimated at full production of the two stand-alone production plants respectively.

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[7] Assumed efficiency of 80%

Table 4.15 Annual operating costs for the two stand-alone production plants.

	Annual operating cost [Million €]
Stand-alone EtOH production	193
Stand-alone Ethylene production	201

4.3.2.2 Biorefinery – Ethylene production from lignocellulosic feedstock

In the annual operating costs for the different biorefinery configurations all the expenses for the corresponding biorefinery are included, see Section 3.5.2. Assumed prices used in the estimation are shown in Table 4.14. See Appendix K for exchange rates used. In all biorefinery configurations investigated ethanol is directly delivered to the ethylene production plant, eliminating the ethanol purchase requirement. Additionally, the MP steam requirement for direct injection into the ethylene reactor feed is produced in the CHP plant. It should be noted that due to the increased MP steam extraction in the CHP plant the fresh water feed to the CHP plant is increased to 135 tonne/h. Note that no income is taken into consideration in the annual operating cost estimation, but it is treated in a separate section, see Section 4.3.3. The parameters affecting the operating cost between the different biorefinery configurations are:

- External fuel requirements (to separate furnace)
- Electricity deficit
- Capital cost of corresponding biorefinery configuration (due to cost estimation assumption of maintenance and administration and insurance)

Table 4.16 presents the estimated annual operating costs for the alternative biorefinery configurations at full production.

Table 4.16 Annual operating cost estimations for the different biorefinery configurations investigated.

	Annual operating cost [Million €]
Biorefinery	208.5
Bio-F	206.7
Bio-MVR	216.4
Bio-VHP	209.9

Investigating the impact flue gas integration with the ethylene reactors (i.e. elimination of separate furnace) has on the annual operating cost, a comparison between the Biorefinery and Bio-F is conducted. The results indicate that the elimination of the separate furnace, by integrating the ethylene reactors with CHP plant flue gases, decreases the annual operating cost. This is mainly due the elimination of external fuel requirement (i.e. elimination of a purchase requirement), see Table 4.11.

The results indicate that implementation of a MVR on the rectifier reflux (i.e. introducing an additional electricity consumer to biorefinery) results in comparatively high annual operating cost. The increase in annual operating cost is due to the need of purchasing external electricity, see Table 4.11.

Investigating the influence VHP steam delivery to the cluster has on the annual operating cost, a comparison between the Biorefinery and Bio-VHP is conducted. The results show that annual operating cost is increased when delivering VHP steam to the cluster. This is mainly due to the fact that the capital cost is increased when delivering VHP steam to cluster (i.e. the CHP plant size increases), hence increasing the maintenance and administration costs.

The distribution of the different parameters contributing to the annual operating cost is investigated. Figure 4.20 illustrates the operating cost contribution for different parameters in the Biorefinery (i.e. without modifications). The largest contributor is shown to be the raw material (accounting for 73%). Similar results are obtained for the other biorefinery configurations. Hence, the results indicate that annual operating cost for the biorefinery is considerably dependent on the raw material (in this case spruce) price.

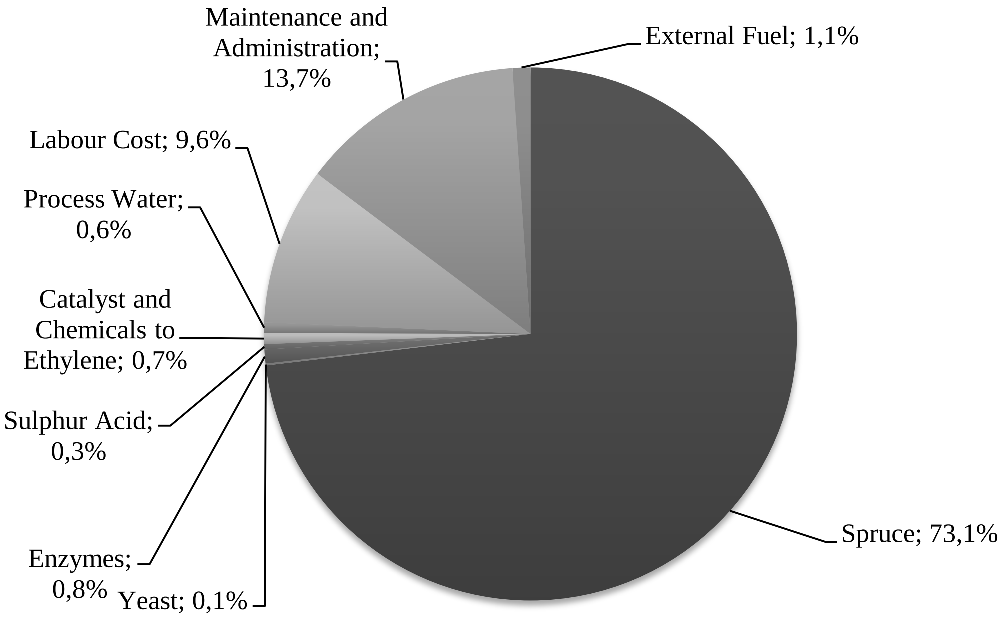

Figure 4.20 Operating cost distribution for the Biorefinery (i.e. without modifications).

4.3.3 Annual revenue estimation

4.3.3.1 Stand-alone lignocellulosic ethanol and stand-alone ethanol dehydration to ethylene production

In the annual revenue estimation for the stand-alone lignocellulosic ethanol and the stand-alone ethanol dehydration to ethylene production plants all the income sources for the two stand-alone production plants respectively are included, see Table 4.11. Table 4.17 presents assumed prices in the estimation.

Table 4.17 Assumed prices for the co-products used in the revenue estimation.

	Price		Reference
Solid-residues (Pellets)	34.9	€/MWh	(Karlsson, 2009)
Steam	41.1	€/MWh	Based on natural gas price[8]
Electricity	91.9	€/MWh	(Spetz, 2011)
By-products (Ethylene Column)	32.9	€/MWh	Based on natural gas price

The income sources taken into consideration in the stand-alone lignocellulosic ethanol production plant are ethanol, excess solid residues, and net electricity production. The selling price of ethanol is estimated from the minimum production cost, see Section 4.3.4.1. The only income source taken into consideration in the stand-alone ethanol dehydration to ethylene production is the ethylene product. The selling price of ethylene is estimated from the minimum production cost, see Section 4.3.4.1.

The annual sales incomes for the stand-alone lignocellulosic ethanol production and the stand-alone ethanol dehydration to ethylene production plant at full production are estimated at 242 million € and 212 million € respectively, see Table 4.18.

Table 4.18 Annual revenue estimations for the two stand-alone production plants.

	Annual revenue [Million €]
Stand-alone EtOH production	242
Stand-alone Ethylene production	212

4.3.3.2 Biorefinery – Ethylene production from lignocellulosic feedstock

In the annual revenue estimation for the different biorefinery configurations all the income sources for the corresponding biorefinery are included; ethylene (the same for all biorefinery configurations), excess solid residues, net electricity production, ethylene column by-products (for Bio-F), and VHP steam (for Bio-VHP), see Table 4.11. The selling price of ethylene is estimated from the minimum production cost, see Section 4.3.4.2. Table 4.17 presents assumed prices in the estimation. Table 4.19 presents the annual sales incomes for the different biorefinery configurations at full production.

Table 4.19 Annual revenue estimations for the different biorefinery configurations investigated.

	Annual revenue [Million €]
Biorefinery	258
Bio-F	257
Bio-MVR	264
Bio-VHP	262

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[8] Assumed efficiency of 80%

As can be seen in Table 4.19 the flue gas integration with the ethylene reactors slightly reduces the annual revenue of the biorefinery (i.e. comparing the Biorefinery and Bio-F). This is mainly due to the increased solid residue load to the CHP plant, reducing the amount of excess solid residues. The results indicate that the introduciion of a MVR on the rectifier reflux increases the annual revenues (i.e. comparing the Biorefinery and Bio-MVR). This is mainly an effect of the increased amount of solid residues due to a reduced hot utility demand of the process. Comparing the Biorefinery and Bio-VHP it can be seen that the annual revenues of the biorefinery is increased when producing VHP steam for the cluster. As a consequence an additional income source is introduced (at the expense of excess solid residues) and the co-generated electricity production in the CHP plant is increased.

Figure 4.21 illustrates the contribution of the different income sources to the annual revenues of the different biorefinery configurations investigated in the thesis. The results indicate that ethylene is the main income source of the biorefinery, accounting for approximately 82% of the total annual revenues of the different biorefinery configurations.

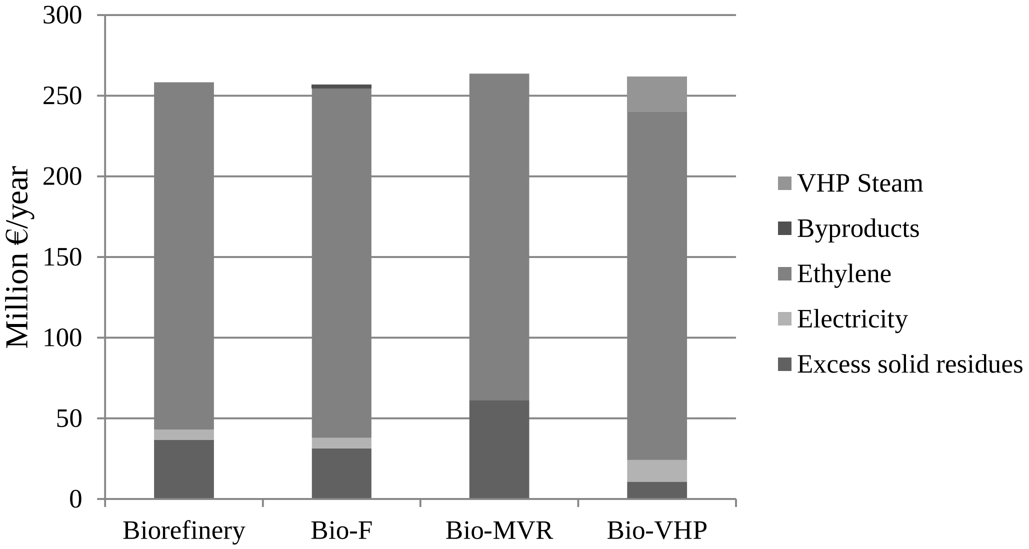

Figure 4.21 Annual revenue distributions for the different biorefinery configurations.

4.3.4 Production cost estimation

4.3.4.1 Stand-alone lignocellulosic ethanol and stand-alone ethanol dehydration to ethylene production

The total capital costs, annual operating costs, and annual revenues for the stand-alone lignocellulosic ethanol and the stand-alone ethanol dehydration to ethylene production plants are identified. The costs and revenues are used to estimate the ethanol and ethylene production costs respectively, using a discount cash flow analysis, see Section 3.5.3. The ethanol production cost for the stand-alone lignocellulosic ethanol production is estimated at 0.53 €/kg ethanol (93 wt%). The ethylene production cost for the stand-alone ethanol dehydration to ethylene production is estimated at 1.06 €/kg ethylene. Both production costs are presented in Table 4.20.

Table 4.20 Production costs for the two stand-alone production plants.

	Production cost [€/kg]
Stand-alone EtOH	0.53 €/kg ethanol
Stand-alone Ethylene	1.06 €/kg ethylene

The results indicate that the production cost of ethanol from softwood feedstock is higher than the assumed ethanol purchase price, see Table 4.14.

4.3.4.2 Biorefinery – Ethylene production from lignocellulosic feedstock

The total capital costs, annual operating costs, and annual revenues for the different biorefinery configurations are identified in order to estimate the ethylene production cost using a discount cash flow analysis, see Section 3.5.3. Parameters affecting the production cost between the different biorefinery configurations are:

- Total capital cost
- Annual operating cost (including: external fuel requirements and net electricity deficit)
- Revenues (including: excess solid residues, net electricity production, ethylene by-products, and VHP steam delivery to the cluster)

It should be noted that the ethylene production cost estimation is highly dependent on price assumptions made for relevant parameters. For example purchased electricity price is assumed to be 68.9 €/MWh and the selling price 91.9 €/MWh. The difference is due to the fact that the biorefinery produces electricity from a renewable energy source and is thereby eligible for support in the form of tradable “Green” certificates. See Table 4.14 and Table 4.17 for price assumptions used in ethylene production cost evaluation. Figure 4.22 presents the ethylene production cost for the stand-alone ethanol dehydration to ethylene production plant and the different biorefinery configurations.

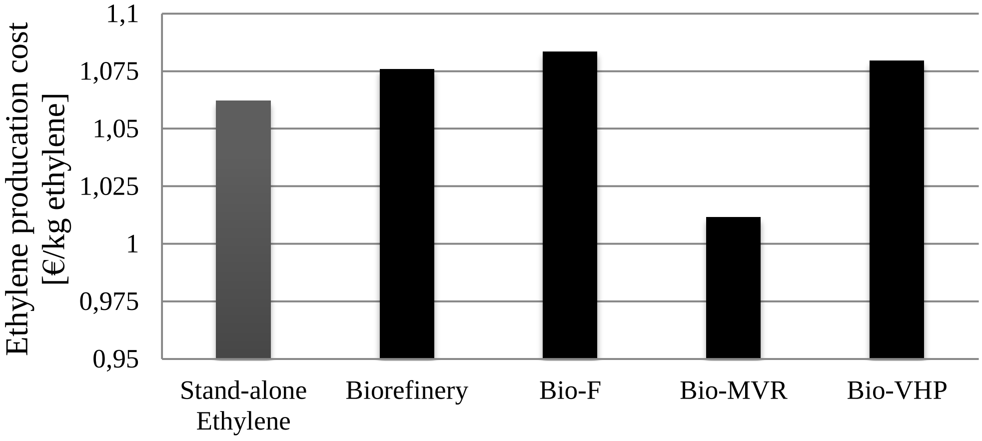

Figure 4.22 Ethylene production cost for the stand-alone ethylene plant, and the different biorefinery configurations investigated.

The estimated ethylene from lignocellulosic feedstock production cost varies between 1.012 €/kg and 1.084 €/kg, see Table 4.21.

Table 4.21 The ethylene production cost for the stand-alone ethylene plant and the different biorefinery configurations investigated.

	Ethylene production cost [€/kg]
Stand-alone Ethylene	1.062
Biorefinery	1.076
Bio-F	1.084
Bio-MVR	1.012
Bio-VHP	1.080

Investigating the impact the flue gas integration with the ethylene reactors has on the ethylene production cost, a comparison between the Biorefinery and Bio-F is conducted. The economical evaluation indicates that the reduced capital cost (i.e. the elimination of a separate furnace) and the enabling of selling by-products from the ethylene column as product do not result in a lower ethylene production cost within the given economical life time of 20 years.

In the Bio-MVR the implemention of a MVR on the rectifier reflux is investigated. The results indicate that the heat pump introduction significantly reduces the minimum hot utility demand of the biorefinery, and consequently increases the amount of excess solid residues. The reduced hot utility demand leads to a reduced steam production, and consequently the amount of co-generated electricity is reduced. Conversely, the electricity consumption of the biorefinery increases (due to MVR compressor work) resulting in a requirement of externally produced electricity. Taking all parameters into consideration, the results indicate that the ethylene production cost is reduced by the introduction of a MVR system in the biorefinery (i.e. comparing the Biorefinery and Bio-MVR), see Figure 4.22 and Table 4.21.

Investigating the influence VHP steam delivery to the cluster has on the ethylene production cost, a comparison between the Biorefinery and Bio-VHP is conducted. As illustrated in Figure 4.22 the ethylene production cost is slightly increased when the biorefinery delivers VHP steam to the cluster. The increased steam production in the CHP plant results in an increased electricity production (i.e. increased income). However, the amount of excess solid residues available for sale is reduced. The results indicate that the VHP steam delivery to the chemical cluster increases the total capital cost, the annual operating cost, the annual revenue, and the ethylene production cost. This indicates that (with assumed prices) it is not profitable to produce VHP steam in the CHP plant by firing of excess solid residues. It should be noted that selling price of steam is based on steam production of natural gas. Hence, no credit is accounted for the fact that the VHP steam produced in the CHP plant can be considered as renewable.

The results indicate that the ethylene production cost is lower in the stand-alone ethylene production plant (using purchased ethanol as feedstock) compared with the biorefinery (using lignocellulosic feedstock) without modifications, see Table 4.21. However, results also indicate that the introduction of a MVR system in the biorefinery

(Bio-MVR) can reduce the ethylene production cost (mainly due to substantial reduction in minimum hot utility demand) of the biorefinery. A 59% minimum hot utility demand reduction in the biorefinery corresponds to an ethylene production cost reduction of 6% (i.e. comparing the Biorefinery and Bio-MVR). This is due to the fact that the cost of raw material purchase is the largest contributor (i.e. 73%) to the annual operating cost of the biorefinery. Additionally, ethylene is the main income source (i.e. approximately 82%) of the biorefinery. The results indicate that the ethylene production using softwood feedstock in a biorefinery can be more profitable than purchasing ethanol (produced in Europe) to a stand-alone ethylene production plant, if introducing a MVR system in the biorefinery.

5 Conclusion

The results show that 277.6 kg ethanol per tonne dry wood can be produced in the stand-alone lignocellulosic ethanol plant. The results indicate that the process can cover the minimum hot utility (112 MW) and steam for direct injection into process streams (42 MW and 9 MW) by firing of lignin-rich solid residues in a CHP plant. The stand-alone ethanol production results in excess of solid residues (86 MW) and electricity (24 MW_{el}).

The results show that 0.57 kg ethylene per kg ethanol can be produced in the stand-alone ethanol dehydration to ethylene plant. The results indicate that the process requires external fuel (16 MW) to cover the minimum hot utility demand after implementation of a FEHX and firing of by-products (7.5 MW). Additionally, electricity (4 MW_{el}) and steam for direct injection (25 MW) must be produced externally.

The results indicate that 158.2 kg ethylene per tonne dy wood can be obtained combining the stand-alone lignocellulosic ethanol and the stand-alone ethanol dehydration to ethylene production into a biorefinery producing ethylene from lignocellulosic feedstock. The integration of the two stand-alone processes into a biorefinery results in a minimum hot and cold utility demand of 79 MW and 141 MW respectively, which corresponds to 40% and 28% reduction respectively. The reduction is mainly due to reuse of excess heat available in the ethylene production plant. By introducing a MVR on the rectifier reflux (Bio-MVR) the minimum hot utility demand of the biorefinery can be further reduced by 59%, corresponding to a 75% reduction compared with the two stand-alone processes.

The results indicate that the amount of lignin-rich solid residues generated by the ethanol production process is sufficient to cover the minimum hot utility, steam for direct injection, and electricity demand of the biorefinery. Moreover, the results show that the excess solid residues can eliminate the external fuel requirement of the catalytic ethylene reactors by integration of flue gases. Alternatively, the excess solid residues can be utilised in the CHP plant producing VHP (41 bar) steam to cover the heat deficit (i.e. 62 MW after site wide energy efficiency measures) in the cluster.

The results indicate that the ethylene production cost in the biorefinery without modifications is higher compared with the stand-alone ethylene production using purchased ethanol as feedstock. Additionally, the results indicate that it is not profitable to use excess solid residues in a CHP plant to eliminate the separate furnace. The results also show that it is not profitable to produce VHP steam for the chemical cluster by firing solid residues. However, the results indicate that the introduction of a MVR heat pump on the rectifier reflux in the biorefinery reduces the ethylene production cost by 6% (i.e. from 1.076 to 1.012 €/kg ethylene). The substantial energy savings achieved by the introduction of a MVR in the biorefinery also results in a lower ethylene production cost compared with the stand-alone ethylene production plant. Hence, the results indicate that the ethylene production in a biorefinery using softwood feedstock can be more profitable than in a stand-alone ethylene production plant purchasing ethanol (produced in Europe), if introducing a MVR system in the biorefinery. Figure 5.1 illustrates an overview of main material and energy streams in Bio-MVR.

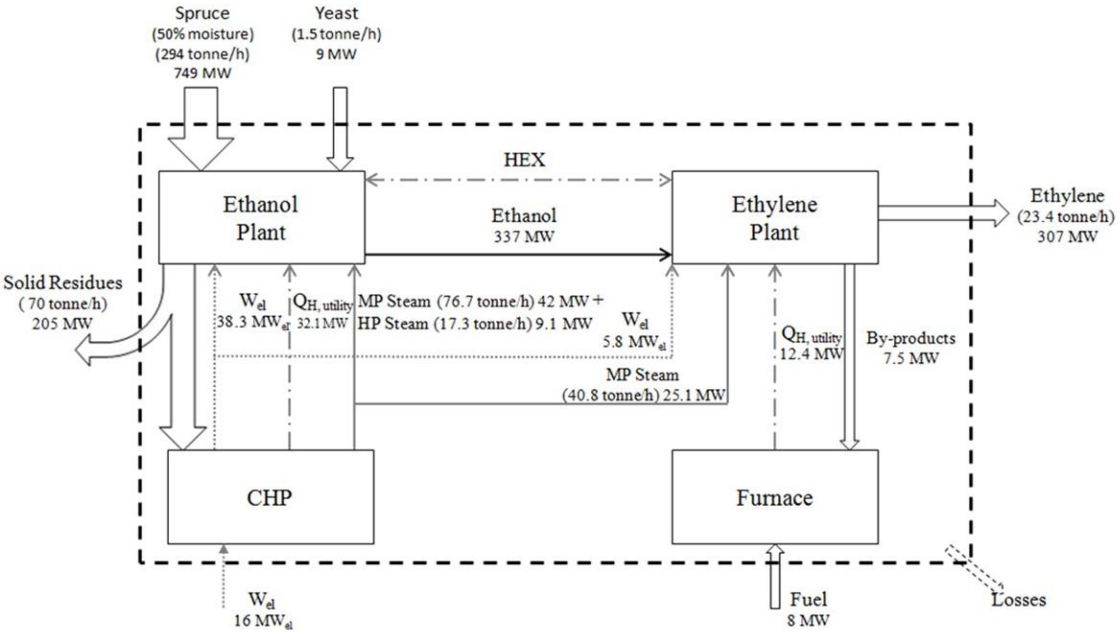

Figure 5.1 Overview of material (black and solid grey arrows for material and steam for direct injection respectively) and energy (dotted and dashed grey arrows for electricity and heat exchange or utility respectively) streams in the Bio-MVR process configuration.

6 Further work

6.1 Flue gas integration with ethylene reactors

The solution to eliminate the ethylene reactor furnace by heat integration with flue gases presented in the thesis may have certain implementation problems. The opportunity to combine a furnace with a steam boiler must be further investigated. For example, the ethylene reactors require high temperatures (450˚C) which may imply material problems in the flue gas channels. How the integration can be conducted practically, and at what cost, must also be investigated.

6.2 Integration opportunities with the chemical cluster

The opportunity to integrate the biorefinery with the chemical cluster in Stenungsund is investigated in the thesis. The integration opportunity investigated is based on results obtained in a TSA study after site wide energy efficiency measures (i.e. a hot utility deficit of 62 MW which can be covered with 41 bar steam). Different integration opportunities with the chemical cluster should be further investigated. For example, different modification scenarios of the chemical cluster, affecting e.g. the pressure levels of the hot utility deficit, should be investigated and how the biorefinery can be integrated to cover the hot utility demand of the cluster. Other more advanced, intelligent integration opportunities in Stenungsund may also be investigated.

6.3 District heating

The pinch temperature of the biorefinery is 95.9°C. Hence, the biorefinery has a potential to deliver excess heat below the pinch to a district heating network. Figure 6.1 illustrates the district heating potential for the biorefinery with a MVR introduced on the rectifier distillate, where the blue line represents the water in the district heating system. As can be seen in Figure 6.1 the biorefinery with a MVR has a potential to deliver approximately 24 MW (Q_{DH}) to a district heating system (assuming a supply temperature of 90°C and a return temperature of 50°C). The biorefinery without any modifications has the potential to deliver approximately 64 MW. It should be noted that flue gas condensation is not included in the district heating potential evaluation.

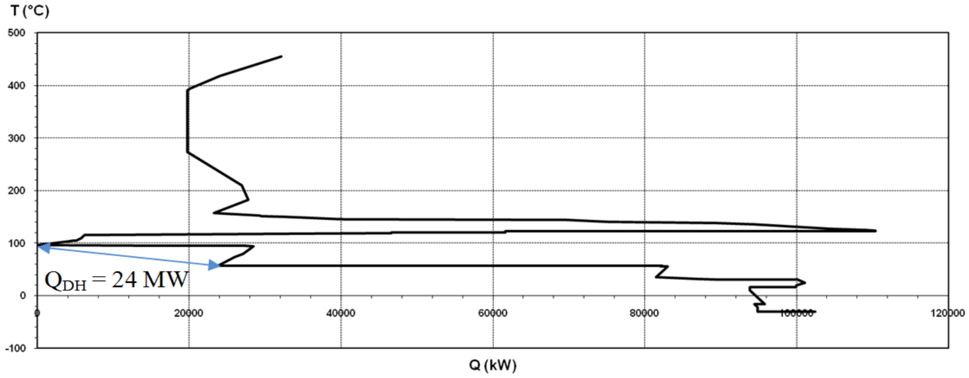

Figure 6.1 GCC for the biorefinery with a MVR introduced on the rectifier distillate, illustrating the district heating potential (blue line).

Currently there is no demand for expanding the existing district heating network in Stenungsund. If developing new technologies enabling district heat delivery on longer distances the district heating potential of the biorefinery could be further investigated. The district heating could bring in an extra income to the biorefinery.

6.4 Sustainable ethylene?

Furthermore, a thorough investigation is required to decide whether the produced ethylene can be considered to be sustainable. A more detailed analysis needs to be conducted to decide which is the most sustainable: a biorefinery in Stenungsund producing ethylene from lignocellulosic feedstock or a stand-alone ethylene production plant in Stenungsund purchasing ethanol feedstock. Parameters to be investigated include differences in CO_2 emissions, electricity production/consumption, and climate impact. The availability of sufficient amounts of lignocellulosic raw material in the area needs to be investigated when studying the alternative of introducing a biorefinery in Stenungsund. One question to ask may be if the produced ethylene can be considered to be sustainable if the raw material (in this case ethanol) is transported from far distances (e.g. from South America) and the electricity demand is covered by electricity produced from non-renewable resources in Europe?

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Appendix A: Alternative pretreatment methods

Hemicellulose and cellulose in lignocellulosic raw material can be made accessible for the downstream hydrolysis through addition of a base catalyst, i.e. undergo alkali pretreatment. The addition of a base catalyst, such as sodium-, calcium-, potassium hydroxide, or ammonia, affects the lignin association with hemicellulose and cellulose. The alkaline pretreatment achieves high efficiencies for agricultural residue and some hardwood species (Galbe, et al., 2002). The achieved effect is highly dependent on the lignin content of the feedstock. The efficiency decreases with increasing lignin content (Galbe, et al., 2002; Sun, et al., 2002; Holtzapple, et al., 1992).

The alkali pretreatment method is followed by some environmental concerns. The process requires high concentrations of salts, as a consequence a costly chemical recovery step is necessary. Also additional expenses concerning wastewater treatment and solid residue deposition may occur, e.g. due to incorporated salts into the biomass (Mosier, et al., 2005). However, one advantage with the process is the mild operating conditions (Carvalheiro, et al., 2008).

A combination of alkaline pretreatment and steam explosion can also be applied to lignocellulosic raw material, i.e. Ammonia Fiber Explosion (AFEX). The pretreatment method obtains very high sugar yields for both hemicellulose and cellulose (over 90% hydrolysis) for low lignin-containing agricultural residues. The method shows moderate success for hardwood. Furthermore, it is not an efficient pretreatment method handling softwood feedstock (Sun, et al., 2002). Some drawbacks with the AFEX pretreatment are the safety issues concerning handling ammonia and the need for chemical recovery. However, when employing the AFEX pretreatment method no sugar degradation occurs, leading to a higher overall sugar recovery and no inhibition in the downstream hydrolysis or fermentation steps. (Mosier, et al., 2005)

The recalcitrance of biomass can also be overcome by the organosolv pretreatment, i.e. the addition of an organic solvent and an inorganic catalyst. Examples of organic solvents are ethanol, methanol, and acetone. Common catalysts used are HCl and H_2SO_4. The conversion of cellulose in downstream hydrolysis step has been shown to be successful for large amount of different feedstocks. Some studies suggest that this also applies to hardwood and softwood (Zhu, et al., 2010). However, in order to avoid inhibition in the subsequent hydrolysis and fermentation step the solvent needs to be removed (Sun, et al., 2002). The resulting solid residue, i.e. lignin, obtains very high purity and quality when employing the organosolv pretreatment (Pan, et al., 2005).

Appendix B: User defined components – Input data

Input data for user defined components HMF and soluble lignin (LGNSOL) are based on information in Aspen Plus file "corn_stover_to_ethanol" developed by National Renewable Energy Laboratory (NREL) (National Renewable Energy Labratory, 2004).

Chemical Formula

Components\Specification\User Defined\Formula

- HMF $C6H6O3$

Properties\Molecular Structure

- LGNSOL $C10H13.9O1.3$

Pure Component Parameters

Properties\Estimation\Input

- Do not estimate any parameters

Properties\Parameters\Pure Component

- CPIG (Coefficients for the ideal gas heat capacity equation): HMF and LGNSOL
- PLXANT (Coefficients for the Extended Antoine vapor pressure equation): HMF and LGNSOL
- DHVLWT (Coefficients for the Watson Heat of Vaporization equation): LGNSOL
- USRDEF: HMF and LGNSOL, see Table B1

Table B1 User defined parameters for HMF and soluble lignin (LGNSOL) respectively. TB - Normal Boiling Point; OMEGA - Pitzer acentric factor; TC - Critical Temperature; PC - Critical Pressure; VC - Critical Volume; RKTZRA - Parameter for the Rackett liquid molar volume model; DGFORM - Ideal gas Gibbs free energy of formation at 298.15 K; DHFORM - Ideal gas heat of formation at 298.15 K. (National Renewable Energy Labratory, 2004)

Data set	Units	HMF	LGNSOL
TB	C	259,00	552.25
OMEGA		0.99	2.57
TC	C	457.86	737.95
PC	atm	51.67	61.19
VC	cc/mol	342.50	416.50
RKTZRA		0.20	0.36
DGFORM	cal/mol	-56821.44	-
DHFORM	cal/mol	77340.45	-469000,00

Appendix C: Stand-alone ethanol from lignocellulosic feedstock production - Reactions

Table C1 Reactions assumed to occur in the first pretreatment reactor and assumed fractional conversion of glucan, mannan, galactan, xylan, arabinan, acetate, and lignin respectively. (Nguyen, et al., 2000; Wingren, et al., 2004; Aden, et al., 2002)

Reaction	Stoichiometry	Conversion
1	Glucan + Water →Glucose	0.21
2	Glucan → Levulinic acid + Formic acid	0.1
3	Glucan → HMF + 2 Water	0.01
4	Mannan + Water → Mannose	0.79
5	Mannan →Levulinic acid + Formic acid	0
6	Galactan + Water → Galactose	0.79
7	Galactan → Levulinic acid + Formic acid	0
8	Xylan + Water → Xylose	0.79
9	Xylan →Furfural + 2 Water	0
10	Arabinan + Water → Arabinose	0.79
11	Arabinan → Furfural + 2 Water	0
12	Acetate → Acetic acid	1
13	Lignin → Soluble lignin	0.05

Table C2 Reactions assumed to occur in the second pretreatment reactor and assumed fractional conversion of glucan, mannan, galactan, xylan,and arabinan respectively. (Nguyen, et al., 2000)

Reaction	Stoichiometry	Conversion
1	Glucan + Water →Glucose	0.38
2	Glucan → Levulinic acid + Formic acid	0.01
3	Glucan → HMF + 2 Water	-
4	Mannan + Water → Mannose	0.05
5	Mannan →Levulinic acid + Formic acid	0.16
6	Galactan + Water → Galactose	0.05
7	Galactan → Levulinic acid + Formic acid	0.16
8	Xylan + Water → Xylose	0.05
9	Xylan →Furfural + 2 Water	0.16
10	Arabinan + Water → Arabinose	0.05
11	Arabinan → Furfural + 2 Water	0.16

Table C3 Reactions assumed to occur in the SSCF reactor and assumed fractional conversion of glucose, mannose, galactose, xylose,and arabinose respectively. The sugar degradation to lactic acid is assumed to be 0.002. However, in the total conversion rate of 0.032 the assumption that 3% of the fermentable sugars are lost to contamination is included. One major excluded reaction is the conversion of xylose to xylitol, where the fractional conversion of xylose can be assumed to be 0.046 (wt%). (Aden, et al., 2002)

Reaction	**Stoichiometry**	**Conversion**
1	Glucose → 2 Ethanol + 2 CO_2	0.90
2	Glucose → 2 Lactic acid	0.032
3	Glucose → 3 Acetic acid	0.015
4	Glucose + 2 CO_2 → 2 Succinic acid + O_2	0.006
5	Glucose + 2 Water → 2 Glycerol + O_2	0.004
6	Mannose → 2 Ethanol + 2 CO_2	0.90
7	Mannose → 2 Lactic acid	0.032
8	Mannose → 3 Acetic acid	0.015
9	Mannose + 2 CO_2 → 2 Succinic acid + O_2	0.006
10	Mannose + 2 Water → 2 Glycerol + O_2	0.004
11	Galactose → 2 Ethanol + 2 CO_2	0.90
12	Galactose → 2 Lactic acid	0.032
13	Galactose → 3 Acetic acid	0.015
14	Galactose + 2 CO_2 → 2 Succinic acid + O_2	0.006
15	Galactose + 2 Water → 2 Glycerol + O_2	0.004
16	3 Xylose → 5 Ethanol + 5 CO_2	0.80
17	3 Xylose → 5 Lactic acid	0.032
18	2 Xylose → 5 Acetic acid	0.014
19	3 Xylose + 5 CO_2 → 5 Succinic acid + 2.5 O_2	0.009
20	3 Xylose + 5 Water → 5 Glycerol + 2.5 O_2	0.003
21	3 Arabinose → 5 Ethanol + 5 CO_2	0.80
22	3 Arabinose → 5 Lactic acid	0.032
23	2 Arabinose → 5 Acetic acid	0.014
24	3 Arabinose + 5 CO_2 → 5 Succinic acid + 2.5 O_2	0.009
25	3 Arabinose + 5 Water → 5 Glycerol + 2.5 O_2	0.003

Table C4 Combustion reactions assumed to occur in the steam boiler with assumed fractional conversion. a) Molar extent (kmol/h). (National Renewable Energy Labratory, 2004)

Reaction	**Stoichiometry**	**Conversion**
1	Glucan + 6 O_2 → 6 CO_2 + 5 H_2O	1
2	Mannan + 6 O_2 → 5 H_2O + 6 CO_2	1
3	Galactan + 6 O_2 → 5 H_2O + 6 CO_2	1
4	Xylan + 5 O_2 → 5 CO_2 + 4 H_2O	1
5	Arabinan + 5 O_2 → 5 CO_2 + 4 H_2O	1
6	Lignin + 12.825 O_2 → 10 CO_2 + 6.95 H_2O	1
7	Yeast + 1.2 O_2 → 0.9 H_2O + CO_2 + 0.1 N_2	1
8	Glucose + 6 O_2 → 6 CO_2 + 6 H_2O	1
9	Mannose + 6 O_2 → 6 H_2O + 6 CO_2	1
10	Galactose + 6 O_2 → 6 H_2O + 6 CO_2	1
11	Xylose + 5 O_2 → 5 H_2O + 5 CO_2	1
12	Arabinose + 5 O_2 → 5 H_2O + 5 CO_2	1
13	Ethanol + 3 O_2 → 3 H_2O + 2 CO_2	1
14	Soluble Lignin + 12.825 O_2 → 6.95 H_2O + 10 CO_2	1
15	HMF + 6 O_2 → 3 H_2O + 6 CO_2	1
16	Furfural + 5 O_2 → 2 H_2O + 5 CO_2	1
17	Acetic Acid + 2 O_2 → 2 H_2O + 2 CO_2	1
18	Lactic Acid + 3 O_2 → 3 H_2O + 3 CO_2	1
19	Glycerol + 3.5 O_2 → 4 H_2O + 3 CO_2	1
20	Succinic Acid + 3.5 O_2 → 3 H_2O + 4 CO_2	1
21	H_2SO_4 → H_2O + 0.5 O_2 + SO_2	1
22	CO_2 → 0.5 O_2 + CO	0.0001[a]
23	SO_2 + 0.5 O_2 + H_2O → H_2SO_4	0.01

Appendix D: Stand-alone ethanol dehydration to ethylene production - Reactions

Table D1 Reactions assumed to occur in the stoichimetric reactor and obtained selectivity.

Reaction	Stoichiometry	Selectivity
1	Ethanol → Ethylene + Water	0.988
2	2Ethanol → Diethyl ether + Water	0.00052
3	Ethanol → Acetaldehyde + Hydrogen	0.002
4	2Ethanol + Hydrogen → 2Ethane + 2Water	0.0027
5	3Ethanol → Propylene + 3Water	0.0006
6	2Ethanol → Butadien + 2Water	0.005
7	Ethanol → Carbon monoxide + Methane + Hydrogen	0.00007
8	Ethanol + Water → Carbon dioxide + Methane + Hydrogen	0.0011

Appendix E: Stream data for the stand-alone lignocellulosic ethanol production

Table E1 Stream data for the stand-alone lignocellulosic ethanol production plant.

Name	Type	T_{start} [°C]	T_{target} [°C]	Q [kW]	Comments
1	Hot	278	155	24018	FG cooler, soft
2	Hot	145.5	143.5	11122	Condensing flash steam, soft
3	Hot	100.9	99.6	27898	Condensing flash steam, soft
4	Hot	99.5	99	1087	Condensing flash steam, soft
5	Hot	100.1	35	26342	Cooler liquid fraction to SSCF
6	Hot	99.6	37	4589	Cooler flash steam, to WWT, soft
7	Hot	109.4	37	6155	Cooler effect #2 (evap. cond.), soft
8	Hot	87.5	87.4	53828	Condenser Rectifier column
9	Hot	62.2	62.1	58615	Condenser flash steam, soft
10	Hot	60.1	60	944	Condenser Beer column
11	Hot	40.1	35	6686	Cooling enzymatic hydrolysis
12	Hot	35.1	35	10805	Cooling fermentation
13	Hot	114.8	37	3629	Cooler Rectifier bottom, soft
14	Hot	79.1	37	5455	Cooler recirculation water, soft
15	Cold	10	205	28087	Air preheater combustion
16	Cold	147	177	8209	Preheater condensate return
17	Cold	14.3	177	19106	Feed water preheater combustion
18	Cold	117.2	117.3	48836	Reboiler Beer column
19	Cold	114.7	114.8	17882	Reboiler Rectifier column
20	Cold	110.4	114.5	40489	Evaporator (effect#1 evaporation)
21	Cold	98.6	110.4	1283.6	Evaporator (effect#1 heating to b.p.)
22	Cold	30.1	100	41845	Preheater Beer column

Appendix F: Stream data for the stand-alone ethanol dehydration to ethylene production

Table F1 Stream data for the stand-alone ethanol dehydration to ethylene production plant.

Name	**Type**	**T_{start} [°C]**	**T_{target} [°C]**	**Q [kW]**	**Comments**
1	Hot	428	172	13251.4	Reactor effluent #1
2	Hot	172	156.77	25128.0	Reactor effluent #2
3	Hot	156.7	140.4	7699.8	Reactor effluent #3
4	Hot	140.4	114.9	5707.1	Reactor effluent #4
5	Hot	114.9	84	4151.6	Reactor effluent #5
6	Hot	132.9	38	1844.7	Midcooler#1 Compressor
7	Hot	128	38	1287.9	Midcooler#2 Compressor
8	Hot	129.4	38	1294.0	Midcooler#3 Compressor
9	Hot	61.2	20	1939.4	Cooler Quench tower
10	Hot	56.5	15	532.1	Cooler before dryer
11	Hot	15	-17.2	2337.3	Precooler C2 splitter
12	Hot	-25	-25.1	7578.7	Condenser C2 splitter
13	Cold	169	450	21244.2	Furnace #1
14	Cold	385.6	450	3562.0	Furnace #2
15	Cold	386.9	450	3476.0	Furnace #3
16	Cold	389	450	3345.0	Furnace #4
17	Cold	11.2	11.3	6091.2	Reboiler C2 splitter
18	Cold	-21.4	-21.3	1379.5	Reboiler Stripper
19	Cold	25	135	4274.4	Preheat Ethanol feed

Appendix G: Stream data for the Biorefinery – Ethylene from lignocellulosic feedstock production

Table G1 Stream data for the Biorefinery (without modifications) producing ethylene from lignocellulosic feedstock.

Name	**Type**	**T_{start}** [°C]	**T_{target}** [°C]	**Q** **[kW]**	**Comments**
1	Hot	278	155	20903	FG cooler, soft
2	Hot	145.5	143.5	11122	Condensing flash steam, soft
3	Hot	100.9	99.6	27898	Condensing flash steam, soft
4	Hot	99.5	99	1087	Condensing flash steam, soft
5	Hot	100.1	35	26342	Cooler liquid fraction to SSCF
6	Hot	99.6	37	4589	Cooler flash steam, to WWT, soft
7	Hot	109.4	37	6155	Cooler effect #2 (evap. cond.), soft
8	Hot	92.1	92	39547	Condenser Rectifier column
9	Hot	62.2	62.1	58615	Condenser flash steam, soft
10	Hot	60.1	60	944	Condenser Beer column
11	Hot	40.1	35	6686	Cooling enzymatic hydrolysis
12	Hot	35.1	35	10805	Cooling fermentation
13	Hot	114.8	37	3629	Cooler Rectifier bottom, soft
14	Hot	79.1	37	5455	Cooler recirculation water, soft
15	Hot	428	223.6	10580.4	Reactor effluent #1
16	Hot	146	145	27798.9	LP waste heat steam generation
17	Hot	156.7	140.4	7699.8	Reactor effluent #3
18	Hot	140.4	114.9	5707.1	Reactor effluent #4
19	Hot	114.9	84	4151.6	Reactor effluent #5
20	Hot	132.9	38	1844.7	Midcooler#1 Compressor
21	Hot	128	38	1287.9	Midcooler#2 Compressor
22	Hot	129.4	38	1294.0	Midcooler#3 Compressor
23	Hot	61.2	20	1939.4	Cooler Quench tower
24	Hot	56.5	15	532.1	Cooler before dryer
25	Hot	15	-17.2	2337.3	Precooler C2 splitter
26	Hot	-25	-25.1	7578.7	Condenser C2 splitter
27	Cold	10	205	24444	Air preheater combustion
28	Cold	147	177	4805	Preheater condensate return
29	Cold	14.3	177	27434	Feed water preheater combustion
30	Cold	117.2	117.3	48836	Reboiler Beer column
31	Cold	114.7	114.8	17882	Reboiler Rectifier column
32	Cold	110.4	114.5	40489	Evaporator (effect#1 evaporation)
33	Cold	98.6	110.4	1283.6	Evaporator (effect#1 heating to b.p.)
34	Cold	30.1	100	41845	Preheater Beer column
35	Cold	213.6	450	12553.6	Furnace #1
36	Cold	385.6	450	3562.0	Furnace #2
37	Cold	386.9	450	3476.0	Furnace #3
38	Cold	389	450	3345.0	Furnace #4
39	Cold	11.2	11.3	6091.2	Reboiler C2 splitter
40	Cold	-21.4	-21.3	1379.5	Reboiler Stripper

Appendix H: Stream data for the Bio-MVR

Table H1 Stream data for the Bio-MVR

Name	**Type**	**T_{start}** [°C]	**T_{target}** [°C]	**Q** **[kW]**	**Comments**
1	Hot	278	155	13935	FG cooler, soft
2	Hot	145.5	143.5	11122	Condensing flash steam, soft
3	Hot	100.9	99.6	27898	Condensing flash steam, soft
4	Hot	99.5	99	1088	Condensing flash steam, soft
5	Hot	100.1	35	26342	Cooler liquid fraction to SSCF
6	Hot	99.6	37	4589	Cooler flash steam, to WWT, soft
7	Hot	109.4	37	6148	Cooler effect #2 (evap. cond.), soft
8	Hot	162.1	128.4	45710	Condenser Rectifier column
9	Hot	62.2	62.1	58615	Condenser flash steam, soft
10	Hot	60.1	60	944	Condenser Beer column
11	Hot	40.1	35	6614	Cooling enzymatic hydrolysis
12	Hot	35.1	35	10119	Cooling fermentation
13	Hot	114.8	37	3629	Cooler Rectifier bottom, soft
14	Hot	79.1	37	3685	Cooler recirculation water, soft
15	Hot	428	223.6	10580.4	Reactor effluent #1
16	Hot	146	145	27798.9	LP waste heat steam generation
17	Hot	156.7	140.4	7699.8	Reactor effluent #3
18	Hot	140.4	114.9	5707.1	Reactor effluent #4
19	Hot	114.9	84	4151.6	Reactor effluent #5
20	Hot	132.9	38	1844.7	Midcooler#1 Compressor
21	Hot	128	38	1287.9	Midcooler#2 Compressor
22	Hot	129.4	38	1294.0	Midcooler#3 Compressor
23	Hot	61.2	20	1939.4	Cooler Quench tower
24	Hot	56.5	15	532.1	Cooler before dryer
25	Hot	15	-17.2	2337.3	Precooler C2 splitter
26	Hot	-25	-25.1	7578.7	Condenser C2 splitter
27	Cold	10	205	16296	Air preheater combustion
28	Cold	147	177	1294	Preheater condensate return
29	Cold	14.3	177	27433	Feed water preheater combustion
30	Cold	117.2	117.3	48836	Reboiler Beer column
31	Cold	114.7	114.8	17882	Reboiler Rectifier column
32	Cold	110.4	114.5	40489	Evaporator (effect#1 evaporation)
33	Cold	98.6	110.4	1283.6	Evaporator (effect#1 heating to b.p.)
34	Cold	30.1	100	41845	Preheater Beer column
35	Cold	213.6	450	12553.6	Furnace #1
36	Cold	385.6	450	3562.0	Furnace #2
37	Cold	386.9	450	3476.0	Furnace #3
38	Cold	389	450	3345.0	Furnace #4
39	Cold	11.2	11.3	6091.2	Reboiler C2 splitter
40	Cold	-21.4	-21.3	1379.5	Reboiler Stripper

Appendix I: Equipment costs for individual unit operations in the lignocellulosic ethanol production

Table I1 *Equipment costs for main unit operations in the ethanol production. (Hamelinck, et al., 2005)*

Unit	**Quantity**	**Base Eq. Cost (C_B) (2003) [Million €]**	**Base Capacity (Q_B)**		**Scaling Factor (M)**	**Installation factor**	**Capacity (Q)**	**Eq. Cost (C_E) (Base Year) [Million €]**	**Eq. Cost (2010)**	**Capital Cost (2010) [Million €]**
Mechanical pretreat, Feeders, Conveyer	2	4.44	83.3	tonnedry/h(input)	0.67	2	73.5	8.2	11.3	22.6
Pretreatment 1 (Steam Explosion)	1	1.41	83.3	tonnedry/h(input)	0.78	2.36	147	2.2	3.0	7.2
Solid Separation after pretreat	9.1	1.05	10.1	tonnedry/h(input)	0.65	1.69	92.0	40.2	55.5	93.8
Pretreatment 2 (Steam Explosion)	1	1.41	83.3	tonnedry/h(input)	0.78	2.36	92.0	1.5	2.1	5.0
SSCF	40.4	0.67	1.04	tonne/h ethanol	0.8	1.88	1.0	27.2	37.6	70.7
Distillation system	2.2	2.96	18466	kg/h ethanol	0.7	2.75	41214.8	11.6	16.0	44.0
Solid Separation after beer column	5.3	1.05	10.1	tonnedry/h(input)	0.65	1.69	53.5	16.4	22.7	38.4

Table I2 Equipment costs for main pumps in the ethanol production. (Aden, et al., 2002)

Unit	Quantity	Base Eq. Cost (C_B) (2003) [Million €]	Base Capacity (Q_B)		Scaling Factor (M)	Installation factor	Capacity (Q)	Eq. Cost (C_E) (Base Year) [Million €]	Eq. Cost (2010)	Capital Cost (2010) [Million €]
Pump 1	1	10600	171056	kg/h	0.79	2.8	215403	0.009	0.013	0.037
Pump 2, Sulphuric Acid	1	4800	3289	kg/h	0.79	2.8	1470	0.002	0.003	0.005
Pump 3, Sulphuric Acid	1	4800	3289	kg/h	0.79	2.8	735	0.001	0.002	0.003
Pump 4	1	10600	171056	kg/h	0.79	2.8	90805	0.005	0.007	0.013
Pump 5	1	10600	171056	kg/h	0.79	2.8	25984	0.002	0.002	0.005
Pump 6, Rotary Pump	1	61368	428764	kg/h	0.7	2.8	616155	0.057	0.082	0.160
Pump 7, Rotary Pump	1	61368	428764	kg/h	0.7	2.8	655006	0.060	0.085	0.167

Table I3 Equipment costs for evaporation effects in the ethanol production. (Aden, et al., 2002)

Unit	Quantity	Base Eq. Cost (C_B) (2003) [Million €]	Base Capacity (Q_B)		Scaling Factor (M)	Installation factor	Capacity (Q)	Eq. Cost (C_E) (Base Year) [Million €]	Eq. Cost (2010)	Capital Cost (2010) [Million €]
Evaporation 1	1	435650	22278	ft^2	0.68	2.1	16958.1	0.26	0.38	0.80
Evaporation 2	1	435650	22278	ft^2	0.68	2.1	43629.2	0.50	0.72	1.52
Evaporation 3	1	435650	22278	ft^2	0.68	2.1	52303.9	0.56	0.82	1.72
Evaporation 4	1	435650	22278	ft^2	0.68	2.1	48484.9	0.53	0.78	1.63
Evaporation 5	1	435650	22278	ft^2	0.68	2.1	65281.7	0.65	0.95	2.00

Table I4 Equipment costs for flash operations in the ethanol production. (Aden, et al., 2002)

Unit	**Quantity**	**Base Eq. Cost (C_B) (2003) [Million €]**	**Base Capacity (Q_B)**		**Scaling Factor (M)**	**Installation factor**	**Capacity (Q)**	**Eq. Cost (C_E) (Base Year) [Million €]**	**Eq. Cost (2010)**	**Capital Cost (2010) [Million €]**
Flash 1	1	64100	278865	kg/h	0.93	1.2	420477	0.068	0.098	0.12
Flash 2	1	64100	278865	kg/h	0.93	1.2	18782	0.004	0.005	0.01
Flash 3	1	64100	278865	kg/h	0.93	1.2	184154	0.032	0.045	0.05
Flash 4	1	64100	278865	kg/h	0.93	1.2	165372	0.029	0.041	0.05
Flash 5	1	64100	278865	kg/h	0.93	1.2	393948	0.064	0.092	0.11
Flash 6	1	64100	278865	kg/h	0.93	1.2	387791	0.063	0.091	0.11
Flash 7	1	64100	278865	kg/h	0.93	1.2	378989	0.062	0.089	0.11
Flash 8	1	64100	278865	kg/h	0.93	1.2	370761	0.060	0.087	0.10
Flash 9	1	64100	278865	kg/h	0.93	1.2	362000	0.059	0.085	0.10

Appendix J: Equipment costs for the CHP plant and the MVR heat pump

Table J1 CHP plant cost for the different biorefinery configurations, and equipment cost of the MVR system. (Hamelinck, et al., 2005) (Harvey, 2009)

Unit Operation	**Quantity**	**Base Eq. Cost (C_B) (2003) [Million €]**	**Base Capacity (Q_B)**		**Scaling Factor (M)**	**Installation factor**	**Capacity (Q)**	**Eq. Cost (C_E) (Base Year) [Million €]**	**Eq. Cost (2010)**	**Capital Cost (2010) [Million €]**
Boiler Stand-alone	1	27.1	235	tonne/h SH steam	0.73	1.4	275	30.4	42.0	58.8
Steam system + turbine Stand-alone	1	5.36	10.3	MW_{el}	0.7	1.86	55.4	17.4	24.0	44.7
Boiler Biorefinery	1	27.1	235	tonne/h SH steam	0.73	1.4	244	27.9	38.5	53.9
Steam system + turbine Biorefinery	1	5.36	10.3	MW_{el}	0.7	1.86	46.05	15.3	21.1	39.3
Boiler Bio-F	1	27.1	235	tonne/h SH steam	0.73	1.4	365	37.4	51.6	72.3
Steam system + turbine Bio F	1	5.36	10.3	MW_{el}	0.7	1.86	46.39	15.4	21.2	39.5
Boiler Bio-MVR	1	27.1	235	tonne/h SH steam	0.73	1.4	165	20.9	28.9	40.5
Steam system + turbine Bio-MVR	1	5.36	10.3	MW_{el}	0.7	1.86	28.23	10.9	15.0	27.9
Boiler Bio-VHP	1	27.1	235	tonne/h SH steam	0.73	1.4	356	36.7	50.7	70.9
Steam system + turbine Bio-VHP	1	5.36	10.3	MW_{el}	0.7	1.86	54.98	17.3	23.9	44.5
MVR Rectifier reflux (Compressor)	1	0.07	250	kW	0.46	1.9	6170	0.3	0.4	0.8

Appendix K: Exchange rates

Table K1 Exchange rates. (x-rates)

	€	**$**	**SEK**
€	1	0,723327	8,70901
$	1,3825	1	6,29946
SEK	0,114824	0,158744	1