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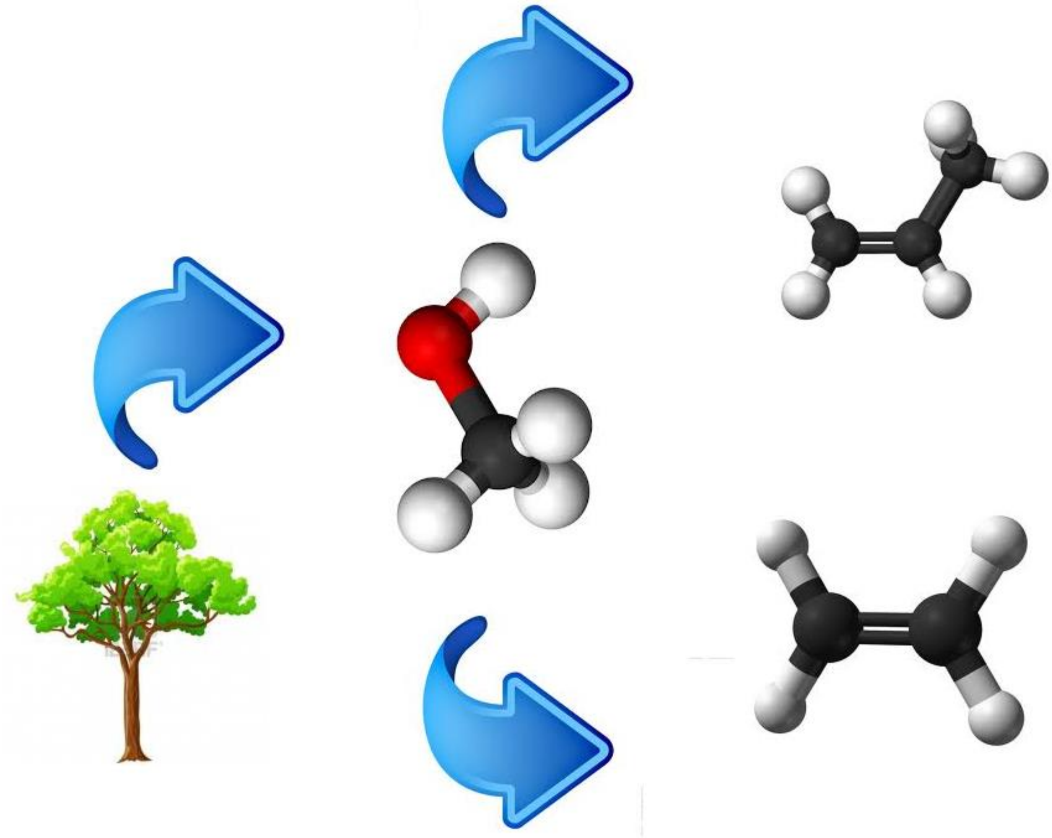

Process integration study of biomass-to-methanol (via gasification) and methanol-to-olefins (MTO) processes in an existing steam cracker plant

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

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CHALMERS UNIVERSITY OF TECHNOLOGY
Göteborg, Sweden 2013

MASTER'S THESIS

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Cover:
Biomass to methanol and methanol to propylene and ethylene

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ABSTRACT

Ethylene and propylene, also referred to as light olefins, are important building blocks within the chemical industry and are used for the production of plastics. They are usually produced via steam cracking of naphtha or other light fractions of petroleum. This process route is a very energy consuming process and consumes non-renewable feedstock and will thus not be sustainable in the long run. Fossil feedstock can be replaced with biomass. Methanol is produced from biomass via gasification and methanol synthesis and then light olefins are produced in a Methanol-to-olefins (MTO) process. Replacing some of the olefins produced today via steam cracking at Borealis in Stenungsund with olefins produced via the MTO process is a first shift towards more sustainable production processes.

The consequences of integrating the MTO process with the existing cracker plant as well as integrating the complete process chain from biomass to olefins with the existing cracker plant have been evaluated based on the potential for heat integration and the potential to produce high pressure steam. The potential for high pressure steam production is particularly relevant given the loss of high pressure steam production from the cracker furnaces when reducing their capacity.

Energy- and mass balances were obtained by creating simulation models for the MTO process as well as the biomass to methanol process. The energy balances obtained were used as input data for a heat integration study using pinch analysis. The opportunities for heat integration with the existing cracker plant were evaluated for different cases. The first case was restricted to heat integration opportunities for the MTO process only. The second case included heat integration opportunities for the complete process chain from biomass to olefins.

From the simulation models an energy yield from biomass to methanol of 0.51 MW/MW was obtained, which is similar to other published studies of this process. The yield going from methanol to olefins was based on yield data for the UOP/Hydro technology.

The heat integration for the MTO and steam cracker case indicates that it is possible to transfer approximately 11.6 MW from the cracker process to the MTO process. Furthermore, it is possible to produce approximately 18 MW of high pressure steam from excess heat from the MTO process, which is not enough to cover the reduced production of high pressure steam from the cracking furnaces. In the biomass to olefins process, heat integration with the steam cracker shows opportunities to recover approximately 22 MW of process heat and produce 175 MW of high pressure steam, which would be enough to cover the loss in high pressure steam production.

Key words: Methanol to Olefins (MTO), Biomass to methanol, heat integration, process integration, pinch analysis, simulation

Processintegrationsstudie av en biomassa till metanol (via förgasning) och en metanol till olefiner (MTO) process i en existerande ångkrackeranläggning
Examensarbete inom masterprogrammet Innovative and Sustainable Chemical Engineering
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SAMMANFATTNING

Eten och propen, även kallade lätta olefiner, är viktiga byggstenar i den kemiska industrin och används exempelvis till produktionen av plast. De produceras ofta genom ångkrackning av nafta eller andra lätta fraktioner av olja. Ångkrackning är en mycket energikrävande process, och det faktum att processen både konsumerar mycket energi och icke förnybara råvaror, kommer denna process ej vara hållbar i längden. Ett sätt att hantera denna fråga är att byta ut den icke förnybara råvaran mot biomassa, vilket kan möjliggöras genom att producera metanol genom att förgasa biomassa och sedan producera metanol i en metanolsyntes process, vilken sedan kan användas i metanol-till-olefiner (MTO) processen. Genom att byta ut en del av de olefiner som produceras via ångkrackning på Borealis med olefiner producerade via MTO processen är det möjligt att skifta mot mer hållbara produkter.

Konsekvenserna som uppstår då MTO processen integreras med befintlig kracker, och då processerna när man går från biomassa till olefinermed befintlig kracker, har utvärderats baserat på potentialen för värmeintegration och potentialen för högtrycksångproduktion. Potentialen för högtrycksångproduktion har utvärderarts på grund av en reducerad ångproduktion från krackern de dess kapacitet minskas och ersätts med MTO processen.

Energi- och massbalanser har erhållits genom att göra simuleringsmodeller för processerna, både för MTO processen och för processerna när man går från biomassa till metanol. Energibalanserna som erhållits har använts i en pinchanalys. Möjligheterna för värmeintegration med den befintliga krackeranläggningen utvärderades för olika fall, ett då endast MTO processen och krackern var inkluderade, och ett då alla processer från biomassa till olefiner samt krackern var inkluderade.

Från simuleringsmodellerna erhölls ett energiutbyte för biomassa till metanol processerna på 0.51 MW/MW, vilket liknar resultat från andra studier gjorda på samma ämne. Utbytet för metanol till olefiner erhölls från utbytedata för UOP/Hydro tekniken.

Värme integrationen för MTO processen med befintlig kracker, resulterade i att det ungefär var möjligt att integrera 11.6 MW och ungefär möjligt att producera 18 MW högtrycksånga, vilket inte är tillräckligt för att täcka reduktionen av högtrycksånga från krackern. Värmeintegrationen för alla processer från biomassa till olefiner med befintlig kracker resulterade i att det ungefär var möjligt att integrera 22 MW och ungefär möjligt att producera 175 MW högtrycksånga, vilket skulle vara tillräckligt för att täcka reduktionen av ångproduktion från krackern.

Nyckelord: Metanol-till-olefiner (MTO), Biomassa till metanol, värmeintegration,
processintegration, pinchanalys, simulering

Contents

Preface

This study investigates opportunities for heat integration between a biomass to methanol process, a methanol-to-olefins (MTO) process, and an existing naphtha steam cracker plant.

This Master thesis was carried out at the Department of Energy and Environment, Division of Heat and Power Technology, Chalmers University of Technology, Sweden in cooperation with Borealis in Stenungsund.

I would like to thank my supervisors Maria Arvidsson and Roman Hackl at Chalmers, my supervisor Lars Pettersson at Borealis and my examiner Professor Simon Harvey for all help and guidance.

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Göteborg June 2013

Erika Johansson

Notations

Abbreviations

ATR	AutoThermal Reforming
ER	Energy Ratio, net HHV energy efficiency [%]
GCC	Grand Composite Curve
HHV	Higher Heating Value [kJ/kg]
HP	High Pressure steam
LP	Low Pressure steam
MP	Medium Pressure steam
LPMEOH^{TM}	Air Products Liquid Phase Conversion company trade mark for a Liquid phase methanol synthesis process
MTO	Methanol To Olefins
WGS	Water-Gas-Shift

Symbols

$E_{biomass}$	HHV of biomass feed to gasifier [kJ/s]
E_{elec}	HHV of fuel used for electricity production [kJ/s]
E_{fuel}	HHV of fuel/product produced [kJ/s]
E_{heat}	HHV of feed converted to heat [kJ/s]
ΔT_{min}	Minimum temperature difference [K]
Q	Duty [kW]
$Q_{C,min}$	Minimum cold utility required [kW]
Q_{DH}	Potential for district heating delivery [kW]
$Q_{H,min}$	Minimum hot utility required [kW]
Q_{REC}	Heat recovered in the process [kW]
$W_{el.demand}$	Work, needed in the form of electricity, used within the processes to increase the pressure of process flows with pumps and compressors
η_{th}	Thermal efficiency [%]
$\eta_{elec\ or\ heat}$	HHV efficiency of produced electricity or heat [%

1 Introduction

1.1 Background

Ethylene and propylene, also referred to as light olefins, are important building blocks used for producing e.g. polymers (Zimmermann & Walzl, 2009). Ethylene is one of the largest consumed chemicals by volume, and is mostly used as a feedstock in the manufacturing of plastics, fibers, and other organic chemicals. Ethylene is a fundamental building unit in the global petrochemical industry. Products produced from ethylene include polyethylene (PE), polyvinylchloride (PVC) and polyethylene terephthalate (PET) (Global Industry Analysts, Inc, 2008). Propylene is also an important feedstock for industrial derivatives such as polypropylene, acrylonitrile, propylene-oxide and phenol. Propylene usage spans over various industries, from automotive and construction to packaging, medical and electronics (CHEMSYSTEMS, 2012). Currently most olefins are produced via thermal cracking of naphtha or other light fractions of petroleum with steam, which is often referred to as steam cracking. During the process the hydrocarbon feedstock, usually of fossil origin, is cracked into smaller molecules. The process is very energy demanding. The resulting product mix from the cracking process, which varies depending on the process conditions, must then be separated into the desired products by using a sequence of separation and other chemical treatment steps (Zimmermann & Walzl, 2009).

Increased emissions of greenhouse gases are leading to global climate change, affecting humans as well as other species. Most greenhouse gas emissions are related to the combustion of fossil fuels. Another problem regarding fossil feedstock is that we are facing depletion of them. The scarcity of oil affects both the energy security around the world and the availability of feedstock used in the chemical industry worldwide. As mentioned above, olefins are important building blocks in the chemical industry. Thus, since the usual way of producing them both consumes a lot of energy and non-renewable carbon sources such as oil, the method will not be sustainable in the long run. One way to deal with this issue is to replace the non-renewable feedstock with biomass. One opportunity to achieve this transition is to utilize methanol produced via gasification of biomass and methanol synthesis, followed by the production of olefins in a methanol-to-olefin (MTO) process (Holmgren, et al., 2012; Hackl & Harvey, 2010). In the MTO process methanol is converted to ethylene and propylene via catalysis. Operating conditions of the reactor, e.g. temperature and pressure will influence the product ratio between ethylene and propylene. Therefore it is possible to maximize the production towards ethylene or propylene.

Olefins are currently produced via steam cracking at Borealis located in Stenungsund. Borealis is part of a chemical cluster in Stenungsund, and their steam cracker plant is the heart of this cluster (Hackl, et al., 2011). Within this chemical cluster they have a common vision that “in 2030 Stenungsund industry park will be the hub for the manufacturing of sustainable products within the Swedish chemical industry” (Business Region Göteborg, 2011). A major challenge in this vision is to shift towards renewable feedstocks and energy carriers. There is also a need for energy efficiency and energy integration within the cluster (Business Region Göteborg, 2011). A first transition towards this vision at Borealis could be to replace a part of the olefins produced via steam cracking with olefins produced via the MTO technology. Methanol can be produced both from biomass and from fossil feedstocks, and most of the methanol currently available on the world market today is produced from coal or natural gas. To meet the vision it is important that the methanol used is produced from renewable biomass feedstock.

This master thesis will investigate the consequences of replacing part of the olefins produced via steam cracking of naphtha with the methanol to olefins process (MTO). The thesis will investigate the option of operating the MTO process with methanol purchased on the world market, as well as a complete conversion chain including biomass gasification with downstream methanol synthesis which is thereafter fed to the MTO process. The investigation uses flowsheeting software to generate heat and mass balances for the different process configurations investigated and pinch analysis to evaluate heat integration opportunities.

1.2 Aim and Scope

The aim of this master thesis is to identify the consequences of integrating a biomass to methanol process and/or an MTO process to produce light olefins with the existing steam cracker plant, which partly replaces todays` fossil feedstock. Focus will be on heat integration opportunities of the new MTO unit with the existing plant and the analysis of the resulting change in energy balance i.e. reduced steam production when decreasing the capacity of the conventional steam cracker. The analysis of the resulting change in energy balance at the steam cracker plant is also evaluated in order to be able to evaluate the effects of implementing process integration. In this study has also the possibilities for heat integration within the MTO process as well as within the biomass to methanol processes been investigated to be able to evaluate effects of process integration between the processes. For the MTO process has also some operating conditions been changed to enable for better process integration alternatives. It is important to utilize excess heat within the processes as efficiently as possible to minimize the need of external energy sources.

The different combinations for process integration investigated can be seen in Figure 1-1, integration within the individual processes, biomass to methanol and methanol to olefins has as mentioned also been investigated.

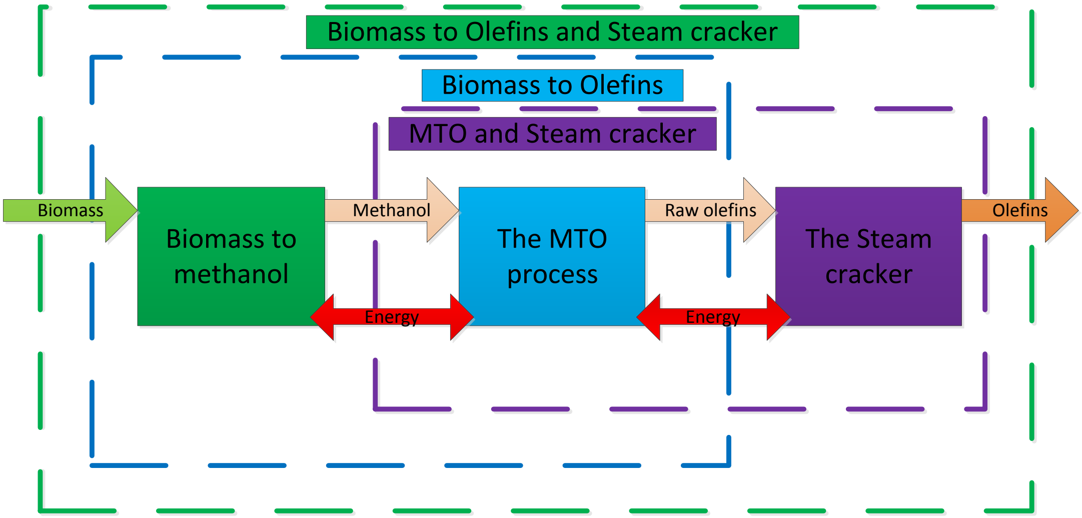


Figure 1-1 Heat integration combinations investigated. Heat integration within biomass to methanol and within the MTO process has also been investigated.

The aim has been met by creating a simulation model of the MTO process using the commercial flowsheeting software Aspen Plus, based on data found in scientific literature. Simulation models used for the processes from biomass to methanol were originally made at the division for Heat and Power Technology at Chalmers University of Technology (Isaksson, et al., 2012). Some of these models were adjusted and developed in accordance with information found in the literature. These models were then used to extract stream data necessary for conducting the heat integration study. Stream data for the existing steam cracker plant was taken from a previous study conducted at the division (Hedström & Johansson, 2008). Additional data for the steam cracker plant was provided by Pettersson (2013). The data obtained was necessary to enable a heat integration study. The heat integration study was made to investigate internal heat recovery potentials and the demands for external heating and cooling.

The MTO process unit was assumed to be sized so as to replace the ethylene production of two cracker ovens at the existing Borealis steam cracker plant. The methanol feed flowrate was selected so as to achieve an ethylene production rate of 200 kt/yr, assuming that the MTO process is designed to maximize ethylene production. Since the reactor operating conditions can be tuned to favor maximum production of propylene, these conditions were also investigated. The calculations were based upon the same methanol feed flowrate to the reactor and the same reactor volume and catalyst quantity. Under these conditions, the reactor product mix produces less than 200 kt/yr of ethylene.

The MTO process product gas is assumed to be fed to the existing separation process train at the steam cracker plant. Given that the product gas from the MTO process has a different composition that that of the product gas from the naphtha steam cracker reactors in the existing process, it is likely that the energy balance profile of the separation train is affected. These effects are however not investigated in this thesis.

2 Process outline

In order to be able to produce olefins from biomass, the biomass (logging residues) is first converted (by pre-treatment, gasification, gas cleaning, and gas conditioning) to synthesis gas (mainly consisting of CO and H_2), before being synthesized to methanol. Methanol is then reformed to olefins in the MTO process, illustrated in Figure 2-1.

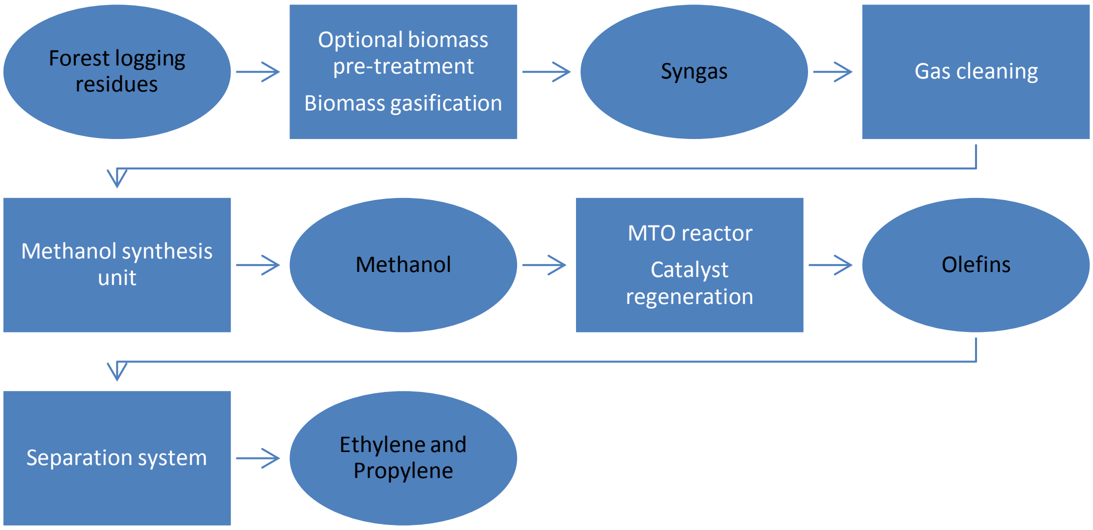


Figure 2-1 Simple process flowsheet, biomass to olefins.

2.1 Biomass to methanol process

Before the biomass is gasified, it can be pre-treated via e.g. drying or pyrolysis. Regarding the gasification technology and the gasification agent, it will differ depending on size, raw material and downstream synthesis reactions, in this case methanol synthesis. Feed gas for the methanol synthesis consists of H_2 and CO, and can be produced via gasification. The gasification process releases high temperature excess heat, which must be recovered in a suitable manner so as to achieve high energy efficiency, decrease the environmental footprint of the process and improve process economics. The gas produced in the gasifier has to be cleaned extensively in order to enable chemicals production. The synthesis gas must additionally be conditioned in order to enable production of methanol. In the methanol synthesis step the H_2 and CO gas are transformed via catalysis to methanol, where temperatures of approximately 250˚C and a pressure of approximately 35 to 90 bar are common (Air Products and Chemicals, Inc, 1998).

2.1.1 Biomass to methanol process specifications

The process flowsheet for the production of methanol from biomass assumed in this thesis is based on the process flowsheet described in Isaksson, et al. (2012), see Figure 2-2.

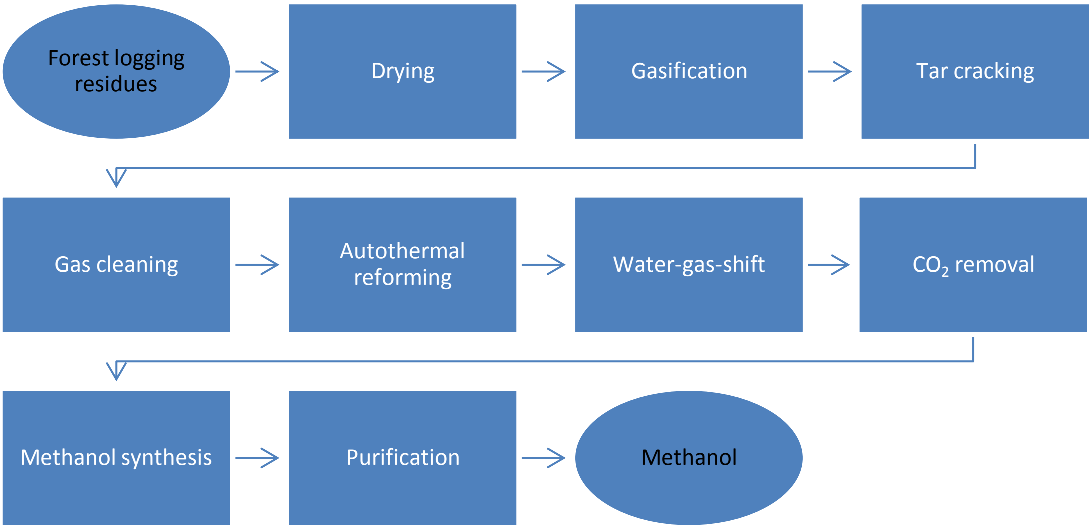


Figure 2-2 Simple process flowsheet, biomass to methanol.

2.1.1.1 Drying

The biomass pre-treatment is identical to that described by Isaksson et al. (2012), i.e. chipping followed by drying using a low temperature air drier. The biomass is assumed to initially have a moisture content of 50 wt% and being dried to a moisture content of 15 wt%. The biomass is then fed to the gasifier.

2.1.1.2 Gasification

It is advantageous to use elevated pressure and oxygen instead of air as the oxidizing media. Elevated pressure makes it possible to use smaller equipment downstream of the gasifier. Using oxygen instead of air also has the advantage of avoiding dilution of the syngas with nitrogen, which is especially important if the purpose is to convert the syngas to chemical products. In this thesis O_2/steam-blown fluidized-bed gasification is assumed.

2.1.1.3 Tar cracking

Tars and other hydrocarbons will form during gasification of biomass, and must be removed prior to methanol synthesis. It is possible to either use “hot gas”, e.g. catalytic tar cracking, or “cold gas”, scrubbing, cleaning. Catalytic tar cracking is assumed in this thesis, as outlined in Isaksson et al. (2012). Catalytic tar cracking has the advantage that heat can be recovered at high temperatures. Furthermore, the tars are catalytically cracked into e.g. CO and H_2, which is beneficial for the downstream methanol synthesis.

2.1.1.4 Wet gas cleaning

Removal of particulates and other impurities in the product gas is necessary since particulates can poison the methanol synthesis catalyst. As in the study by Isaksson et al. (2012), wet gas cleaning is assumed for removal of particulates and other impurities from the product gas. Solid particles are first removed with a cyclone. Particulates and alkalis, which condense on particles, are removed in a bag filter before the gas passes through a wet scrubber and a sulfur guard bed. Using a ZnO bed makes it possible to lower the sulfur concentration to below 0.1 ppm (Hamelinck & Faiij, 2001).

2.1.1.5 Autothermal reforming (ATR)

The methane content in the product gas is relatively large. In order to avoid accumulation of methane in downstream processes it is important to reform the gas prior to methanol synthesis. This can be accomplished using a steam-methane-reformer (SMR) or an autothermal reformer (ATR). In this study an oxygen-blown ATR is assumed. In the ATR, hydrocarbons such as methane, ethane and ethylene are reformed into carbon monoxide and hydrogen. The reforming is based on equilibrium reactions and operating parameters found in the literature (Rostrup-Nielsen, 2002; Rostrup-Nielsen, 1993; Hiller, et al., 2006). In order to provide heat to the highly endothermic reforming reactions, carbon dioxide and water is also formed by oxidizing part of the feed product gas. The temperature range of the ATR is typically 900 to 1100˚C. A water to carbon ratio of 1.5 – 2.5 moles of steam per mole of carbon is possible.

2.1.1.6 Water-gas-shift (WGS)

The final step before the methanol synthesis is to adjust the hydrogen to carbon monoxide ratio to obtain higher methanol yields in the methanol synthesis, which is based on equilibrium reactions. This can be done by utilizing the water-gas-shift reaction by adding steam to the shift reactor, according to 2-1.

$$CO + H_2O \leftrightarrow CO_2 + H_2 \qquad \text{2-1}$$

The desired hydrogen to carbon monoxide ratio is defined by the downstream reaction, and the specified ratio can be met by by-passing the shift reactor with a sub-stream. In the case for methanol synthesis the ratio between hydrogen and carbon monoxide to maximize the methanol yield is 2.1:1 (Hamelinck & Faiij, 2001).

2.1.1.7 CO_2 removal

To further increase the methanol yield in the methanol synthesis, CO_2 can be removed from the syngas. The closer the $(H_2\text{-}CO_2)/(CO+CO_2)$ ratio is to 2.1, the greater is the conversion of the syngas to methanol. It is however advantageous to have some CO_2 in the feed to the reactor to promote the methanol formation from CO, i.e. the CO_2 content of the gas affects the equilibrium reactions within the methanol synthesis. CO_2 in the gas is also advantageous to avoid too much deactivation of the catalyst. A volume fraction of CO_2 of 2 – 10% is suitable (Air Products and Chemicals, Inc, 1998).

CO_2 removal from the syngas can e.g. be achieved via amine absorption (Götz, et al., 2012). The syngas containing CO_2 enters the absorber and contacts an aqueous solution of amine that flows counter-currently to the syngas stream. CO_2 is a weak base and reacts exothermically with the amines, which is a weak acid, and forms water soluble salt. The stream containing the absorption solution and the salt, exits the absorber at the bottom of the absorption column. This stream is then regenerated and recycled back to the absorption column. The "clean" syngas exits at the top of the absorption column (Alie, et al., 2005). When utilizing internal heat exchanging for the absorber and regeneration processes, the required energy input for the absorption of CO_2 can be approximated by the energy requirement for the reboiler in the desorber (Götz, et al., 2012).

2.1.1.8 Methanol synthesis

After the CO_2 absorption process, the gas is transferred to a methanol synthesis unit. There exist different processes for methanol synthesis, e.g. gas-phase methanol synthesis and liquid phase methanol synthesis. The methanol synthesis reaction method assumed in this thesis is the triple-phase methanol synthesis with the trademark LPMEOH^{TM}, which is referred to as a liquid phase methanol synthesis (Air Products and Chemicals, Inc, 1998). The reactor used in this catalytic reaction is a slurry bubble column. Catalyst used is Cu/Zn/Al (Air Products and Chemicals, Inc, 1998; Heydorn & Diamond, 2003). Typical reaction temperature for the LPMEOH^{TM} reaction is in the range of 230 to 270°C (Heydorn & Diamond, 2003). The pressure of the LPMEOH^{TM} reaction is in the range of 35 to 90 bar, where higher pressures results in higher conversions (Air Products and Chemicals, Inc, 1998). The reactions taking place during the methanol synthesis are according to 2-2, 2-3 and the water-gas-shift reaction 2-1.

$$2H_2 + CO \leftrightarrow CH_3OH \tag{2-2}$$

$$3H_2 + CO_2 \leftrightarrow CH_3OH + H_2O \tag{2-3}$$

Reaction 2-3, methanol formation from CO_2, occurs only to a minor extent.

The methanol synthesis is an exothermic reaction. An advantage with the three-phase reactor is that the liquid-phase oil that the catalyst particles are dispersed in serves as a heat removal medium, and permits isothermal operation of the synthesis reaction (Heydorn & Diamond, 2003). The LPMEOH^{TM} process is very flexible when it comes to variations in the syngas composition. It is very advantageous, compared to other technologies, for syngas that is rich in CO. This is due to the ability to control the temperature within the reactor with the heat removal medium. In an ordinary gas-phase reaction, a circulating H_2 rich gas is often required to be able to control the temperature within the reactor. Despite that it is possible to use a CO rich syngas in the LPMEOH^{TM} process, the closer the $(H_2\text{-}CO_2)/(CO+CO_2)$ ratio is to 2.1, the greater is the conversion. Another method of increasing the degree of conversion is to cool down the reaction mixture, resulting in methanol condensation, and to recycle part of the reactor effluent back to the reactor inlet (Air Products and Chemicals, Inc, 1998). This is necessary since the methanol synthesis reaction is limited by chemical equilibrium (Graaf & Beenackers, 1996). According to Air Products and Chemicals (1998), a recycle to fresh feed ratio of 1:1 is usually quite effective when optimizing the methanol production. However, the recycle ratio depends upon whether the syngas is rich in CO or if the syngas is more balanced, $H_2/CO=2.1$. As long as neither the CO nor the H_2 is entirely consumed, the overall conversion into methanol is increased with an increased recycle ratio. If for example using a CO rich syngas where most of the H_2 is consumed in the reactor, it is claimed that little is gained with a recycle ratio above 2:1 (Air Products and Chemicals, Inc, 1998). If this is the case and a higher conversion is desired it is necessary to generate additional H_2, e.g. via a water-gas-shift reaction prior to the methanol synthesis, as assumed in this thesis. It can also be done by adding additional water to the syngas before passing it through the reactor resulting in that the water-gas-shift equilibrium within the methanol synthesis reactor goes towards the H_2 product (Air Products and Chemicals, Inc, 1998). The alternative of not having a separate WGS reaction would require one less process unit. However since the WGS reaction is an exothermic reaction, and the heat formed during reaction can be recovered, the alternative of not having a separate WGS reactor would affect the opportunities for heat recovery. Unreacted gas, which is not recycled back to the methanol synthesis reactor, is assumed to be combusted in a steam-boiler.

After the methanol has been flashed out a first time, another flash is used at a lower pressure to separate methanol from unreacted gas. After the second flash, the methanol is further purified using two distillation columns, reaching a final purity of 99.7 wt% (Isaksson, et al., 2012).

2.1.2 Biomass to methanol product yield

Hamelinck & Faiij (2001) report that methanol can be produced from biomass with a net higher heating value (HHV) energy efficiency between 54 and 58%, and in their study they achieved a HHV net energy efficiency of 55%. Williams et al. (1995) reports net HHV energy efficiencies, Energy ratios (ER), for different gasification technologies varying between 56.6 and 67.7%. Isaksson, et al. (2012) found reported net HHV energy efficiencies in the literature ranging between 50 and 57%, and in their study of a biomass to methanol process, they achieved a net HHV energy efficiency of 51%. The Energy ratio, or net HHV energy efficiency, is calculated as defined in equation 2-4.

$$ER = \frac{E_{fuel}}{E_{biomass}} \qquad \text{2-4}$$

$$E_{fuel} = HHV\ fuel\ \left[\frac{kJ}{kg}\right] * fuel\ output\ [\frac{kg}{s}]$$

$$E_{biomass} = HHV\ biomass\ \left[\frac{kJ}{kg}\right] * biomass\ input\ \left[\frac{kg}{s}\right]$$

Another measurement of the yield of methanol from biomass is the thermal efficiency, η_{th}. The thermal efficiency is defined as the energy content (HHV basis) of the methanol product divided by the sum of the energy content of all primary-energy inputs to the process, which includes the biomass feedstock, plus additional feed used to produce electricity and heat that must be supplied from external sources. It can be calculated according to equation 2-5.

$$\eta_{th} = \frac{E_{Products}}{E_{biomass} + \frac{E_{Elec}}{\eta_{elec}} + \frac{E_{heat}}{\eta_{heat}}} \qquad \text{2-5}$$

$E_{Elec} = Net\ quantity\ of\ external\ electricity\ required$

$E_{heat} = Net\ quantity\ of\ external\ heat\ required$

$\eta_{elec\ or\ heat} = HHV\ efficiency\ of\ producing\ the\ electricity\ or\ heat$

Williams, et al. (2001) reported Thermal efficiencies for different gasification technologies of between 53.9 and 61.0%.

The HHV value for methanol is 22.9 MJ/kg (Biomass Energy Data Book, 2011).

2.2 Methanol-to-olefins (MTO) process

In this section some history and process specifications regarding the MTO technology will be addressed.

2.2.1 MTO process background

UOP/Norsk Hydro developed the technology of producing olefins from methanol using a catalyst based on silicoaluminophosphate molecular sieve technology. At their demonstration unit at Norsk Hydro´s Porsgrunn facility in Norway it is claimed that they achieve near perfect methanol conversion rates, i.e. almost all methanol fed to the reactor is converted into olefins and other by-products (Hamblett, 1996). The demonstration unit, which processed 0.5 tons/day of methanol (in 1995), showed stability of the catalyst even after more than 450 cycles of reaction and regeneration. In 1995 Norsk Hydro and UOP announced that the technology was available for license (Hamblett, 1996). However, in 2009 the MTO process was still unproven at commercial scale. Several projects are currently ongoing in China, where it is possible to exploit cheap and abundant coal via gasification and methanol synthesis (CHEMSYSTEMS, 2009). The first commercial scale installation of the UOP/Hydro MTO process was announced in 2011 and is planned to start up in 2013 (UOP Honeywell, 2011). According to Håvard (2011), the MTO technology will soon be commercialized in large scale. An industrial scale demonstration MTO process plant has been built by the French oil and gas company Total in Belgium (Håvard, 2011). The Honeywell UOP company announced in November 2012 that they got a third technology license for starting a new MTO project at a company in China (UOP Honeywell, 2012). The major MTO technologies include the UOP/Hydro MTO process, the Lurgi process, and the DMTO (methanol or DME as feedstock) process (Ding & Hua, 2012). The main difference between the UOP/Hydro process and the Lurgi process is that in the UOP/Hydro process the catalyst used is highly selective for conversion of methanol into ethylene and propylene, whereas in the Lurgi process the aim is mostly to produce propylene (CHEMSYSTEMS, 2002). The DMTO process differs from the other two in the way that it is possible to utilize both methanol and dimethylether (DME) as feedstock.

2.2.2 MTO process specifications

In the MTO process, methanol fed to the reactor is converted to light olefins with carbon selectivity at about 75 to 80% towards ethylene and propylene. Product ratio of ethylene and propylene is in the range of 0.7 to 1.4, depending on different process parameters such as operating temperature (where higher temperatures leading to higher ethylene to propylene ratios), pressure (where higher pressure leads to higher propylene ratio) and water content, possible to use up to 20 mole% water (where higher water content leads to higher ethylene ratio) in the feed (Vora, et al., 2001). A schematic process layout for the MTO process is shown in Figure 2-3.

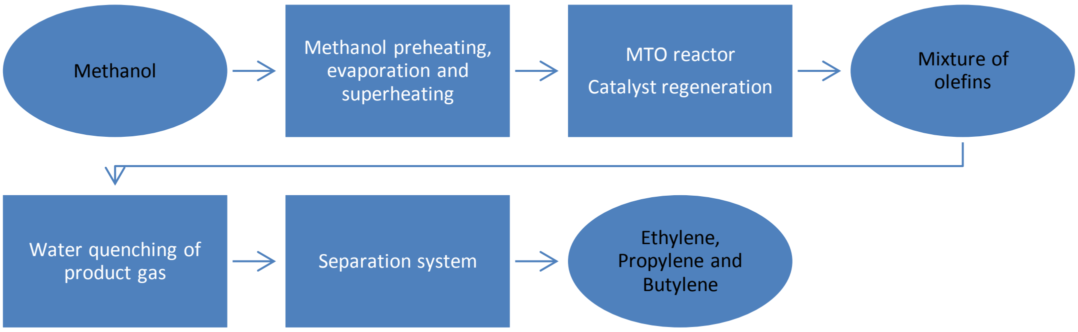


Figure 2-3 Schematic process layout for the MTO process.

The operating conditions of the reactor will not only have an effect on the performance of the catalyst, it will also have an effect on the requirements of the feed stream and on downstream processes such as the separation system. The operating temperature will influence the heat and temperature required to heat up the feed stream. The separation equipment will be affected by the operating conditions when it comes to specifications such as size. The operating conditions will also influence the amount and temperature of the heat that is needed to perform the separation and the amount and temperature of the heat that will be available for other applications, thereby influencing the heat integration possibilities.

In the MTO process, the methanol that is fed to the reactor is converted to light olefins and the reaction takes place in the presence of catalysts. According to Chen et al. (2012) the SAPO-34 catalyst is the most promising industrial catalyst for the MTO process. This is mostly due to its high selectivity towards ethylene and propylene, and it is also the catalyst used in the UOP/Hydro technology (Vora, et al., 2001). The catalyst particle consists of molecular sieve, matrix and binder. The weight of the binder is 7 to 15% of the weight of the catalyst particle. The weight of the molecular sieve is in the range of 25 to 60% of the catalyst particle. An example of catalyst particle composition is 60% matrix and binder and 40% molecular sieve (Clem, et al., 2006).The main challenge with this catalyst is however the coke formation during reaction. The coke has a deactivating effect on the catalyst (Vora, et al., 2001), and therefore is there a need for catalyst regeneration, as indicated in Figure 2-3.

After the reaction step the different products in the product stream have to be separated using different separation techniques. The UOP/Hydro MTO process, including the downstream separation sequence, can be seen in Figure 2-4. First a water quench configuration is utilized to separate some of the water present and other impurities. After the water quench the product gas is fed to a sequence of gas purification processes.

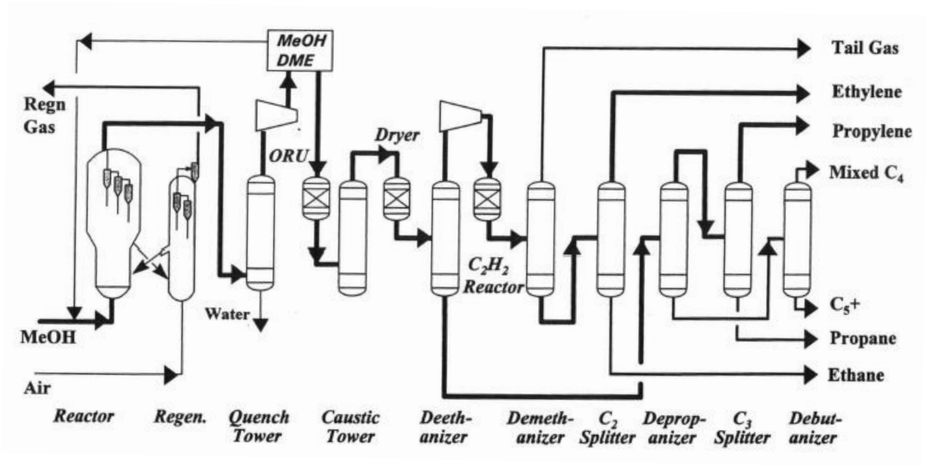


Figure 2-4 UOP/Hydro MTO process flow scheme (Eng, et al., 1998).

2.2.2.1 MTO reactor and regeneration

When converting methanol into light olefins in the MTO reaction it is beneficial to use a circulating fluidized bed with catalyst regeneration, as shown in Figure 2-5. A fluidized bed reactor is suitable since this technology normally provides the best opportunities for catalyst circulation to a separate regenerator where the coke can be combusted. Furthermore, since both the MTO process and the combustion of coke are exothermic, this reactor type is suitable because it enables removal of heat that is generated (Vora, et al., 2001). Also at the demonstration plant in Norway they utilize a fluidized-bed reactor with a fluidized-bed regenerator due to the high heat of reaction and the frequent regeneration of catalyst (Hamblett, 1996).

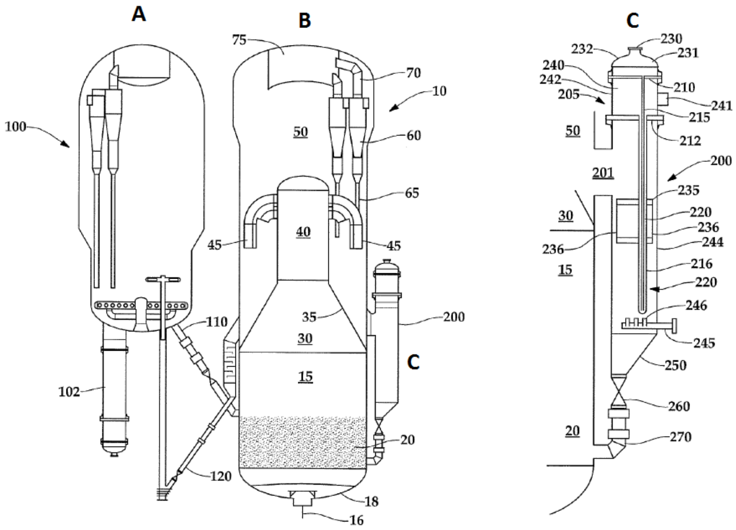


Figure 2-5 MTO reactor, circulating fluidized bed, B, with catalyst cooling, C, and catalyst regeneration, A, (Miller, 2011).

Methanol and DME are the preferred feedstocks for the MTO process. The feed is introduced into the reactor and to the catalyst via a fluidized feed stream. The products of the MTO reaction depend upon the feed stream, catalyst and conditions within the reactor. The products will however preferably contain light olefins, ethylene and propylene.

Operating conditions of the reactor will influence the ratio of ethylene/propylene and coke formation. An increased pressure may favor the production of higher propylene ratios. Also the temperature will influence the ratio of ethylene and propylene, and a higher temperature gives a higher ratio. However, a higher temperature will also reduce the selectivity towards light olefins (Vora, et al., 2001). Temperature of the reaction is preferably between 400 and 550˚C. To maximize the production of ethylene a temperature between 475 and 550˚C, or more preferably between 500 and 520˚C may be used. To maximize the production of propylene a temperature between 350 and 475˚C, or more preferably between 400 and 430˚C may be used (Miller, 2011). The pressure of the reactor is between 1 and 3 barg (Eng, et al., 1998).To maintain the selectivity towards light olefins, a non-reactive diluent may be used in the feed stream. The diluent can for example consist of helium, nitrogen, steam or carbon dioxide. The amount of diluent used in the feedstock can vary considerably and may vary between 5 and 90 mole%. The feed stream may also contain water, and may consist of 0 to 35 wt% water (Miller, 2011). It is possible to use crude methanol as feed, which nominally contains 20 wt% of water (Eng, et al., 1998).

The reaction of converting methanol into olefins is exothermic. Excess heat from the reaction will disrupt the optimal conditions of the reaction by raising the temperature to levels that are too high. Therefore it is of utmost importance to control the temperature within the reactor to be able to optimally convert the methanol into olefins and minimize the formation of by-products. The temperature can be controlled by removing heat from the reactor during the process. One way of doing this is to cool the catalyst used in the conversion reaction. Another way of controlling the heat of the reaction is to adjust the temperature of the feed stream. However, adjusting the temperature of the feed stream will not quickly change the temperature of the reaction since the catalyst within the reactor is very massive and voluminous. The catalysts will not response to changes in temperature of the feed stream (Miller, 2011).

When the catalyst is exposed to the reacting species coke, carbonaceous material, is generated and deposited on the catalyst. Accumulation of coke on the catalyst will interfere with the catalyst ability to convert the reactants into products, and will result in a spent catalyst. As the coke deposit increases, the catalyst loses its activity and less of the feed will be converted into the desired olefins (Miller, 2011). This is also in accordance with Soundararajan, et al. (2001). The methanol conversion decreases significantly with an increase of coke on the catalyst and the coke formed during reaction causes partial or complete pore plugging, which reduces the active sites available for the reagent molecules. Coke having deactivating effect is classified as inactive coke (Soundararajan, et al., 2001). Regeneration of the catalyst, e.g. via coke combustion in air, is therefore necessary. Formation of coke is dependent on temperature and water content in the feed, and will be higher with higher temperatures and lower with water content. However, the coke does not just have deactivating effects, active coke also increases the ethylene selectivity (Vora, et al., 2001; Soundararajan, et al., 2001). An optimum catalyst operation, depending on wanted products, is found at a certain equilibrium level of coke (Vora, et al., 2001). Soundararajan, et al., (2001) showed that the etylene selectivity increases from 11.3 mole% on fresh catalyst to about 20.1 mole% with 12.3 wt% coke deposited on the catalyst. This phenomena arises because the deposited coke increases the shape selectivity of the SAPO-34 catalyst by inducing steric hindrance (Soundararajan, et al., 2001). According to Kuechler, et al. (2005) it is important to design the reactor so that a relatively high average level of coke is maintained within the reactor, and a preferred average level of coke range from about 2 to about 20 wt%. A high average level of coke can be maintained by just regenerating a part of the catalyst (Kuechler, et al., 2005). The step of regenerating the catalyst by removing the coke via combustion with oxygen will restore the catalytic activity of the catalyst (Miller, 2011). To increase the selectivity to light olefins it is preferred to have an average level of coke between 2 and 7 wt% based on the overall weight of the catalyst (molecular sieve plus matrix and binder) (Cao, et al., 2011). Therefore only a fraction of the catalyst material will be regenerated and the remaining fraction will be cooled (Miller, 2011).

The reactor utilized in the MTO reaction, part B in Figure 2-5, consists of an upper disengaging chamber and a lower reaction chamber. The lower reaction chamber contains a dense phase zone, which operates within a superficial velocity of about 0.5 and 1.5 m/s (Miller, 2011). The transition phase zone is located above the dense phase zone and extends from the lower reaction chamber into the upper disengaging chamber. The superficial velocity of the transition zone is within the range of 0.5 to 3 m/s (Miller, 2011). As the gas, unreacted feedstock and products, travels through the reactor chamber to the disengaging chamber, it carries partially coked catalyst particles with it. When the mixture of catalyst particles and reaction product reaches the top of the reactor chamber, distributor arms discharge the catalyst particles and the reaction product to the bottom of the disengaging chamber by gravitational force. Catalyst particles that remain in the reaction product stream continue upwardly to phase separators such as cyclones, which separates the catalyst from the product vapor. The product vapor is transferred to the product recovery section (Miller, 2011).

The catalyst separated from the product vapor via cyclones is transferred to the bottom of the disengaging chamber. A portion of the catalyst settled inside the disengaging chamber will be directed to a catalyst cooler, seen in part C of Figure 2-5, and another portion will be directed to the regenerator, seen in part A of Figure 2-5. The portion directed to the catalyst cooler is heat exchanged in a flow-through type of catalyst cooler. At least two catalyst cooler is preferred. The catalyst cooler has a diameter of 1.8 to 2.5 m with a preferred amount of cooling tubes ranging from 75 to 200 (Miller, 2011). The use of cooling tubes makes it possible to recover and remove excess heat from the catalysts and produce steam that can be used elsewhere. To control the amount of catalyst exiting from the reactor and thus entering the catalyst cooler a recirculation valve is utilized, and it is therefore possible to control the temperature in the reactor. The temperature of catalyst material exiting the catalyst cooler can be 40˚C lower than the average reactor temperature (Williams & Vaughn, 2003).

The catalyst material transferred to the regenerator, part A in Figure 2-5, is heated in the presence of oxygen to a temperature between 550 and 780˚C (Clem, et al., 2006). The amount of oxygen left in the flue gas after combustion should be 0.1 to 5 vol% (Miller, 2011). At these temperatures the coke deposited at the catalyst will be combusted. To achieve complete regeneration of the catalyst particles, and achieve complete combustion, a temperature inside the reactor of 730˚C is required (Sadeghbeigi, 2011).

The catalyst material and the regeneration gas, often air, flows upward from the lower combustion zone towards the upper combustion zone. As the mixture of catalyst and gas flows through the regenerator and the coke is burned off, the heat generated is absorbed by the relatively carbon free catalyst. To control the temperature inside the regenerator and to return the catalyst to the reactor at a suitable temperature, a back-mixed type of catalyst cooler is used, number 102 in Figure 2-5 (Cetinkaya & Myers, 1986). The regenerated catalyst particles can be returned to the reactor at a temperature 80˚C lower then when the catalyst material left the reactor, disengaging chamber (Beech & Walter, 2007). The average level of coke on the regenerated catalyst particles should be less than 0.2 wt% of the molecular sieve in the catalyst particle (Clem, et al., 2006). The temperature of the regenerator can be controlled by withdrawing regenerated catalyst and passing it through the catalyst cooler to form a cooled regenerated catalyst composition. The cooled catalyst material transferred back to the regenerator will be mixed with catalyst material containing coke and work as an inert material absorbing heat released during the combustion (Cao, et al., 2011). The regenerated catalyst material will be transferred through the catalyst cooler, and thereby it is possible to produce steam (Cetinkaya & Myers, 1986). A portion of the catalyst material transferred through the catalyst cooler will be returned to the reactor and another portion will be returned to the regenerator.

To increase the heat transfer between catalyst material and cooling tubes, a fluidizing gas is transported through the catalyst coolers. An inert gas such as nitrogen, steam or a hydrocarbon gas is used and the flow rate of the fluidizing gas is sufficiently high to accomplish fluidization. There are two ways to control the temperature of the recirculated catalyst material, one can either control the amount of catalyst travelling through the catalyst cooler or vary the fluidizing gas in the catalyst cooler. All catalyst particles that enter the catalyst cooler are transferred back to the dense phase of the reactor chamber (Miller, 2011). By adjusting the amount of fluidizing gas, more or less of the heat available can be used to produce steam, too much fluidizing gas will result in more heat leaves with the fluidizing gas, and too little will decrease the heat transfer from the catalyst particles. It is at least possible to recover 80% of the incoming heat and produce steam (Reh, et al., 1979).

The amount of catalyst transferred to the regenerator should be between 5 and 200%, or a preferred amount between 30 and 50% of the amount transferred to the catalyst cooler at the reactor (Clem, et al., 2006). The catalyst material continuously circulates through the reaction zone and recirculation zone at a mass ratio of the catalyst in the reaction zone to the total amount of catalyst in the reaction and recirculation zone at a value of 0.3-0.7:1. The recirculation rate is 10 to 50 times the total feed rate of methanol to the reaction zone (Williams & Vaughn, 2003). Catalyst, comprising both sieve and other material, is removed from the reactor to the regenerator at a rate from about 0.1 to 0.3 times the total methanol feed rate (Beech & Walter, 2007).

2.2.2.2 Water quench configuration

Due to the high content of water, and the content of catalyst particles and dust in the product vapor, the vapor is quenched in a water tower to separate the catalyst dust and some of the water vapor from the product gas. An operating temperature of the water quench of 95 to 115°C is suitable (Wang, et al., 2011). Since catalyst particles and dust are present in the product vapor it is not possible to heat exchange the product gas below the dew point, the catalyst dust will then stick to the heat exchanger wall (Fuglerud, 2013).

To be able to separate the product gas from the entrained catalyst fines, to remove water and any heavy by-products such as C_6+ hydrocarbons, the gas coming from the reactor is quenched using a two-stage process. A two-stage process is used since the reactor effluent can contain small amounts of acetic acid, which could build up in a conventional quench process scheme (Miller & Senetar, 2002). An example of the two-stage quench process can be seen in Figure 2-6.

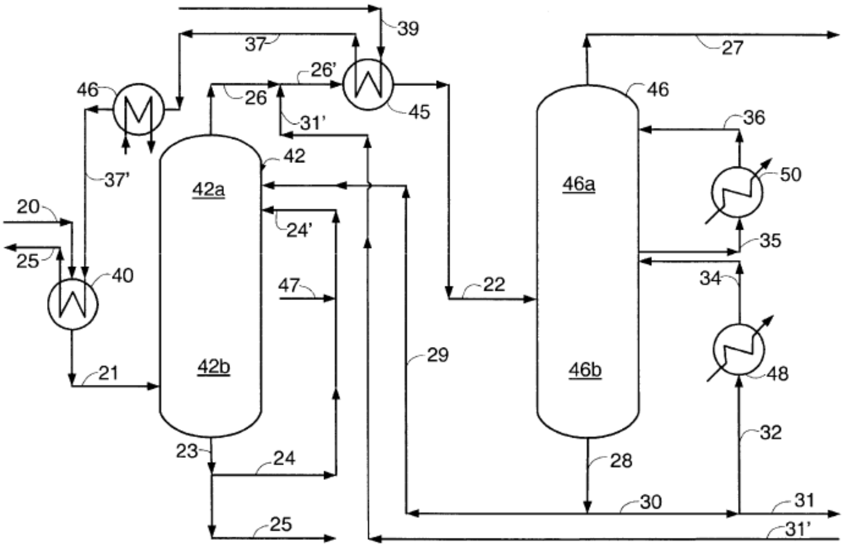


Figure 2-6 Two-stage quench process (Miller & Senetar, 2002).

To recover the heat of the reactor effluent it is first heat exchanged. However, the effluent cannot be cooled below its dew point since the catalyst fines then will stick to the heat exchanger wall. The cooled reactor effluent is then passed to the first quench tower, number 42 in Figure 2-6, where the effluent is contacted with a relatively pure aqueous stream and a neutralizing agent, which is introduced at the top of the tower. This configuration will result in a hydrocarbon vapor stream leaving at the top of the quench tower and a waste water stream leaving at the bottom. The waste water stream will contain the heavy by-products, neutralized organic acid components, and the catalyst fines present in the reactor effluent. Part of the waste water stream leaving at the bottom may be recycled back to the quench tower at a point above where the reactor effluent is entering. The other part of the waste water stream will be withdrawn and the catalyst fines present will be recovered (Miller & Senetar, 2002). In the first quench tower it is preferred that not more than 5% of the water present in the reactor effluent is removed. The amount of quench medium used in the first quench tower to the reactor effluent stream is preferred to be in the range 0.3-0.47:1. The temperature of the quench medium should be less than 90˚C, and preferably about 35˚C. After the first quench tower, the amount of water in the overhead vapor stream is preferred to be between 30 to 50% based on the total weight of the overhead stream (Beech, et al., 2006).

The vapor stream leaving the first quench tower is first heat exchanged indirectly in an intercondenser, where the vapor stream is partially condensed. The partially condensed reactor effluent is passed further to the second quench tower, number 46 in Figure 2-6. The reactor effluent is partially condensed before the second quench tower both because one can utilize some of the heat available and because this configuration will require less quench water to reduce the amount of water in the reactor effluent. At the top of the second quench tower, the light olefin vapor is recovered and passed on to the separation processes. At the bottom of the quench tower, a relatively pure aqueous stream is recovered. A portion of the bottom product will be returned to the first quench tower, a portion will be heat exchanged and recycled back to the second quench tower, and the last portion will be passed to a water stripper zone. In the stripper zone any remaining oxygenates and small hydrocarbons, such as propane, will be removed from the water stream as a stripper overhead stream and passed to the reactor effluent leaving the first quench tower. A purified water stream will leave the stripper at the bottom (Miller & Senetar, 2002). The vapor leaving at the top of the second quench tower should contain little more water than the saturation level of the remaining dewatered effluent stream. Preferably it should contain less than 3% of the total amount of water present in the gas leaving the reactor (Beech, et al., 2006).

2.2.2.3 Gas purification

To obtain “clean” process streams of the light olefins, a number of separation processes are required. The separation process used after the water quench configuration is similar to the separation process utilized in steam cracking. The separation process used in the MTO process can be seen in Figure 2-4, and consists of a caustic tower, a dryer, a deethanizer, a demethanizer, a C_2 splitter, a depropanizer, a C_3 splitter and a debutanizer. Since it is assumed that the MTO product gas leaving the water quench is transferred to the existing gas purification processes at the existing cracker plant, this will not be further elaborated.

2.2.3 Methanol to olefins product yield

Mass product yield obtained with the UOP/Hydro technology can be seen Table 2-1 and Table 2-2. The mass product yields for the UOP/Hydro technology have been found in literature, but to be noticed is that information regarding specific operating conditions and results thereof is almost nonexistent in the literature, i.e. no specified operating conditions for the MTO yields found, Table 2-1 and Table 2-2, were specified. Since methanol is catalytically converted to olefins (such as ethylene and propylene) it would have been desirable to describe the MTO process kinetically. However, satisfactory kinetic expressions to describe the UOP/Hydro process could not be found in literature, and therefore the yields seen in Table 2-1 and Table 2-2 were utilized in this thesis.

Table 2-1 Mass product yield and carbon selectivity for the UOP/Hydro technology, High Ethylene case (Vora, et al., 1997).

	Feed kton/yr	Products kton/yr	%yield on C
Methanol	2330		
Ethylene		500	49
Propylene		325	32
Butylenes		100	10
C_5+		22	2
H_2, C_1, C_2, C_3 saturates		35	3.5
CO_X		5	0.5
Coke		31	3.0
Water		1310	
Total	2330	2330	100

Table 2-2 Mass product yields for the UOP/Hydro technology, High Ethylene and High Propylene case (Eng, et al., 1998).

	High Ethylene, 1000 kton/yr	High Propylene, 1000 kton/yr
Methanol Feed	2502	3368
Products		
Ethylene	500	500
Propylene	325	665
Mixed C_4`s	105	178
C_{1-}	45	24
C_2 and C_3	17	25
C_5+	60	74
Total	1052	1466

2.3 Existing steam cracker plant

The existing cracker plant produces approximately 930 kt/yr of olefins (640 kt/yr ethylene, 200 kt/yr propylene and 90 kt/yr butylene/butadiene) from 9 cracker ovens. Of the 640 kt/yr ethylene that is produced, approximately half is produced via steam cracking of ethane. Cracking of ethane almost only results in the production of ethylene, i.e. almost no other kinds of olefins are produced. The rest of the ethylene, propylene and butylene/butadiene are produced via steam cracking of butane, propane and naphtha (Pettersson, 2013). At the cracker plant are there different kinds of cracker ovens, one kind where only ethane is cracked, one kind where only naphtha is cracked, and one kind where it is possible to shift between the different feeds, flex ovens (ethane, butane, propane and naphtha). The reason why Borealis uses different kinds of cracking feeds is that it results in flexibility, i.e. it is to some extent possible to choose feed depending on current feed and product prices and thereby maximize process plant profit.

Reduction of the steam cracker capacity, when replacing it with the MTO process, will be accomplished by reducing the cracking of butane, propane and naphtha, by replacing two cracking furnaces. This means that 200 kt/yr of ethylene produced via MTO will replace 200 kt/yr of the 320 kt/yr (i.e. 62.5%) of the ethylene produced via cracking of butane, propane and naphtha, see above. The reason why the cracking of ethane not will be replaced stems from the fact that cracking of ethane almost only generates ethylene and it is ethylene that is in highest demand on the market. Another reason is that the ovens that solely crack ethane are new, whereas other ovens (e.g. the flex ovens) are older and more energy demanding and two of these may be replaced with the MTO process (Pettersson, 2013).

The utility system, seen in Table 2-3, used in Stenungsund and at Borealis (Pettersson, 2013) consists of high pressure (HP) steam, medium pressure (MP) steam and two low pressure (LP) steam levels. The different steam levels used and their respective saturation and superheating temperature can be seen in Table 2-3.

Table 2-3 Utility system used in Stenungsund and at Borealis.

	T [˚C] saturated	**T [˚C] superheated**
HP steam 85barg	300	485
MP steam 8.8barg	179.2	240
LP steam 2.7barg	141	160
LP steam 1.8barg	131	-
Boiler feed water	130/170	-

Currently in the existing cracker plant approximately 215 MW HP steam is used for different processes. HP steam is produced in two ways, approximately 195 MW, 250 t/h, is produced from the steam crackers and minimum 30 MW, 39.3 t/h, or maximum 80 MW from a boiler. A reduction of the steam cracker capacity will consequently reduce the generation of HP steam from the steam cracker. The steam produced from the boiler can be increased to 80 MW to be able to some extent cover the HP steam demand. At the existing cracker plant it is approximated that the production of 100 t/h olefins results in the production of 180 MW, 230 t/h, HP steam (Spetz, 2013). The existing cracker plant produces 930 kt/yr of olefins per year, if the reduction would be made accordingly, see above, the total production of olefins from the steam cracker plant would be 548.7 kt/yr per year, which is a total reduction of 41% (Pettersson, 2013). Since the production of steam from the steam crackers is approximated with 230 t/h per 100 t/h produced olefins, independent of raw material or product, see above, the total amount of steam that is produced from the steam cracker can be reduced by 41%. The HP steam production from the steam crackers will therefore be reduced from 195 MW to 115 MW, or 250 t/h to 147.5 t/h.

Generated steam and electricity as well as exported, imported and used steam at the steam cracker plan are reported in Table 2-4.

Table 2-4 Approximate steam/energy balance of the Steam cracker plant.

	Steam generated at the cracker plant [MW]	**Generated power [MW_{el}]**	**Exported steam [MW]**	**Imported steam [MW]**	**Steam used within the processes at the cracker plant [MW]**	**Dilution steam used in the steam crackers [MW]**
HP (85 barg)	226		5.2			
MP (8.8 barg)					22.7	64.6
LP (2.7 barg)	10.7				4.7	
LP (1.8 barg)				29.1	89.5	
MW_{el}		41.3				

To be able to meet the demand of the processes at the steam cracker plant, to meet the demand of the other plant, and without reducing the amount of electric power generated at the plant, the total amount of HP steam production must be the same. To be able to cover the loss in HP steam production from the steam crackers, one can either increase the production of HP steam from the boiler, or generate HP steam resulting from the integration with the MTO process, or the biomass to methanol processes. Hot streams currently not utilized in heat exchanging at the Borealis plant can possibly be used to heat streams within the MTO process and within the biomass to methanol processes at a more appropriate temperature so that the high temperature streams within the MTO process and biomass to methanol processes can be utilized in a more valuable way. The streams that can be utilized for this purpose is today cooled with either air or cooling water. Stream data can be seen in Table 8-24 in Appendix C.

All the existing processes, except the steam production capacity from the steam cracker, will be assumed to be unchanged even though this will not be the case in reality if the steam cracker partly would be replaced with the MTO process. This reasoning is partly based on the fact that the product stream from the MTO process will contain a higher content of the wanted olefins than the product stream from the steam crackers, i.e. the purity of the product stream from the MTO process will be higher. This will affect the following separation processes. The reasoning is also based on the fact that the dilution steam needed for the steam cracking will decrease. The produced fuel gases from the steam cracker will also be reduced when decreasing the capacity of the steam cracker.

3 Methodology

A simulation model of the biomass to methanol processes and the MTO process has been created in Aspen Plus in order to establish mass and energy balances. Input data for the model was obtained from the literature. The simulation model was used to establish stream data that was used as input for investigating opportunities for heat integration using pinch technology tools.

3.1 Data gathering

The model used for the biomass to methanol process in this thesis is based on previous work performed at the division (Isaksson, et al., 2012) with additional developments and improvements, based on findings in the literature. Special attention for modeling and simulation development was focused on the gasification, autothermal reforming (ATR), CO_2 removal and methanol synthesis steps.

Since the MTO process is a novel technology, see Section 2.2.1, a literature review was conducted in order to obtain necessary process parameter values for the MTO process. Terje Fuglerud at INEOS (Hydro) provided recommendations and hints regarding the UOP/Hydro MTO process technology. Data for the MTO process was needed to be able to as accurately as possible create a simulation model of the MTO process. Data used included suitable operating temperatures, properties of the catalyst, such as the catalyst deactivation due to coke formation, suitable process reactors and different properties related to the process design.

Since the separation units utilized after the quench towers in the MTO process are similar to the units used within the cracker plant, and the produced olefins are assumed to be separated in the same separation system as the product gas from the steam cracker at Borealis, the separation system was not simulated.

3.2 Process simulation

Aspen Plus is a comprehensive chemical process modeling tool used to design and improve process plants (Aspentech, n.d.). It is a software package designed to allow the user to build and run a process simulation model. A process model is based upon the complete layout of the engineering system. The layout includes flowsheet, chemical components and operating conditions. The flowsheet maps the entire system showing e.g. reaction and separation units as well as inlet and outlet streams, both component and energy streams. The chemical components, reactants, products, energy, of the system are specified in the model. The operating conditions must be specified e.g. temperature and pressure at specific locations within the process.

The simulations models were used in order to generate data for the pinch analysis and heat integration study. However, before the data can be used in a pinch analysis the results obtained from the simulation have to be validated to assure accuracy in the simulation models and in the results obtained. The validation will be made by comparing simulation results with results from experiments and simulation studies reported in the literature.

3.2.1 Biomass to methanol

The simulation models for the biomass to methanol process steps used in this thesis were originally made at the department of Energy and Environment by Maria Arvidsson, Johan Isaksson (Isaksson, et al., 2012), Jean-Florian Brau and Stefan Heyne (Heyne, 2013), but some additional changes have been made in accordance with literature found on the subject.

3.2.1.1 Components

The processes from biomass to methanol involve conventional components such as carbon monoxide, carbon dioxide, hydrogen, oxygen and water as well as other hydrocarbons, for the specific components used in the different processes, see Table 8-5 and Table 8-7 in Appendix A. Since the raw material used is biomass, a non-conventional component was created.

The non-conventional component biomass is modeled using enthalpy and density properties. The model used to describe the enthalpy is the HCOALGEN model, which requires ULTANAL, PROXANAL and SULFANAL. To describe the density DCOALIGT is used, which requires ULTANAL and SULFANAL. HCOALGEN is the general coal model for computing, and includes correlations for heat of combustion, heat of formation and heat capacity, and will be calculated based on specified ULTANAL, PROXANAL and SULFANAL. All the option codes are as default. The DCOALIGT model gives the density of coal on a dry basis based on specified ULTANAL and SULFANAL.

ULTANAL is described as the ultimate analysis in wt%. In ULTANAL the different weight percentages of the compounds present must be specified. PROXANAL is described as the proximate analysis in weight%. In PROXANAL the moisture content of the component, the percentage of fixed carbon, percentages of volatile matter and the percentage of ash have to be specified. SULFANAL described the different forms of sulfur present.

The composition for the non-conventional component biomass (Heyne, 2013), input to the dryer and to the gasifier, can be seen in Table 3-1.

Table 3-1 Specifications for the non-conventional component biomass, before drying/after drying.

	ULTANAL		**SULFANAL**		**PROXANAL**
Ash	2.18	Pyritic	0.0124	Moisture	50/15
Carbon	50.3032	Sulfate	0.0124	FC	20
Hydrogen	5.4283	Organic	0.0124	VM	77.82
Nitrogen	0.4695			Ash	2.18
Chlorine	0.0147				
Sulfur	0.0372				
Oxygen	41.5681				

Since the biomass contains ash, a non-conventional component is specified for the ash that forms after gasification of the biomass, and contains 100% ash.

To be able to handle conventional, solid and non-conventional components, three sub-streams are used. The vapor-liquid stream (MIXED), the solid stream (CISOLID) and the non-conventional stream (NC) are required, and therefore the stream class used in the simulation is MIXCINC.

3.2.1.2 Drying

The simulation model of the low temperature air drier is based based on Holmberg & Ahtila (2005), with the exception that no recycle is used (Holmberg, 2012).

For the drying model the Peng-Robinson (PENG-ROB) property method is used, which is recommended for hydrocarbon processing applications such as gas processing, refinery and petrochemical processes.

A moisture content of 50 wt% was assumed before drying. The biomass is assumed to be dried to a moisture content of 15 wt%. For biomass compositions used in the simulation see Table 3-1. Drying of the biomass will take place at atmospheric pressure. Incoming air is assumed to have a temperature of 15˚C, and is heated to 70˚C, which is assumed to be enough to be able to dry the biomass (Holmberg & Ahtila, 2005). The temperature of the incoming biomass is assumed to be 15˚C. Internal heat exchange within the drying process is assumed.

3.2.1.3 Gasification

The type of gasifier implemented in the simulation model is an O_2/steam blown gasifier, and based on a simulation model made by Hannula & Kurkela (2012), which was validated by comparing their results with experimental data. Hannula & Kurkela (2012) report that their model agrees fairly well with the experimental data for the main gas components, i.e. H_2, CO, CO_2 and H_2O. They obtained an average relative error for the concentrations of the main components of 12%, while the magnitude of experimental error in the dada was expected to be around 5%. The simulation model for the gasifier was using the same assumptions as for the model proposed by Hannula & Kurkela (2012), and the results obtained were in accordance with the results in Hannula & Kurkela (2012), a comparison can be seen in Figure 8-1 in Appendix A. When the simulation model had been validated, some input to the simulation model was changed. In this thesis, another HHV estimation model was used, i.e. the estimation model proposed by Sheng & Azevedo (2005) instead of the one proposed by Channiwala & Parikh (2002). Another HHV estimation model was used because this HHV estimation model was used in other studies at the Heat and Power Technology Division at Chalmers University of Technology (Heyne, 2013; Arvidsson, et al., 2012) and also with the incentive to be able to compare the results with other studies that will be made in the future at the division. In Hannula & Kurkela (2012) they discuss that a commercial-scale gasifier, target case, has heat losses at around 1%. In accordance with the discussed “target case”, i.e. commercial scale, in Hannula & Kurkela (2012), the amount of oxygen added to the gasifier was specified so that the resulting heat losses, at a specified temperature, were 1% of the higher heating value, HHV, (Sheng & Azevedo, 2005) of the biomass fed to the gasifier, see Appendix A. The added steam flow to the gasifier was set so that the steam to oxygen mass ratio was 1:1, in accordance with the target case. Since biomass contains 15 wt% moisture when it is fed to the gasifier, the total amount of steam that is present within the gasifier will be higher than the flow entering with the oxygen.

For the gasification model the RK-SOAVE property method was used, which is appropriate for high temperature and high pressure applications, as well as for hydrocarbon processing applications or other supercritical extractions.

To be able to model gasification of biomass, the biomass is first divided into its elemental components, such as carbon and hydrogen, using a yield reactor (RYield). After the yield reactor a stoichiometric reactor (RStoic) is used where some of the carbon and hydrogen (originally from the biomass) is used to form different hydrocarbons, to a specific molar extent. After the stoichiometric reactor, a Gibbs reactor (RGibbs) is used. In this reactor possible reaction products were specified as well as the inert components, see Table 8-2 in Appendix A. The chemical and phase equilibrium composition is accomplished by Gibbs energy minimization.

The gasification is assumed to be performed at 25 bar and at a temperature of 886˚C. The oxygen is assumed to be delivered to the plant at a pressure of 25 bar and at a temperature of 15˚C. The oxygen is heated to 200˚C before it was transferred to the gasifier. Steam is produced by pumping water at 15˚C to a pressure of 25 bar. The water is then heated to the saturation point, evaporated and superheated by 5˚C. The resulting temperature of the steam entering the reactor was 228˚C.

3.2.1.4 Tar cracking

The simulation model for the tar cracker is based on the model proposed by Spath, et al., (2005) and used in Isaksson, et al. (2012).

For the tar cracking model the RK-SOAVE property method with Boston Mathias modifications is used, which is suitable for hydrocarbons and light gases, and is consistent in the critical region.

The tar cracker is simulated as an adiabatic equilibrium reactor (REquil) with specified equilibrium reactions, and molar conversions, where tars and other hydrocarbons, such as methane, ethane and larger hydrocarbon chains are cracked to carbon monoxide and hydrogen. For the specific reactions see Appendix A. The tar cracker is operated with a pressure drop of 0.207 bar. The incoming syngas has a temperature of 886˚C. No heating or cooling is needed for the tar cracker. The tar cracker is however simulated adiabatically, and the reactions are endothermic.

3.2.1.5 Wet gas cleaning

The simulation model for the wet scrubber is based on (Hamelinck & Faiij, 2001) and used in Isaksson, et al. (2012).

The property method used in the wet gas cleaning model was the ENRTL-RK, which can handle liquid electrolyte solutions containing water.

Prior to the filter and scrubber, the syngas is cooled from 650˚C to the dew point. The syngas is scrubbed with water at a temperature of 25˚C and with a specified pressure drop of 3%. The scrubber is simulated as a flash in Aspen plus. The scrubbing water leaving the scrubber is cooled to 25˚C.

The sulfur guard bed is simulated by separating as much sulfur so that the mole fraction of H_2S was reduced to $1*10^{-6}$ (see Section 2.1.1.4).

3.2.1.6 Autothermal reforming (ATR)

For the autothermal reforming simulation model the PR-BM property method was used, which can handle hydrocarbon processing, and reasonable results can be obtained at al temperatures and pressures.

The reactions taking place inside the ATR reactor are equilibrium reactions (HALDOR TOPSOE, u.d.). A Gibbs reactor (RGibbs) was therefore used where possible products are specified, see Table 8-4 in Appendix A. A pressure drop for the reactor is specified to 0.5 bar. The reactor is also operating under adiabatic conditions. The feed to the reactor has a temperature of 550˚C. In order to conduct the reforming reactions oxygen and steam is added. In order to reform methane to a suitable level for downstream methanol synthesis a temperature level of 1100˚C was required. This was obtained by adding enough preheated oxygen (200 ˚C). Steam is added to the reactor with a steam to carbon ratio of 2.5, see Section 2.1.1.5. A figure of the simulation model for the ATR process can be seen in Figure 8-2 in Appendix A.

3.2.1.7 Water-gas-shift (WGS)

The model for the water-gas-shift was based on that used in Isaksson, et al. (2012).

In the water-gas-shift simulation the PENG-ROB property method was used, which can handle high temperatures and pressures, hydrocarbon processing, and gases.

The water-gas-shift reactor was simulated using a Gibbs reactor (RGibbs), where the equilibrium reaction taking place is in accordance with reaction 2-1. Remaining components in the feed gas is assumed to be inert in the reactor. Part of the gas coming from the ATR is transferred to the WGS reactor and part of the gas is bypassed. The amount of gas going via bypass is varied so that a H_2/CO molar ratio of 2.1 is achieved before the gas is entering the methanol synthesis reactor. Steam and feed gas is added to the WGS reactor at 330˚C. The pressure of the incoming feed streams (21 bar) resulted from specified pressure drops (2%) in the heat exchangers used in the simulation model. Steam is added to the reactor so that the total amount of moles H_2O in the reactor corresponds to three times the amount of CO in the reactor. The resulting reaction in the WGS reactor is exothermic and the reactor is operated adiabatically.

3.2.1.8 CO_2 removal

CO_2 was removed to get a balanced feed gas (fresh feed plus recycled gas) to the methanol synthesis, $(H_2\text{-}CO)/(CO_2+CO)=2.1$, to get as high overall methanol yield as possible, and to purge as little unreacted gas as possible. Before the removal of CO_2 by absorption, the gas was cooled down to 40˚C, which is an appropriate temperature for CO_2 removal (Alie, et al., 2005). Due to high water content in the gas, most of the water was flashed out prior to the CO_2 absorption step.

The CO_2 absorption was simulated using a RadFrac column in Aspen plus with 6 stages. The absorption of CO_2 was enabled in the column by specifying reactions and their rate constants. The absorption simulation was made with the incentive to obtain temperature data for the outgoing syngas stream and estimate the CO and H_2 loss in the absorption process. A figure of the simulation model for the CO_2 absorption process can be seen in Figure 8-3 in Appendix A.

Approximately 95% of the CO_2 was removed from the feed gas to achieve the ratio of $(H_2\text{-}CO)/(CO_2+CO)=2.1$ of the feed gas to the reactor. Removal of 95% of the CO_2 resulted in that the feed gas to the reactor approximately contained 6.4 mole% CO_2, which is in the range of 2 to 10 mole%, see Section 2.1.1.7. Removal of 95% of the CO_2, resulted in that approximately 0.1% of the CO and H_2 left the absorption column with the absorption solution. Energy input for the absorption of CO_2 was approximated with 3.3 MJ/kg absorbed CO_2 (Götz, et al., 2012).

3.2.1.9 Methanol synthesis

After the CO_2 removal, the feed gas was compressed to 90 bar and cooled down to a temperature of 240˚C prior the methanol synthesis reactor.

The simulation model for the methanol synthesis was made using an equilibrium reactor (REquil), with the SRK property method, and with specified reactions. Due to linear dependence between the reactions for the methanol synthesis, only reactions 2-1and 2-2, seen in Section 2.1.1.8, was used in the simulation. The REquil calculates equilibrium by solving stoichiometric chemical and phase equilibrium equations, and the equilibrium constants are calculated from the Gibbs free energy. When using this type of reactor, one can allow each reaction to reach equilibrium, or one can restrict the reactions by specifying extent of reaction or the temperature approach of the equilibrium reactions. To find an appropriate temperature approach and to validate the simulation model, input from a commercial-scale demonstration unit of the LPMEOH^{TM} process (Air Products and Chemicals, Inc, 1998) was simulated and the output was compared with the output from the commercial-scale demonstration unit of the LPMEOH^{TM} process. The feed gas for the case used to find an appropriate temperature approach and to validate the model differs from the feed gas used in this study in the way that it was a CO-rich syngas instead of a balanced syngas. A temperature approach of 27 K for the two reactions resulted in similar conversions, seen in Table 8-6 in Appendix A, as in the commercial-scale demonstration unit of the LPMEOH^{TM} process, and was therefore found appropriate. The simulation differed somewhat from the results from the demonstration unit in the sense of obtaining higher CO_2 content, where the feed to the reactor (due to recirculation of unreacted gas) in the simulation model contained about 2.5% more CO_2 and the product out of the reactor contained about 7% more CO_2. This was however accepted. The simulation results for the commercial-scale demonstration unit of the LPMEOH^{TM} process can be found in Table 8-6 in Appendix A.

The remaining parts of the simulation was originally based on Hamelinck & Faiij (2001) and used by Isaksson, et al. (2012).

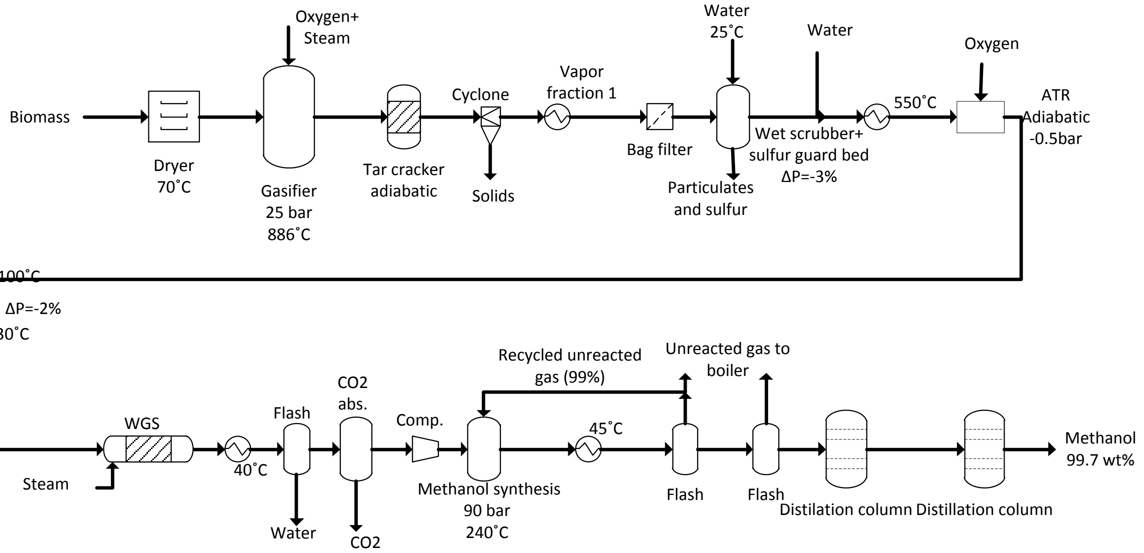
After the reactor the product gas was cooled down to 45˚C to enable flash out of the methanol. The gas leaving at the top of the flash, unreacted gas, was either recycled back to the reactor or was sent to purge. To get as high overall yield as possible, 99% of the unreacted gas was recycled and only 1% was sent to purge. 99% recovery was chosen to get as high overall methanol yield as possible, and at the same time reduce build-up of process gas within the process. The recycled gas was compressed and heated to reach the requirement of 240˚C and 90bar.

After the first flash, the pressure of the methanol stream was lowered using a valve. The methanol was then again allowed to enter a flash to separate some of the unreacted gas dissolved in the methanol. The methanol stream was then transferred to a stripper, which was simulated using 3 stages where a mass recovery of the methanol of 99% was specified. After the stripper the methanol was fed to a distillation column, which was simulated using 29 stages where a mole recovery of methanol of 99.8% and a mole purity of the methanol of 99.5% was specified.

A figure of the simulation model for the methanol synthesis process can be seen in Figure 8-4 in Appendix A.

3.2.1.10 Flowsheet for the process from biomass to methanol

A process flowsheet for the process from biomass to methanol can be seen in Figure 3-1. The different process steps require different temperatures, as shown in the figure. It will e.g. therefore be possible to utilize heat that must be removed from the process gas to heat the process gas where it is required. The production of methanol from biomass also requires input of electricity to run pumps and compressors.



Dryer	Heat required to dry the biomass
Gasification	Steam production and oxygen heating, increase of syngas temperature
Tar cracker	No heating nor cooling demand, adiabatic
Wet gas cleaning	Require lower temperature than the Tar cracker
ATR	Oxygen heating, exothermic reaction, increase of the syngas temperature
WGS	Lower temperature than the ATR, steam production
CO2 abs.	Lower temperature than the WGS, water removal, flash
Methanol synthesis	Exothermic reaction, cooling of reactor
Methanol separation	Heat sink and Heat source

All heat exchangers used are not included!

Figure 3-1 Flowsheet, biomass to methanol, some important modeling assumptions are included.

3.2.2 Simulation model of the Methanol to olefins (MTO) process

The property method used in the simulation is based on the recommendations in Aspen plus. The Peng-Robinson equation of state is recommended for hydrocarbon processing applications such as gas processing, refinery and petrochemical processes. To be able to simulate the combustion in the regenerator the Boston Mathias alpha function is recommended. So, the property method used is the PR-BM method.

3.2.2.1 Components

The process involves conventional components such as methanol, ethylene and water. It also involves solids in the form of catalyst material, which will be approximated using solid aluminum, as recommended by Fuglerud (2013). The solid material, aluminum, is only used in the simulation to be able to properly simulate the energy balance of the process. Since coke is formed during the reaction, a non-conventional component was created. All components used can be seen in Table 8-8 in Appendix B.

The non-conventional component coke is modeled using enthalpy and density properties. The model used to describe the enthalpy is the HCOALGEN model, which requires ULTANAL, PROXANAL and SULFANAL (see Section 3.2.1.1). Since the heat of combustion of coke was found in literature, option code number 6 was selected for the heat of combustion, the remaining option codes were set as default. When option code number 6 is used one has to specify a HCOMP parameter. The HCOMP can be specified in kJ/kg coke, and a heat of combustion of 33 537.2 kJ/kg (Ortega, et al., 1997) was used. The value of the heat of combustion was based on values for different C/H ratios of the coke.

Specifications for the non-conventional component coke can be seen in Table 3-2, and is based on the carbon hydrogen relation in coke, 1:0.8, which was suggested by Fuglerud (2013).

Table 3-2 Specifications for the non-conventional component coke, carbon hydrogen relation 1:0.8.

	ULTANAL		**SULFANAL**		**PROXANAL**
Ash	0	Pyritic	0	Moisture	0
Carbon	93.709	Sulfate	0	FC	100
Hydrogen	6.291	Organic	0	VM	0
Nitrogen	0			Ash	0
Chlorine	0				
Sulfur	0				
Oxygen	0				

To enable handling of conventional, solid and non-conventional components, three sub-streams are used. The vapor-liquid stream (MIXED), the sold stream (CIPSD) and the non-conventional stream (NCPSD) are required, and therefore the stream class used in the simulation is MCINCPSD.

3.2.2.2 The MTO process

The methanol feed to the reactor is vaporized and superheated to a temperature below 350˚C. At a temperature above 350˚C the methanol can dissociate into carbon monoxide and hydrogen. Since no kinetic expressions found in the literature (Bos, et al., 1995; Chen, et al., 2007; Fatourehchi, et al., 2011; Gayubo, et al., 2000; Hu, et al., 2010; Najafabadi, et al., 2012) were able to describe the MTO reaction corresponding to the UOP/Hydro technology and due to the complexity of the MTO reaction, the reactor was simulated as a yield reactor based on the mass yields obtained with the UOP/Hydro technology, Table 2-1 and Table 2-2 seen in section 2.2.3. The flowsheet for the process from methanol to quench product of the technology can be seen in Figure 3-2.

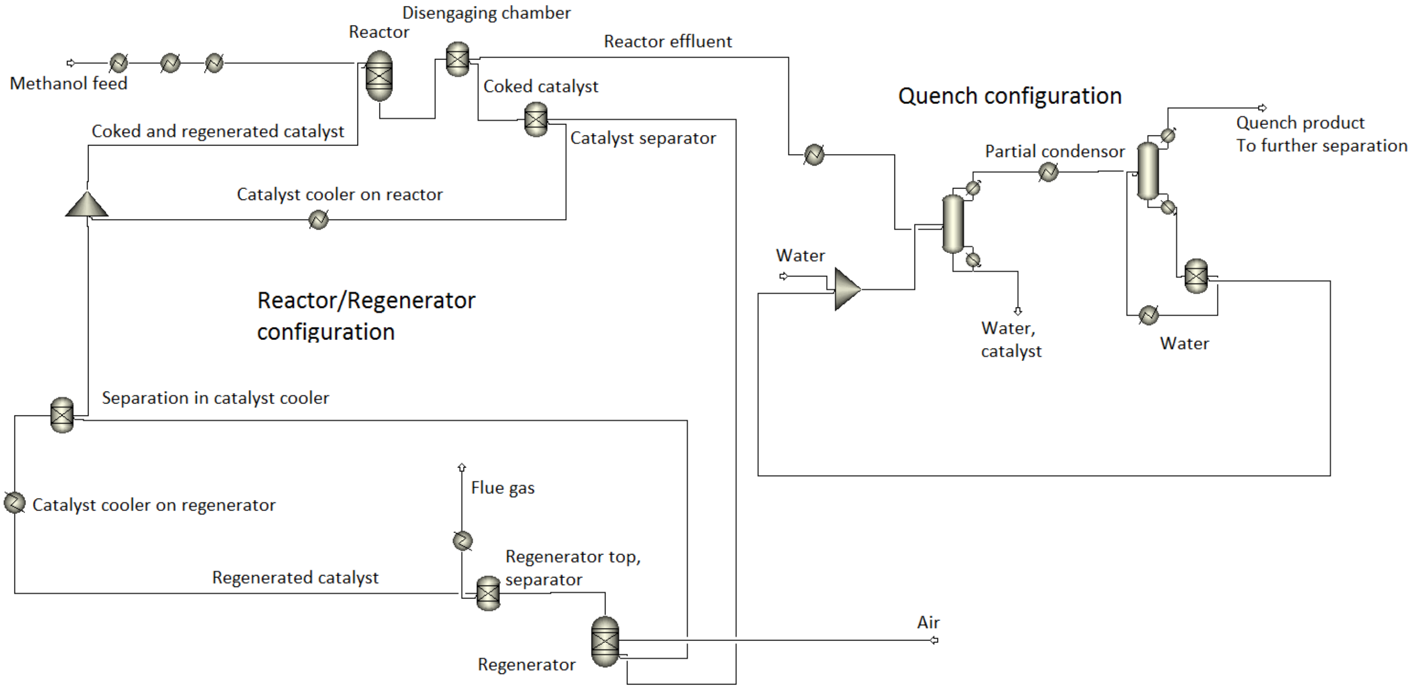


Figure 3-2 Flowsheet for the process from methanol to quench product from Aspen plus.

The reaction was simulated for two different cases, one case where the reaction conditions are set so that the production of ethylene is maximized and one where the production of propylene is maximized. Specifications for these two cases are described in the following sections. The amount of methanol fed to the process is based on the amount required to produce 200 kt ethylene/y in the high ethylene case.

Temperature and component flow specifications for the two cases can be seen in Section 3.2.2.2.1 and 3.2.2.2.2 and a summary of some specifications can be seen in Table 3-3.

Table 3-3 Summary of some modeling specifications regarding the MTO process for the high ethylene and the high propylene case.

	High ethylene case	**High propylene case**
MTO reactor outlet temperature (˚C)	540	445
Carbon selectivity for coke formation (%)	3	2.5
Catalyst material transferred to regenerator (t/h)	31.1	25.9

3.2.2.2.1 High ethylene case

The mass yields for the reaction was based on Table 2-1 and Table 2-2, and the mass yields used can be seen in Table 8-9 in Appendix B. All C_4 and C_5 components seen in the tables have been assumed to be butylene and pentene respectively. To be able to get the atom balance for carbon, hydrogen and oxygen to add up, the different component yields have been slightly adjusted, i.e. the yield of some components have been slightly increased or decreased, compared to Table 2-1 and Table 2-2. For example, in the high ethylene case, was a mass yield for ethylene of 21.45% used instead of 21.46%, a mass yield for propylene of 14.01% used instead of 13.95% and a mass yield of water of 55.82% used instead of 56.22%.

The temperatures used in the high ethylene case are based on the temperature to maximize the ethylene production, see Section 2.2.2, and specifications in Section 2.2.2.1. Temperature of the methanol feed to the reactor was set to 340˚C, to not exceed 350˚C. To gain an average temperature in the reactor of between 500 and 520˚C, the temperature of the outflow of the reactor was set to 540˚C. Since the temperature of the reactor is controlled by the amount and temperatures of the ingoing methanol feed and recycled catalyst material, these parameters were adjusted to meet the requirement of the outlet temperature. For further specifications see Appendix B.

3.2.2.2.2 High propylene case

The mass yields for the reaction was based on Table 2-1 and Table 2-2, and the mass yields used can be seen in Table 8-10 in Appendix B. All C_4 and C_5 components seen in the tables have been assumed to be butylene and pentene respectively. To be able to get the atom balance for carbon, hydrogen and oxygen to add up, the different yields have been slightly adjusted. No data for the coke yield for the high propylene case was found. Since a lower temperature will result in a lower coke yield, a coke yield was selected that is a bit lower than the selectivity for coke in the high ethylene case. As can be seen in Table 2-1, the selectivity for coke in the high ethylene case is 3%, a coke selectivity of 2.5% was chosen in the high propylene case, which was also recommended by Fuglerud (2013).

The temperatures used in the high propylene case are based on the temperature to maximize the propylene production, see Section 2.2.2, and specifications in Section 2.2.2.1. The average temperature in the reactor for the high propylene case should be in the range of 400 to 430˚C, therefore an outlet temperature of the reactor of 445˚C was chosen. To be able to easily change from the configuration of the high ethylene case to the high propylene case, in reality, the amount of catalyst entering the reactor was set to the same amount as in the high ethylene case in the simulation model. The amount of catalyst material was set depending on temperature specifications for the catalyst material, maximum 40˚C lower than the average temperature of the reactor, and the maximum temperature of the ingoing methanol feed. The temperature of the ingoing methanol feed in the high ethylene case was set at maximum, in order to maximize the amount of catalyst material that can absorb heat. The maximum temperature of the methanol feed was chosen so that the temperature of the methanol feed in the high propylene case does not get too low. If a lower amount of catalyst material had been used, less material can absorb the reaction heat, which means that the temperature of the methanol feed must be lower. This implies that the two parameters that one can adjust to meet the temperature requirement of the reactor outlet, are the temperature of the ingoing methanol and the ingoing catalyst material. For further specifications see Appendix B.

3.2.2.3 The regenerator

The regenerator of the process is simulated using a yield reactor, where all of the coke that is formed is completely combusted into CO_2 and H_2O. Oxygen is fed to the regenerator in the form of air in an amount corresponding to 20 mole% oxygen excess. The amount of catalyst material that is fed to the reactor is calculated based on a preferred level of coke on the catalyst particle, seen in Section 2.2.2.1. It is preferred to have a coke level of between 2 and 7 wt% based on the total weight of the catalyst particle (Cao, et al., 2011), therefore an average level of 4.5 wt% is used.

To be able to control the temperature within the regenerator, where a temperature of 730˚C is needed to fully combust the coke into CO_2 and H_2O, cooled regenerated catalyst material is fed into the regenerator, see Section 2.2.2.1. The catalyst material coming from the reactor to the regenerator, is regenerated, cooled down and then recycled back to the reactor at a desired temperature. For specifications regarding the two cases, high ethylene and high propylene see the following sections.

3.2.2.3.1 High ethylene case

The weight of catalyst material transferred to the regenerator in the high ethylene case were calculated accordingly, see Appendix B. The weight of the catalyst material were calculated to 31 094.2 kg/h. The weight of catalyst particles fed to the regenerator per hour corresponds to 0.2667 of the methanol feed per hour. As can be seen in Section 2.2.2.1, should the amount of catalyst particles fed to the regenerator be in the interval of 0.1 to 0.3 (Beech & Walter, 2007). The amount of catalyst particles going to regeneration relative to the amount that is just cooled down and recycled back to the reactor is approximately 6%, which is within the interval of 5 to 200% (Clem, et al., 2006) seen in Section 2.2.2.1. For calculations see Appendix B.

The amount of catalyst particles that are cooled and recycled back to the regenerator was adjusted so that the regenerated catalyst particles and the flue gas coming out of the regenerator had a temperature of 730˚C.

3.2.2.3.2 High propylene case

The weight of catalyst material transferred to the regenerator in the high ethylene case were calculated accordingly, see Appendix B. The weight of the catalyst material were calculated to 25 911.9 kg/h. The weight of catalyst particles fed to the regenerator per hour corresponds to 0.2222 of the methanol feed per hour. As can be seen in Section 2.2.2.1, the amount of catalyst particles fed to the regenerator should be in the interval of 0.1 to 0.3 (Beech & Walter, 2007). The amount of catalyst particles going to regeneration relative to the amount that is just cooled down and recycled back to the reactor is approximately 5%, which is within the interval of 5 to 200% (Clem, et al., 2006) seen in Section 2.2.2.1. For calculations see Appendix B.

To be able to easily shift operating conditions, and thereby shift between the two cases, the amount of catalyst particles that are cooled and recycled back to the regenerator are the same as in the high ethylene case. This implies that the only thing controlling the temperature within the regenerator is the temperatures of the incoming feeds, air, coked catalyst particles and cooled regenerated catalyst particles.

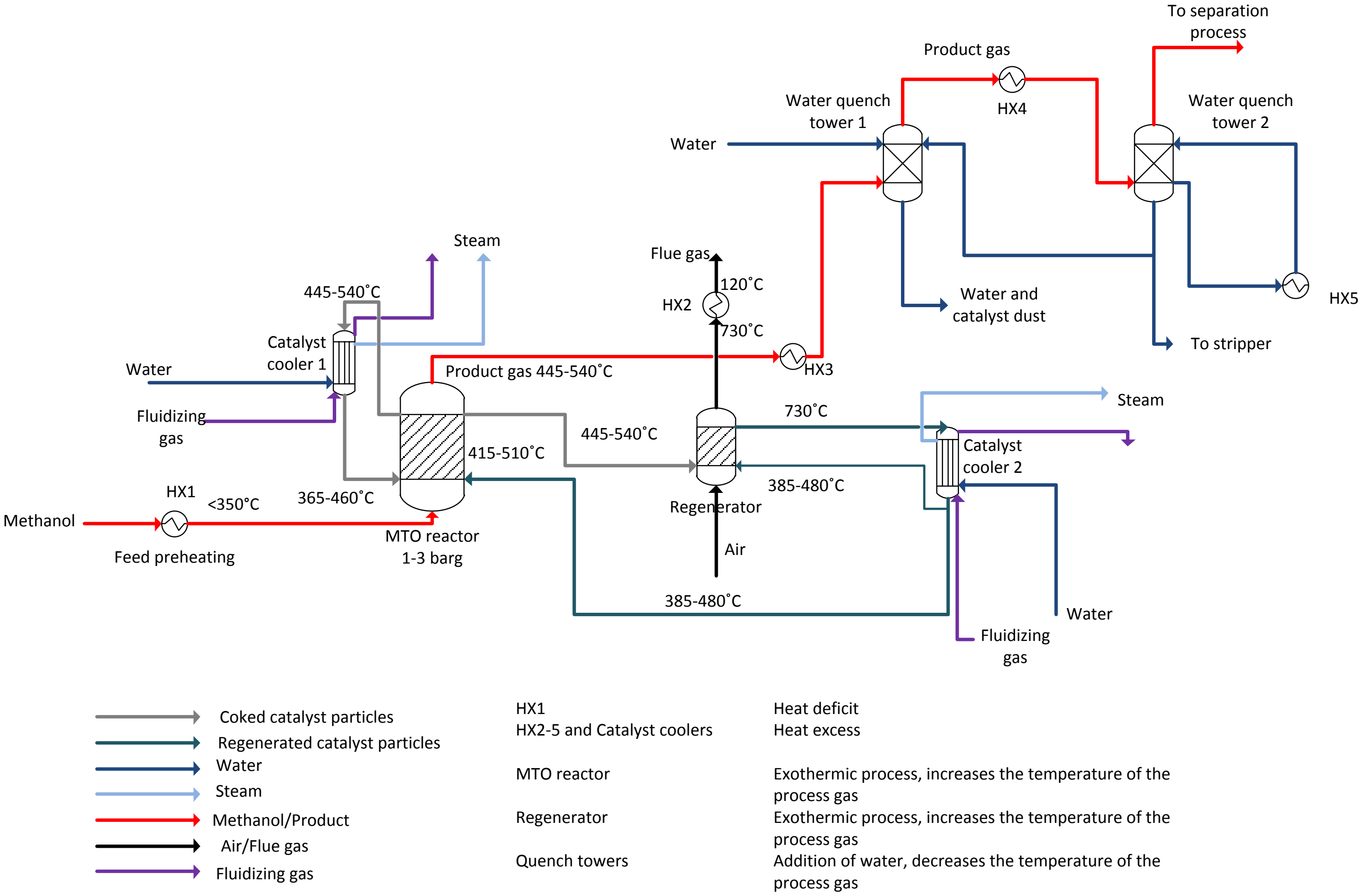
3.2.2.4 The two-stage quench process

The quench towers were modeled using specifications found in the literature, see Section 2.2.2.2. The quench towers were modeled using RadFrac columns with an equilibrium model. No condenser and no reboiler were used in this simulation. Number of stages in the different columns was chosen so that a temperature gradient did exist in the entire column. The reactor effluent is fed on the bottom stage of the column and the water stream is fed on the top stage of the column. To account for some pressure drop through the process, a top stage pressure of 2 bar in the first quench tower was chosen and a top stage pressure of the second quench tower of 1.5 bar was chosen. The amount of ingoing water, or quench medium, to the first tower related to the ingoing reactor effluent was set to 0.47:1 (Beech, et al., 2006). Prior to the first quench tower the reactor effluent was heat exchanged to utilize as much of the available heat as possible. One restriction for this heat exchanger was that the gas was not allowed to be cooled below the dew point. The duty of the heat exchanger was set so that the requirement of water leaving at the first quench tower was met, 5% (Beech, et al., 2006) of the water present in the reactor effluent should leave with the bottom stream. This was done with a design specification in Aspen Plus. Since most of the water, or quench medium, entering the first quench tower is recycled from quench tower number two, the temperature of the ingoing water was set to the outlet temperature of the water of quench tower two. The gas leaving the first quench tower is then partially condensed to be able to utilize as much heat as possible. The amount of water entering the second quench tower was set so that the requirement of maximum 3% (Beech, et al., 2006) of the water present in the original reactor effluent is left in the outgoing gas stream. This was done with a design specification in Aspen Plus. The outgoing water of quench tower number two, is both recycled to quench tower one and back to quench tower two. The water recycled back to quench tower two is heat exchanged down to 35˚C (Beech, et al., 2006), see Section 2.2.2.2. For further specifications regarding the quench tower configuration regarding the two different cases, see Appendix B.

Different property methods were tested to see which property method describing the system as accurate as possible. According to The Engineering ToolBox pure ethylene has solubility in water of 0.12 g/kg at atmospheric pressure and 30˚C, with a pattern of decreased solubility with increased temperature. Therefore, a quench tower was simulated using 30˚C, atmospheric pressure, pure ethylene and pure water. The property method closest to the solubility of ethylene in water was the RKSWS, Redlich-Kwong-Soave-Wong Sandler, property method. With this property method the ethylene had solubility in the water of 0.32 4g/kg, which is 2.7 times greater than the value provided by the Engineering ToolBox. The RKSWS property method was nevertheless selected since most other property methods gave much more or much less solubility of the ethylene in the water. According to the Aspen Plus user guide, the property method RKS is recommended for a quench tower within an ethylene plant. It is also stated that one can use the RKSWS property method for mixtures of non-polar and polar compounds in combination with gases. Therefore, the RKSWS property method was used when simulating the quench towers.

3.2.2.5 Flowsheet for the MTO process

A process flow sheet for the process from methanol to olefins can be seen in Figure 3-3, temperature specifications and specifications regarding where there is heat excess or deficit are included. After the water quench towers additional separation units are required, which both have heat excess, e.g. condensers, and deficit, e.g. reboilers. After the second quench tower, the pressure has to be increased using compressors.



HX1	Heat deficit
HX2-5 and Catalyst coolers	Heat excess
MTO reactor	Exothermic process, increases the temperature of the process gas
Regenerator	Exothermic process, increases the temperature of the process gas
Quench towers	Addition of water, decreases the temperature of the process gas

Figure 3-3 Flowsheet for the MTO process, including some modeling assumptions.

3.2.2.6 Separation

The heat needed and available in the existing separation system at the cracker plant is assumed to be unaffected when decreasing the cracker plant capacity and replacing it with olefins from the MTO process. This is likely not the case since the product gas from the MTO process has a higher content of the wanted olefins than the product gas from the steam crackers. The composition of the feed gas to the separation system when mixing the two processes will also differ when it comes to the amount of fuel gases that is formed. Both of these changes will have an effect on the energy balance of the system. However, this was not analyzed further within the framework of this thesis project.

3.3 Pinch Analysis and Heat Integration

Pinch analysis is a systematic approach that is used to identify possibilities of heat integration within processes or chemical clusters to minimize the external heating and cooling demand. This is done by increasing the amount of internal heat exchanging. Pinch analysis is used to identify the amount of internal heat exchanging that can be done and the amount of external heating and cooling that is needed.

Before the analysis can start, the hot and cold streams have to be identified. A hot stream is a stream that needs to be cooled and a cold stream is a stream that needs to be heated. When investigating the possibilities of heat exchanging, a ΔT_{min} (minimal temperature difference) has to be chosen for the heat exchanging. When all data for the streams are collected a Grand Composite Curve (GCC) can be plotted. The Grand Composite Curve provides a graphical illustration of excess and deficit heat levels at different temperature levels. An example of a Grand Composite Curve (GCC) can be seen in Figure 3-4. The red streams denote areas of excess heat, and the blue streams areas with net heat deficit.

From the Grand Composite Curve (GCC) it is possible to identify the minimum hot ($Q_{H,min}$) and cold utilities ($Q_{C,min}$) needed at a specific ΔT_{min}.

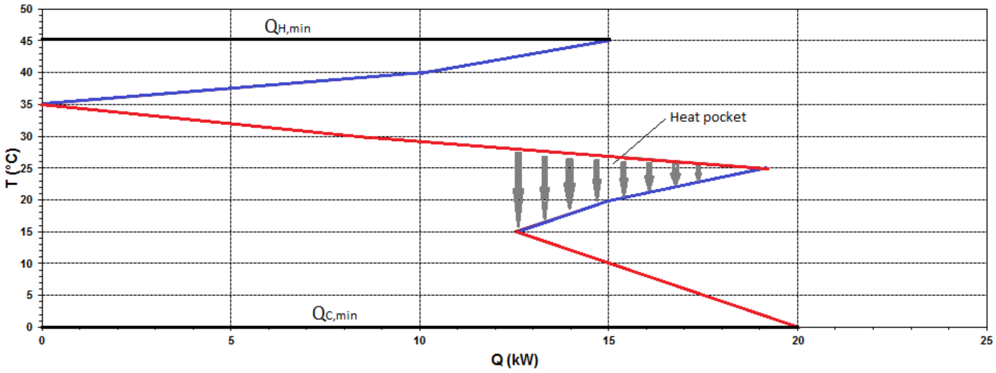


Figure 3-4 Example of a grand composite curve (GCC), red streams representing hot streams (requiring cooling), blue streams representing cold streams (requiring heating).

In the Grand Composite Curve (GCC), see Figure 3-4, the temperature is in shifted temperatures ($\Delta T_{min}/2$ is subtracted from the real temperatures of hot streams, and $\Delta T_{min}/2$ is added to the real temperature of cold streams), in order to obtain a temperature difference of zero at the location(s) where driving forces are at their minimum. The pinch point is located at the temperature where the curve touches the Y-axis. In each temperature interval the total heat excess or deficit can be identified. The process has an overall heat deficit above the pinch, which requires external heating ($Q_{H,min}$), and it has an overall heat excess below the pinch, which is requires external cooling ($Q_{C,min}$). In the GCC it is possible to identify at what temperature(s) utility needs to be provided in order to meet the demand of the process. In a GCC, see Figure 3-4, it is also possible to identify temperature regions where no external heating or cooling is required, and is a heat pocket (represented by grey arrows in Figure 3-4). In this temperature region it is possible to integrate streams with excess of heat with streams that have a deficit of heat. In order to obtain the minimum heating and cooling utility consumption for a process, it is important to follow the three golden rules of pinch technology:

- Do not cool above the pinch
- Do not heat below the pinch
- Do not transfer heat through the pinch

Violation of any of these rules will result in increased energy consumption.

In order to be able to identify integration opportunities for a certain process step with the rest of the process, one can perform a background/foreground analysis. One example of this is the integration of the MTO process with the rest of the chemical cluster. An example of a background/foreground analysis can be seen in Figure 3-5. In this example the blue process can to some extent be integrated with the red process, where all of the heat available in the blue process can be utilized to heat the red process. The heat available in the red process, on the other hand, is not sufficient to heat the entire blue process, external utility is therefore in this case required.

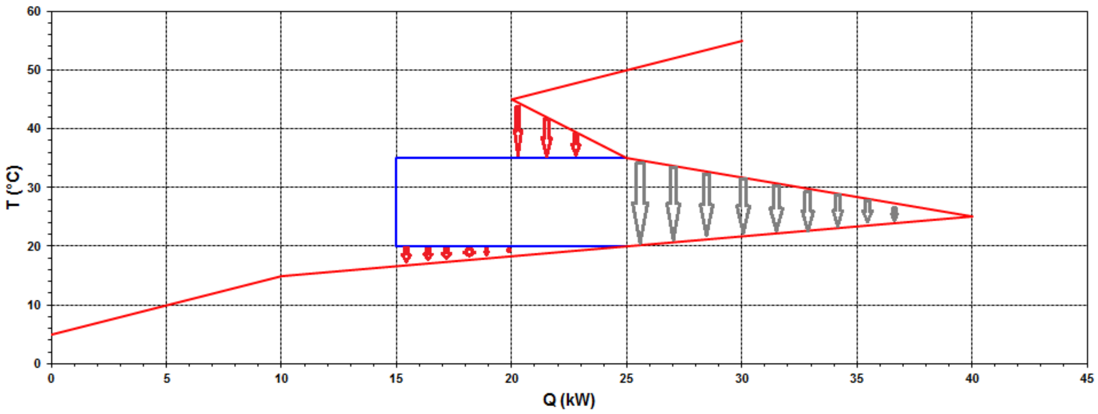


Figure 3-5 Example of a background/foreground analysis.

In order to be able to perform a pinch analysis, process data is generated using the simulation model built in Aspen Plus and will be used as input to the pinch analysis. The pinch analysis will be performed using the Excel add-in Pro Pi. In this program it is possible, among other things, to construct Composite, Grand Composite Curves and background/foreground analysis. In the analysis the minimum demand for hot and cold utilities will be identified as well as opportunities for internal heat exchange. A minimum temperature difference of 10˚C is used in the analysis.

3.3.1 Integration of steam cycles

A process containing high temperature heat (and excess heat) and need heat at low temperatures, may it be appropriate to integrate a steam cycle with the incentive to produce electricity. If the process contains excess heat that does not need to be used for heat integration, it is possible to integrate a steam cycle to utilize this excess heat for electricity production. An example of when it is appropriate to integrate a steam cycle with a process can be seen in Figure 3-6.

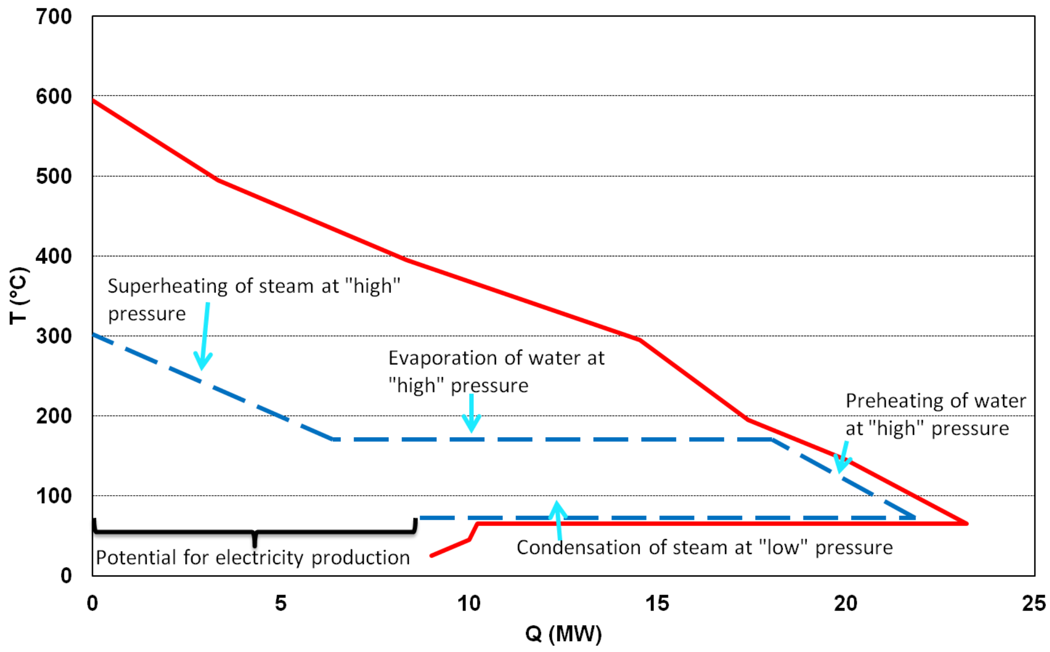


Figure 3-6 Example of an integration of a steam cycle. Red: GCC of a process with high temperature heat in excess and low temperature heat in deficit. Blue: Steam cycle.

It is appropriate to integrate a steam cycle in this process due to the shape of the GCC, the GCC of the process has a large heat pocket and contains excess heat at high temperature levels. When integrating a steam cycle, as seen in the example, one utilizes high temperature heat to produce steam at high pressures (pumping of water from low to high pressure, preheating of water to evaporation point, evaporation of water, and superheating of steam). The steam is then expanded in a steam turbine with the incentive to produce electricity. The potential for electricity production can be seen in the example. The available steam at lower pressure is then used to heat the process, i.e. condensation of the available low pressure steam is used to heat low temperature streams within the process. Depending on what temperature levels that need heat in the process, it is possible to expand the steam to different pressure levels, and thereby also different temperature levels. Seen in the example is just one bleed to one pressure level, but it is possible to have more than one bleed, i.e. one get steam at different pressure levels. To produce as much electricity as possible it is possible to expand the steam to vacuum pressure levels if the temperature level is appropriate, i.e. the temperature level of the condensation should match a temperature level in the need of heat within the process.

Isentropic efficiencies for the turbines were calculated using a performance curve in the Industrial Energy Systems course compendium (Berntsson, 2011), which depend on mass flows and pressure drops in the turbines. The efficiency of the pump was assumed to be 0.8.

3.4 Evaluation of different options for process integration

Possible heat integration opportunities will be influenced by the operating conditions as well as by sizes and heat excess/deficit of different process streams. However, it is important to utilize as much as possible of the heat available to minimize the use of external heat, especially the use of external high temperature heat. One possibility is to integrate the gasifier and the MTO reactor with the cracker making use of the already existing infrastructure such as separation systems and a boiler. There might also be an opportunity to utilize low temperature excess heat within the cracker plant.

The evaluation will be based on heat integration possibilities in five cases, and will be evaluated based on potentials for energy savings and the potential for steam production. This will be done by using background- and foreground curves. An illustration of the process integration possibilities that has been evaluated in this thesis can be seen in Figure 3-7 (also seen in Section 1.2). First the heat integration potentials for two stand-alone cases were investigated. The base case in this evaluation will be the production of methanol to a mixture of raw olefins where methanol is assumed to be imported (stand-alone MTO). The second case has been based on the biomass conversion to methanol process (biomass to methanol). The stand-alone cases were then combined to investigate the potentials for heat integration. The first combined case was based on the process of converting biomass to methanol and the MTO process, methanol to a mixture of raw olefins (biomass to olefins), i.e. the integration of the processes from biomass to methanol and the MTO process. The second combined case was based on the MTO process and the steam cracker plant (MTO and steam cracker).The last case combined all cases, the biomass to methanol processes, MTO process, and the steam cracker plant (biomass to olefins and steam cracker).

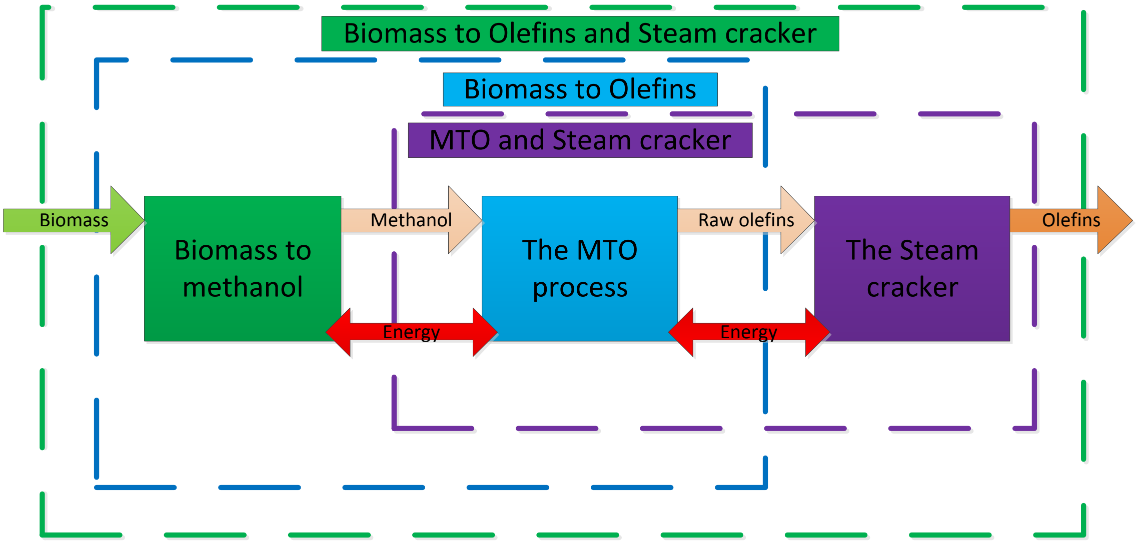


Figure 3-7 Heat integration for the combined cases, Biomass to Olefins, the MTO process and the steam cracker, and Biomass to Olefins and steam cracker.

4 Result and Discussion

4.1 Simulation results

To be able to produce 200 kt/y (350 MW_{HHV}) of ethylene, based on the high ethylene case, and in total approximately 370 kt/y (636MW_{HHV}) of ethylene, propylene and butylene, approximately 117 ton/h (741 MW_{HHV}) of methanol are required (based on 8 000 h/y of plant operation). Results for simulation of production of 117 ton/h methanol from biomass indicate that an input to the dryer of 453ton/h (1 230 MW_{HHV}) biomass (50 wt% moisture) is required. The resulting product yields for the different processes obtained with the simulation models, biomass to methanol, methanol to raw olefins and biomass to raw olefins can be seen in Table 4-1. Olefins included in the yield calculations are ethylene, propylene and butylene.

Table 4-1 Product yields, biomass to methanol, methanol to olefins and biomass to olefins, high ethylene and high propylene case, kg/kg, carbon/carbon and MW/MW.

Yield	**Biomass (dry) to methanol**	**Methanol to olefins (high ethylene)**	**Methanol to olefins (high propylene)**	**Biomass (dry) to olefins (high ethylene)**	**Biomass (dry) to olefins (high propylene)**
kg/kg	0.515	0.398	0.393	0.205	0.202
carbon/carbon	0.383	0.908	0.897	0.348	0.344
MW_{HHV}/MW_{HHV}	0.602	0.858	0.848	0.517	0.511

The resulting Energy ratio for the biomass to methanol models obtained is 60.2%, which corresponds with other studies made on the same subject. Williams, et al. (1995) reported Energy ratios between 56.6 and 67.7% (see Section 2.1.2).

For specific gas compositions after the different process steps from biomass to methanol see Table 8-5 and Table 8-7 in Appendix A.

Electricity demand for the processes, electricity needed to be able to increase to pressure of the process flow with pumps and compressors obtained with the simulation models can be seen in Table 4-2, and is hereafter referred to as process electricity demand, or $W_{el.demand}$.

Table 4-2 Electricity demand for the processes, electricity needed to be able to increase to pressure of the process flow with pumps and compressors obtained with the simulation models, $W_{el.demand}$.

Process/ $W_{el.demand}$	**Biomass to methanol**	**Methanol to raw olefins (high ethylene)**	**Methanol to raw olefins (high propylene)**	**Biomass to raw olefins (high ethylene)**	**Biomass to raw olefins (high propylene)**
MW_{el}	32.1	5.1	4.6	37.2	36.7

4.2 Heat integration results

The utility system regarding the HP steam produced and used in Stenungsund and at Borealis will be utilized in the heat integration analysis. The utility system can be seen in Table 2-3 in Section 2.3. The available boiler at the steam cracker plant has a minimum capacity of 30 MW and a maximum capacity of 80 MW. It is therefore possible to increase the production of HP steam from the boiler by 50 MW.

4.2.1 Biomass to methanol

This section presents results based on the production of 117 ton/h of methanol from 453 ton/h of biomass (50 wt% moisture).

The resulting energy demand for the absorption of CO_2 is 141 MW in the reboiler of the desorber. For the heating of the reboiler, it assumed that pressure level of the LP steam used in Stenungsund is used here as well, which will be included in the heat integration study.

Unreacted gas from the methanol synthesis can be burned in a boiler to produce steam. When assuming 80% efficiency for the steam production from burning of unreacted gas, hereafter referred to as off-gases, it is possible to approximately produce 18 MW steam.

Heat integration of all process steps, from biomass drying to methanol synthesis, results in a GCC that can be seen in Figure 4-1. Stream data for the respective processes can be seen in Table 8-15 to Table 8-20 in Appendix C. No hot utility is required for the processes when implementing maximum integration. The required minimum cold utility for the processes is approximately 112 MW.

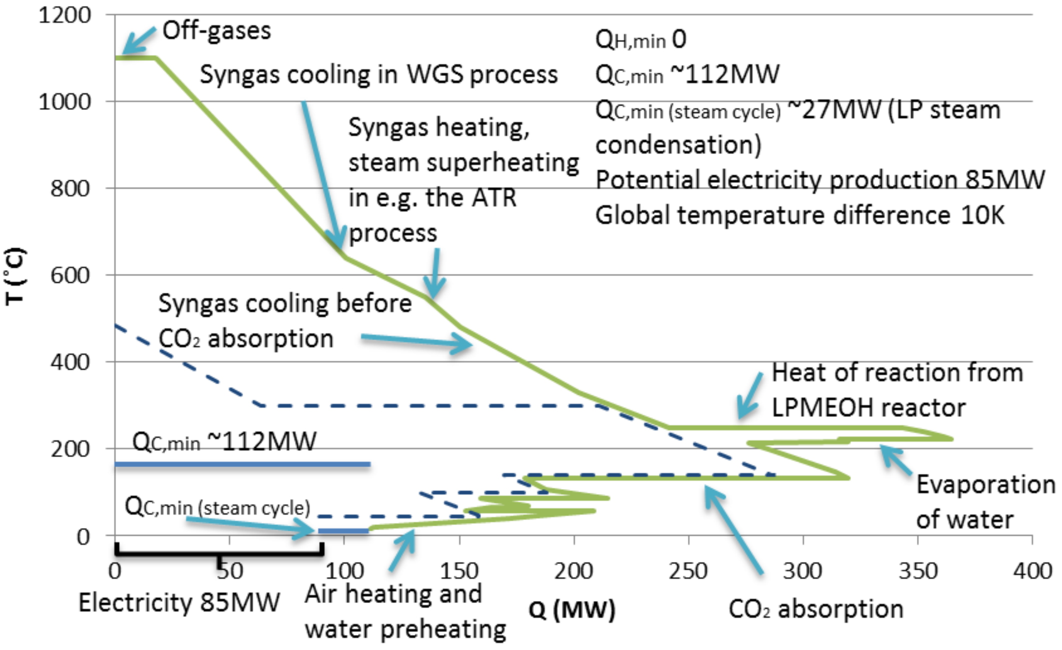


Figure 4-1 GCC of the all process, biomass drying to methanol synthesis (green), from the simulation models, and integration of steam cycle (blue), 378t/h. Included are some important streams affecting the shape of the GCC.

Due to the shape of the GCC, i.e. high temperature excess heat and a large heat pocket, it is suitable to integrate a steam cycle. From the steam cycle integration seen in Figure 4-1, there is a potential to generate 85 MW of electricity. This electricity production is based on the input of 378 t/h steam to a turbine where 198 t/h is expanded from 86 bara to 3.72 bara, 79.2 t/h to 1.05 bara, and 100.8 t/h to 0.1 bara. The steam turbine isentropic efficiencies were assumed to be 0.86, 0.91 and 0.96 respectively, and a pump isentropic efficiency of 0.8. Integration of the processes from biomass to methanol with a steam cycle results in a cooling demand of approximately 27 MW due to that the processes (biomass to methanol) does not need all the resulting heat available from condensation of the LP steam.

A measure of the yield from biomass to methanol is the thermal efficiency,$\eta_{th}\%$, defined in Section 2.1.2, which was based on the energy input in the form of raw material, heat and electricity, as well as the output of energy in the product. Since no heat has to be supplied to the process, and since net electricity generation is positive, $\eta_{th}\%$ is 67.2% (implementing maximum heat integration and the integration of a steam cycle). Williams, et al. (2001) reported Thermal efficiencies for different gasification technologies of between 53.9 and 61.0%. A higher value of $\eta_{th}\%$ was probably obtained due to that maximum heat integration in this case has been applied and due to that a steam cycle has been assumed to be integrated with the processes, and thereby obtaining an additional product in the form of electricity.

4.2.2 Stand-alone MTO

This section presents results for the MTO process, methanol to a mixture of raw olefins. The results are based on the production of 200 kt/y (350 MW_{HHV}) of ethylene, based on the high ethylene case, and in total approximately 370 kt/y (636 MW_{HHV}) of ethylene, propylene and butylene, based on the high ethylene case, which corresponds to the production of olefins from 117 ton/h (741 MW_{HHV}) of methanol.

For the process from methanol to a mixture of raw olefins, the only heat deficit corresponds to the preheating, evaporation and superheating of the methanol. There is heat excess from the two catalyst coolers, the flue gas cooler after the regenerator, and the cooling associated with the quench tower configuration. For specifications regarding the two cases, see Section 4.2.2.1 and 4.2.2.2 below. In this case methanol is assumed to be delivered at atmospheric pressure and at a temperature of 20˚C. Electricity is needed to increase the pressure of the methanol with a pump to 3.1 bara. After the quench tower configuration, the pressure of the olefin mixture must be increased to 18 bara to be able to send it to the separation process.

4.2.2.1 High ethylene case

For duty and stream data for the high ethylene case see Table 8-21 in Appendix C. Resulting GCC for these streams can be seen in Figure 4-2. No hot utility is required for the stand-alone MTO case when maximum integration is implemented. The minimum cold utility for the process is 34.25 MW (6 MW high temperature heat and 28.25 MW low temperature heat).

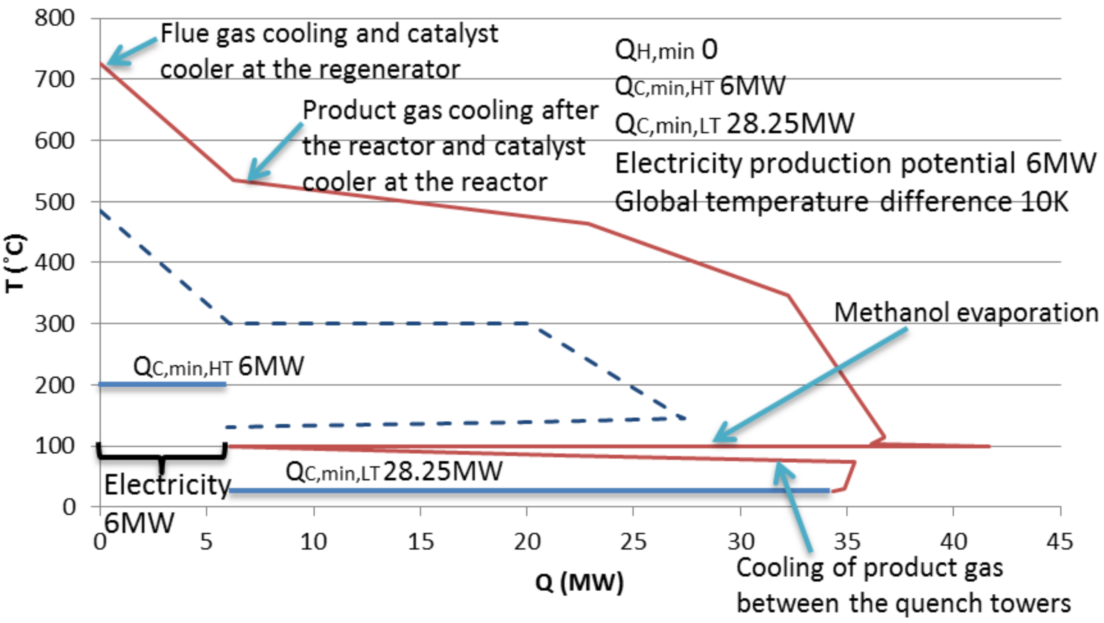


Figure 4-2 GCC for the process from methanol to a mixture of olefins (red), high ethylene case, and the integration of a steam cycle (blue).

Due to the shape of the GCC, i.e. high temperature heat excess and a large heat pocket, it is suitable to integrate a steam cycle, as can be seen in Figure 4-2. The integration resulted in the potential for electricity production of 6 MW, based on the input of 36 t/h steam which was expanded to 2.8 bara with a turbine isentropic efficiency of 0.85 and a pump isentropic efficiency of 0.8. Integration of a steam cycle results in a positive net production of electricity of 1 MW. The minimum cold utility for the MTO process when a steam cycle has been integrated is 28.25 MW (low temperature heat) and no hot utility is required using this setup.

The $\eta_{th}\%$ for the conversion of methanol to raw olefins (ethylene, propylene and butylene), high ethylene case, was estimated to approximately 86%, including the net electricity production.

4.2.2.2 High propylene case

For duty and stream data for the high ethylene case see Table 8-22 in Appendix C. The resulting GCC for these streams can be seen in Figure 4-3. No hot utility is required for the stand-alone MTO case when maximum integration is implemented. The minimum cold utility for the process is 35.8 MW (7.3 MW high temperature heat and 28.5 MW low temperature heat).

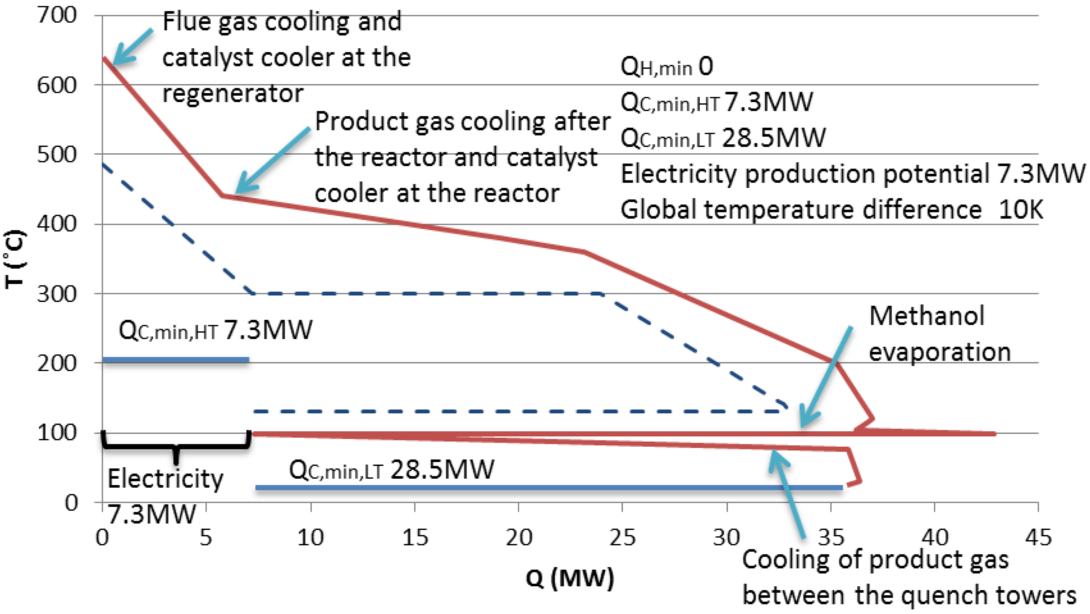


Figure 4-3 GCC for the process from methanol to a mixture of olefins (red), high propylene case, and the integration of a steam cycle (blue).

As for the high ethylene case, see Section 4.2.2.1, the shape of the GCC indicates that there is a possibility to integrate a steam cycle with the high propylene MTO process. The integration results in a potential production of 7.3 MW of electricity, based on the input of 42.84 t/h steam which was expanded to 1.8 barg with a turbine isentropic efficiency of 0.847 and a pump isentropic efficiency of 0.8. Integration of a steam cycle results in a positive net production of electricity in the high propylene case of 2.7 MW. Minimum cold utility for the GCC is 28.5 MW and no hot utility is required when a steam cycle has been integrated.

The $\eta_{th}\%$ for the conversion of methanol to raw olefins (ethylene, propylene and butylene), high propylene case, was estimated to approximately 85%, including the net electricity production.

4.2.2.3 Concluding discussion

When comparing the two cases, the main difference is that the temperature of the methanol feed to the reactor is assumed to be higher in the high ethylene case than in the high propylene case, the load for superheating the methanol is lower in the high propylene case. Another difference is that the temperature of the reaction is higher in the high ethylene case, which results in overall higher temperatures for the high ethylene case. To be noticed is that the temperature of the methanol feed in the high ethylene case was set so that the temperature would not exceed 350˚C. It is however uncertain whether or not a feed temperature of 340˚C in the high ethylene case, and a feed temperature of 195˚C in the high propylene case correspond to reality, i.e. correspond to the temperatures used in a commercial UOP/Hydro MTO process. If the temperature of the feed is too high in the high ethylene case and the temperature is too low in the high propylene case, it will have an impact on the electricity generation potential when integrating a steam cycle.

From the GCC, Figure 4-2 and Figure 4-3, it is possible to see that most of the excess heat that is available is at low temperatures, and cannot be used to for example the production of steam. One possibility to use this excess heat is to utilize it for district heating, Q_{DH}. There is a lot of energy available at this low temperature, and most of the energy comes from the partial condensation of the product gas occurring between the two quench towers.

4.2.3 Biomass to Olefins

Heat integration of the processes from biomass (50% moisture content) to a mixture of olefins will be presented in this section. Since the methanol is assumed to be delivered from the methanol synthesis process, there will be some changes regarding the duty of the methanol preheating, which can be seen in Table 8-23 in Appendix C. The rest of the stream data can be seen in Table 8-15 to Table 8-22 in Appendix C.

4.2.3.1 High ethylene case

The resulting GCC for the integration of the biomass to methanol processes with the MTO process, biomass to raw olefins, for the high ethylene case can be seen in Figure 4-4. The minimum cold utility for the processes is 148 MW (high temperature heat). No hot utility is required for the processes when maximum heat integration is implemented.

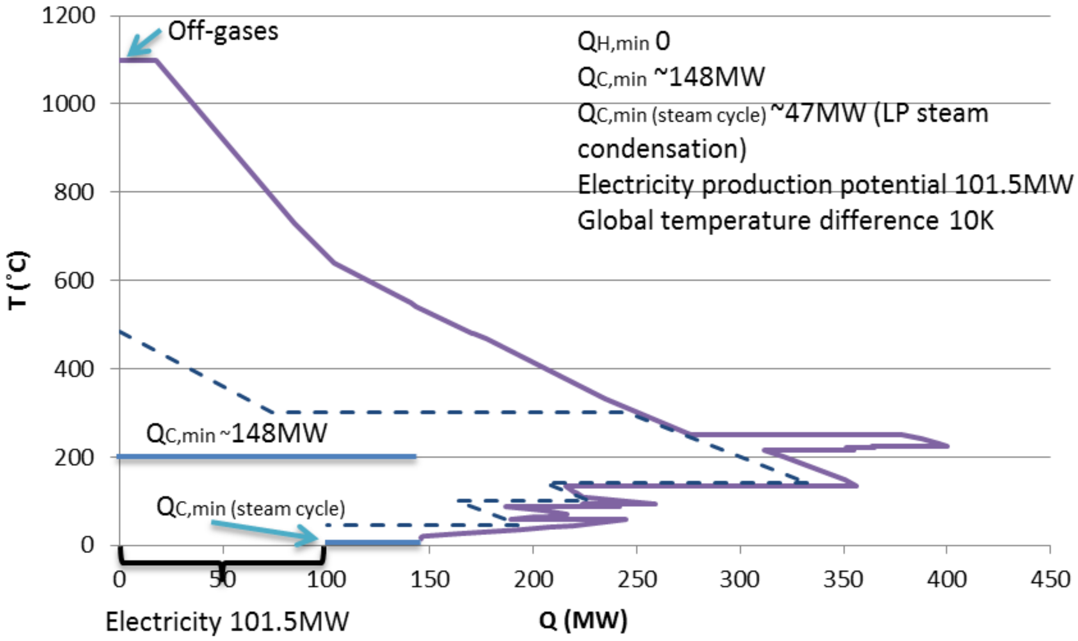


Figure 4-4 GCC for the processes from biomass to a mixture of olefins (purple) in the high ethylene case, from the simulation models and the integration of a steam cycle (blue).

As for the biomass to methanol, Section 4.2.1, and the stand-alone MTO, Section 4.2.2, cases, it is suitable to integrate a steam cycle. The steam cycle integration seen in Figure 4-4, can potentially generate 101.5 MW of electricity. This electricity production is based on the input of 439 t/h steam to a turbine where 216 t/h is expanded from 86 bara to 3.7 bara, 94 t/h to 1.0 bara, and 130 t/h is expanded to 0.1 bara. The electricity produced within the steam cycle had turbine isentropic efficiencies of 0.87, 0.92 and 0.97 respectively and a pump isentropic efficiency of 0.8.

The net electricity production potential from the biomass to olefins processes, high ethylene case, with the integration of a steam cycle is 64.3 MW.

Integration of a steam cycle with the biomass to olefins processes, seen in Figure 4-4, results in the need for approximately 47 MW of cold utility. This is due to the excess heat resulting from the condensation of the LP steam within the steam cycle.

4.2.3.2 High propylene case

The resulting GCC for the integration of the biomass to methanol processes with the MTO process, biomass to olefins, for the high propylene case, and a steam cycle can be seen in Figure 4-5. The minimum cold utility for the processes is 156 MW (high temperature heat). No hot utility is required for the processes when maximum heat integration is implemented.

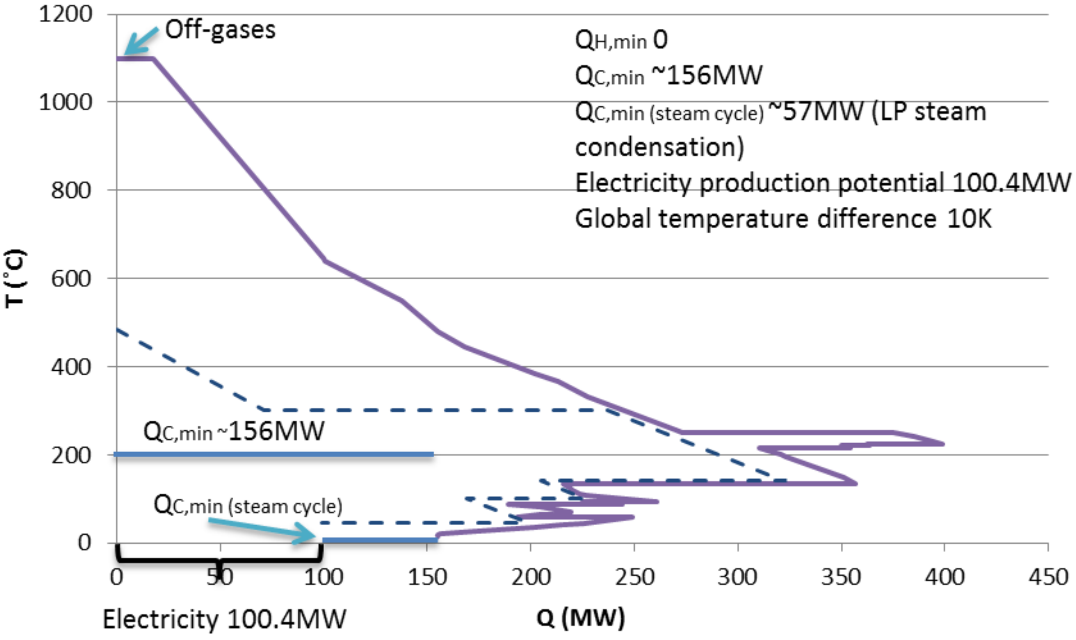


Figure 4-5 GCC for the processes from biomass to a mixture of olefins (purple) in the high propylene case, from the simulation models and the integration of a steam cycle (blue).

The steam cycle integration seen in Figure 4-5, can potentially generate 100.4 MW electricity. This electricity production is based on the input of 425 t/h steam to a turbine where 198 t/h is expanded from 86 bara to 3.7 bara, 83 t/h to 1.0 bara, and 144t/h to 0.1bara. The electricity produced within the steam cycle had turbine isentropic efficiencies of 0.87, 0.92 and 0.97 respectively and a pump isentropic efficiency of 0.8.

Integration of a steam cycle with the biomass to olefins processes, seen in Figure 4-4, results in the need for approximately 57 MW of cold utility. This is due to the excess heat resulting from the condensation of the LP steam within the steam cycle.

The potential net electricity production from the biomass to olefins processes, high ethylene case, with the integration of a steam cycle is 64 MW.

4.2.3.3 Concluding discussion

Comparing the results between the high ethylene and the high propylene case, biomass to olefins, it can be concluded that more electricity can be produced when integrating a steam cycle in the high ethylene case than in the high propylene case, which also can be seen in Figure 4-6. The main difference between high ethylene and high propylene is that the temperatures are higher in the high ethylene case for the MTO process, which results in that more heat is available at high temperatures and can be used for production of electricity from the integration of a steam cycle. As can be seen in Figure 4-4 and Figure 4-5 it is mostly the heat at temperatures above 300°C (evaporation temperature) that is limiting the amount of steam that can be produced, and this limitation is somewhat more clear in the high propylene case than in the high ethylene case.

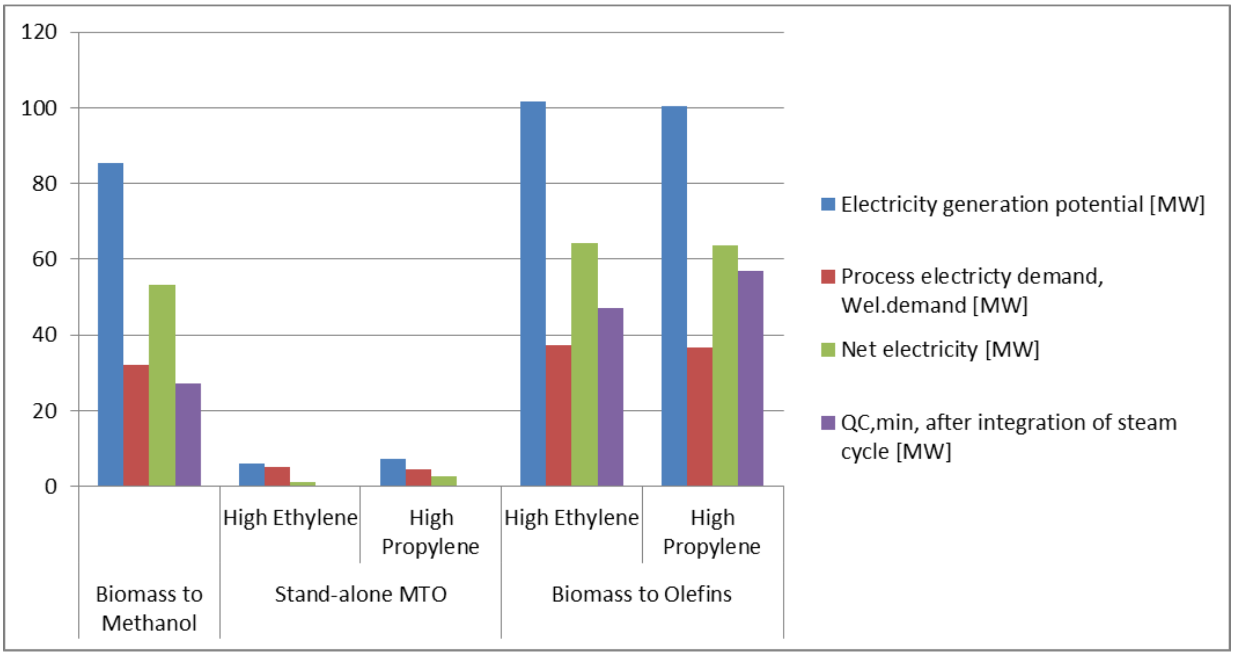


Figure 4-6 Summary of results obtained when integrating the different cases with a steam cycle.

In Figure 4-6 it is also possible to see the process electricity demand. Also shown in Figure 4-6 is the minimum cold utility needed when a steam cycle has been integrated. The cold utility is needed to fully be able to condensate the LP steam so that the pressure of the water used in the steam cycle can be increased using a pump.

From Figure 4-6 it is possible to see that one can gain in amount of electricity produced from integrating all the processes from biomass to olefins, instead of just integrating the processes from biomass to methanol and having a stand-alone MTO. If needed, one would also gain heat at a temperature of 46°C, associated with the condensation of the LP steam when integrating all the processes. These results is due to that better integration opportunities arises when integrating all the processes from biomass to olefins, low temperature heat within the biomass to methanol processes can be used within the MTO process and vice versa, instead of using high temperature heat to heat low temperature process streams.

The heat integration within the two cases, biomass to methanol and stand-alone MTO, both results in excess heat, and both processes alone can cover the process electricity demand. However, when combining the two cases in the same heat integration analysis is the potential to generate electricity higher, and electricity is always needed. This is due to that better integration possibilities arise when combining the processes.

4.2.4 MTO and steam cracker

Since the steam production from the cracker is approximately 230 t/h per 100 t/h of produced olefins, independently of raw material or product, see Section 2.3, the total amount of steam that is produced from the steam cracker is reduced by 41%. The HP steam production from the steam crackers will therefore be reduced from 250 t/h to 147.5 t/h, or 195 MW to 115 MW, see Section 2.3.

The total production of olefins, when integrating the reduced steam cracker plant and the MTO process in the two cases, high ethylene and high propylene, can be seen in Table 4-3.

Table 4-3 Resulting olefin production associated with partial replacement of the steam cracker with the MTO process, and the olefins production at the existing plant.

Olefin	**High ethylene case and reduced steam cracker[kt/y]**	**High propylene case and reduced steam cracker [kt/y]**	**Existing steam cracker [kt/y]**
Ethylene	640	577	640
Propylene	205	257	200
Butylene	81	81	90
Total	**926**	**915**	**930**

This section presents results for the heat integration between the MTO process, two cases, and the available hot streams at Borealis, Table 8-24 in Appendix C.

Heat integration between the two processes has been made with the incentive to, as much as possible, utilize low temperature heat where it is possible, and to get as much excess heat at high temperature as possible to be able to produce as much HP steam as possible. This has been made with the incentive to make-up for the reduced steam production when reducing the steam cracker capacity.

4.2.4.1 High ethylene case

The available hot streams at Borealis can be seen in Table 8-24 in Appendix C. However as can be seen in Table 8-24 in Appendix C and in Figure 4-7 is a lot of the heat available at Borealis at much lower temperatures than is needed in the MTO process, high ethylene case.

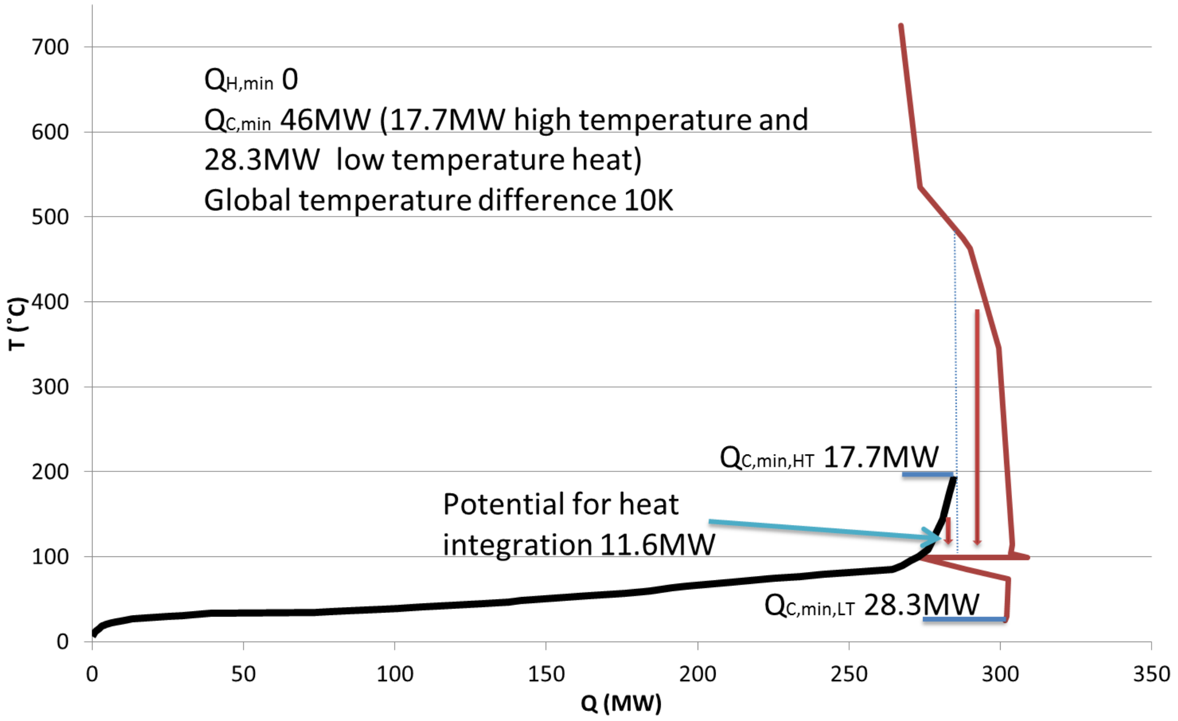


Figure 4-7 Background/Foreground analysis of the MTO process (red), high ethylene case, and the hot streams available at Borealis (black).

From the background/foreground analysis shown in Figure 4-7, the potential for heat integration between the available hot streams at Borealis and the MTO process is approximately 11.6 MW, assuming a minimum temperature difference of 10 K. If 11.6 MW of heat are recovered from the hot streams available at Borealis, the resulting minimum required cold utility for the processes (excluding hot streams from Borealis) is 46 MW, where 17.7 MW is high temperature heat that can be utilized for HP steam production, and 28.3 MW is low temperature heat which cannot be utilized for steam production.

4.2.4.2 High propylene case

The available hot streams at Borealis can be seen in Table 8-24 in Appendix C. However as can be seen in Table 8-24 in Appendix C, and in Figure 4-8, a lot of the heat is available at much lower temperatures than is needed in the MTO process, high propylene case.

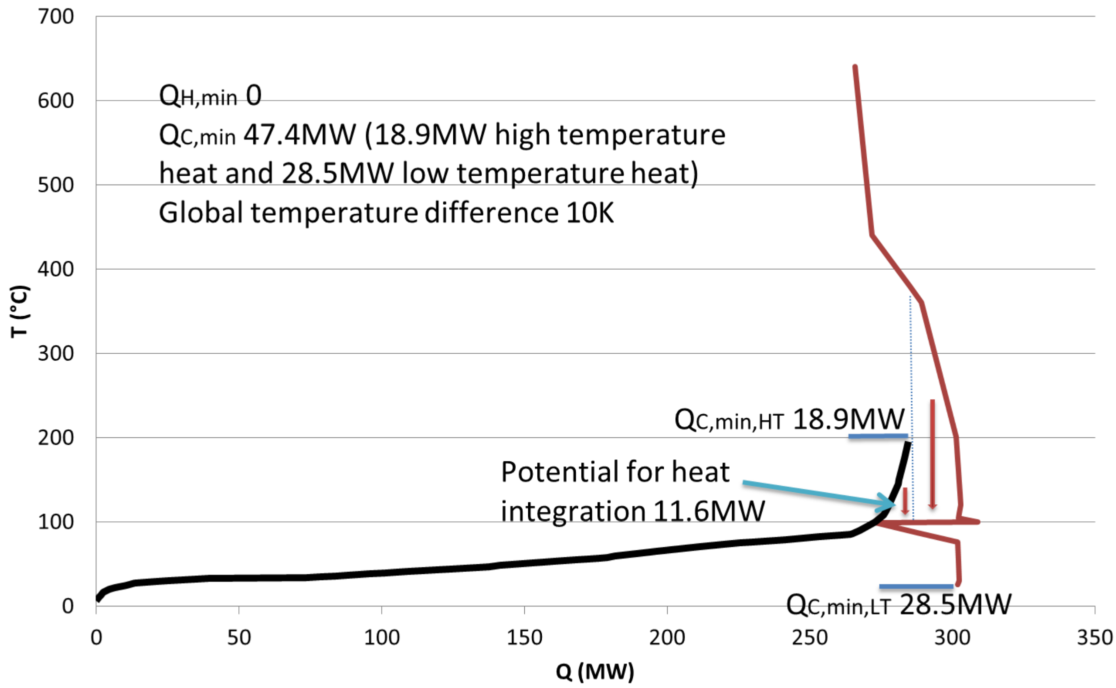


Figure 4-8 Background/Foreground analysis of the MTO process (red), high propylene case, and the hot streams available at Borealis (black).

From the background/foreground analysis shown in Figure 4-8, the potential for heat integration between the available hot streams at Borealis and the MTO process is approximately 11.6 MW, assuming a minimum temperature difference of 10 K. If 11.6 MW of heat are recovered from the hot streams available at Borealis, the resulting minimum required cold utility for the processes (excluding hot streams from Borealis) is 47.4 MW, where 18.9 MW is high temperature heat that can be utilized for HP steam production, and 28.5 MW is low temperature heat which cannot be utilized for steam production.

4.2.4.3 Change in operating parameters in the MTO process to enable better possibilities for heat integration

Since there is much heat available at low temperatures within the MTO process, and from the cracker, as can be seen in for example Figure 4-8, it could be possible to evaporate the methanol in the MTO process at atmospheric pressure, and thereby at lower temperatures. Using this setup, one would first heat the methanol to the boiling point, evaporate the methanol, increase the pressure with a compressor, and then superheat the methanol. However using a compressor instead of a pump both affects the power needed to increase the pressure and the equipment cost where a compressor is much more expensive than a pump.

The GCC for the high ethylene case when evaporating the methanol feed at atmospheric pressure can be seen in Figure 4-9. Using this setup increases the possibility for heat integration within the MTO process and thereby also increases the excess heat at high temperatures from 6 MW to 37.8 MW, an increase of 31.8 MW, in the high ethylene case, which can be used for HP steam production. However, the pump utilized when increasing the pressure of the methanol prior to evaporation approximately demands

0.014 MW of electricity, and when using a compressor to increase the pressure after evaporation, approximately demands 4.75 MW electricity, an increase of 4.74 MW. If approximating that electricity cost three times as much as HP steam, the required increase of steam production to cover the increased electricity demand has to be three times as large. The COP for using the compressor instead of a pump is in the high ethylene case 6.7, which means that you get 6.7 times as much heat as the required electricity demand from using a compressor.

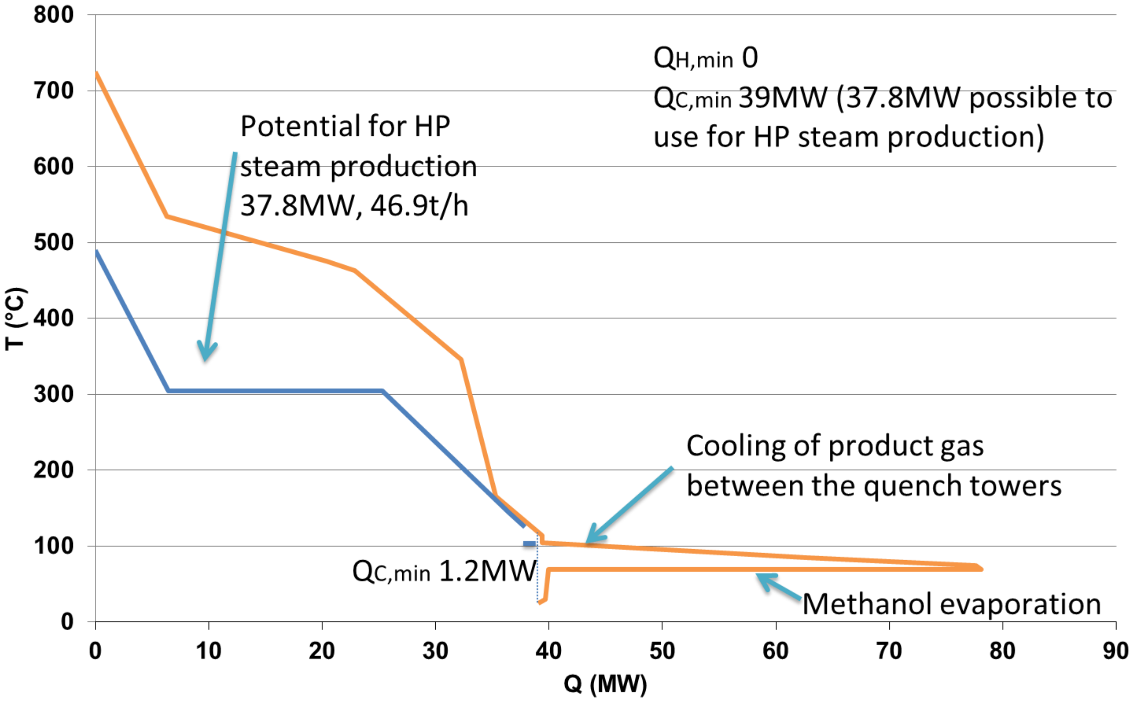


Figure 4-9 Background/Foreground analysis of the MTO process, high ethylene case, evaporation of the methanol at atmospheric pressure (orange), and the potential for excess HP steam production from high temperature heat (blue).

Doing the same analysis for the high propylene case, seen in Figure 4-10, the resulting excess heat at high temperatures increases from 7.3 MW to 38.7 MW, an increase of 31.4 MW that can be used for HP steam production. This corresponds to a COP of 6.6.

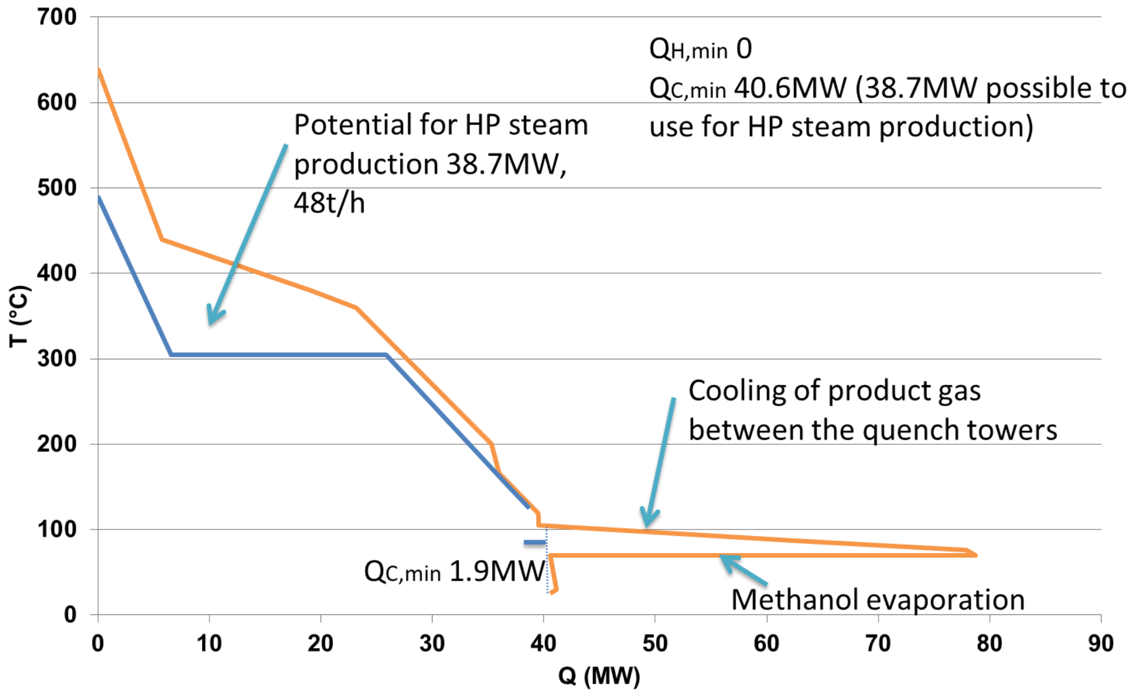


Figure 4-10 Background/Foreground analysis of the MTO process, high propylene case, evaporation of the methanol at atmospheric pressure (orange), and the potential for excess HP steam production from high temperature heat (blue).

Since all heat needed within the MTO process when evaporating the methanol at low temperatures can be covered with low temperature heat within the MTO process, the incentive to integrate this setup with the steam cracker is small, except delivering high temperature heat that can be used for HP steam production. Most of the heat available at low temperatures within the MTO process, and most suitable to use for the evaporation of the methanol is the cooling of the reactor product between the quench towers in the MTO process, which also is a partial condensation. However, since there are often technical considerations regarding which setup is the most appropriate one, different heat integration possibilities should be further examined.

An example of streams that could be utilized from the steam cracker plant to prepare the methanol (evaporation at atmospheric pressure) is streams no.10 to 16 in Table 8-24, which are the top of primary fractionators. A background/foreground analysis of this setup can be seen in Figure 4-11.

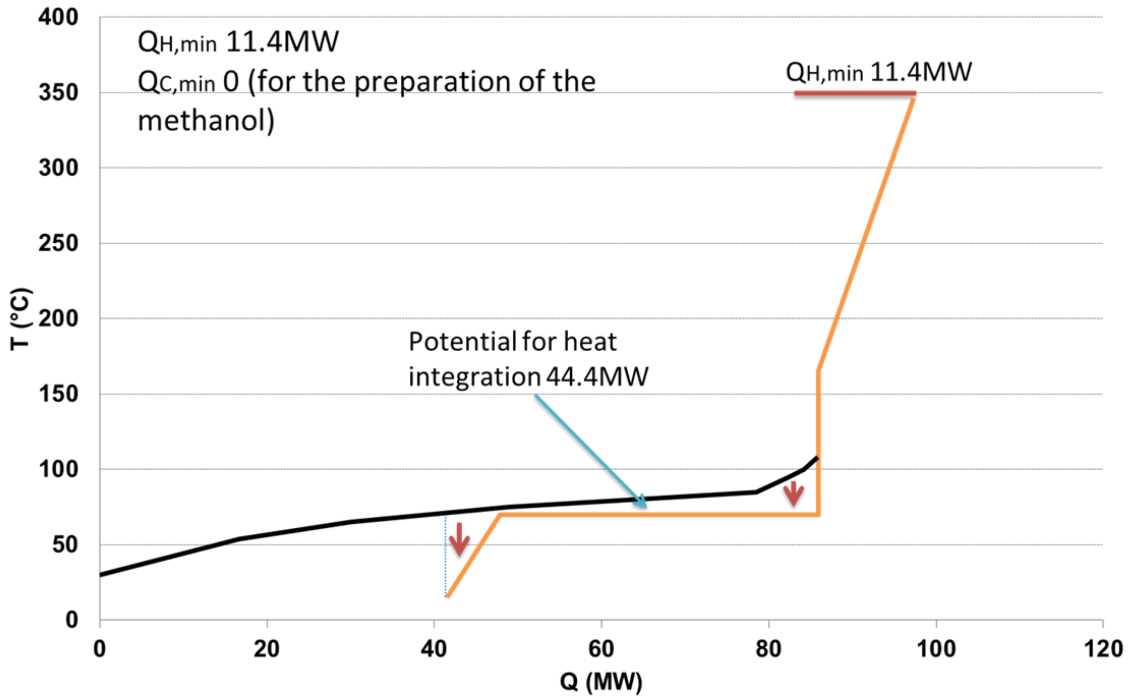


Figure 4-11 Background/Foreground analysis of the preparation of the methanol in the MTO process (orange), evaporation at atmospheric pressure, and 7 streams from the steam cracker plant (black).

In Figure 4-11 it is possible to see that the streams are possible to utilize for the preheating and evaporation of the methanol at atmospheric pressure. However, no streams are available at the steam cracker plant that could be utilized for the superheating of the methanol.

4.2.4.4 Concluding discussion

Comparing the two cases, high ethylene and high propylene, with respect to the potential for heat integration with the steam cracker, it is hard to observe any difference. This is because the processes are almost identical with respect to heat excess and deficits at low temperatures. The main contributing source to heat deficit is the evaporation of methanol, which is identical for the two cases. As can be seen in Figure 4-7 and Figure 4-8, the potential for heat integration is moderate, it would have been more advantageous to be able to integrate more, so that more of the high temperature heat from the MTO process could have been used to produce steam.

One result from a total site analysis made by Hackl et al., (2011), was that site-wide heat integration resulted in excess of LP steam at some of the chemical plants included in the analysis. If it would be possible to utilize this LP steam produced at other chemical plants for the preparation of the methanol in the MTO process, instead of evaporating the methanol at atmospheric pressures, it would be possible to produce more HP steam from the MTO process compared to the original stand-alone MTO case, currently utilized for part of the evaporation and the superheating of the methanol. Compared to when the methanol is evaporated at atmospheric pressures, the demand for electricity is reduced. This would have a great impact on the steam balance of the Borealis plant when the cracker capacity has been reduced.

4.2.5 Biomass to Olefins and steam cracker

In this section will results be presented from the pinch analysis when combining all the processes from biomass to olefins and the steam cracker.

4.2.5.1 Highe ethylene case

A background/foreground analysis was made with the objective of quantifying the change in the maximum potential for steam production from high temperature excess heat when utilizing heat from the available hot streams at Borealis, Table 8-24, in the processes from biomass to olefins. The result from the background/foreground analysis can be seen in Figure 4-12. The potential for heat integration between the biomass to olefins processes GCC and the available hot streams at Borealis can be seen in Figure 4-12, and is approximately 21.7 MW.

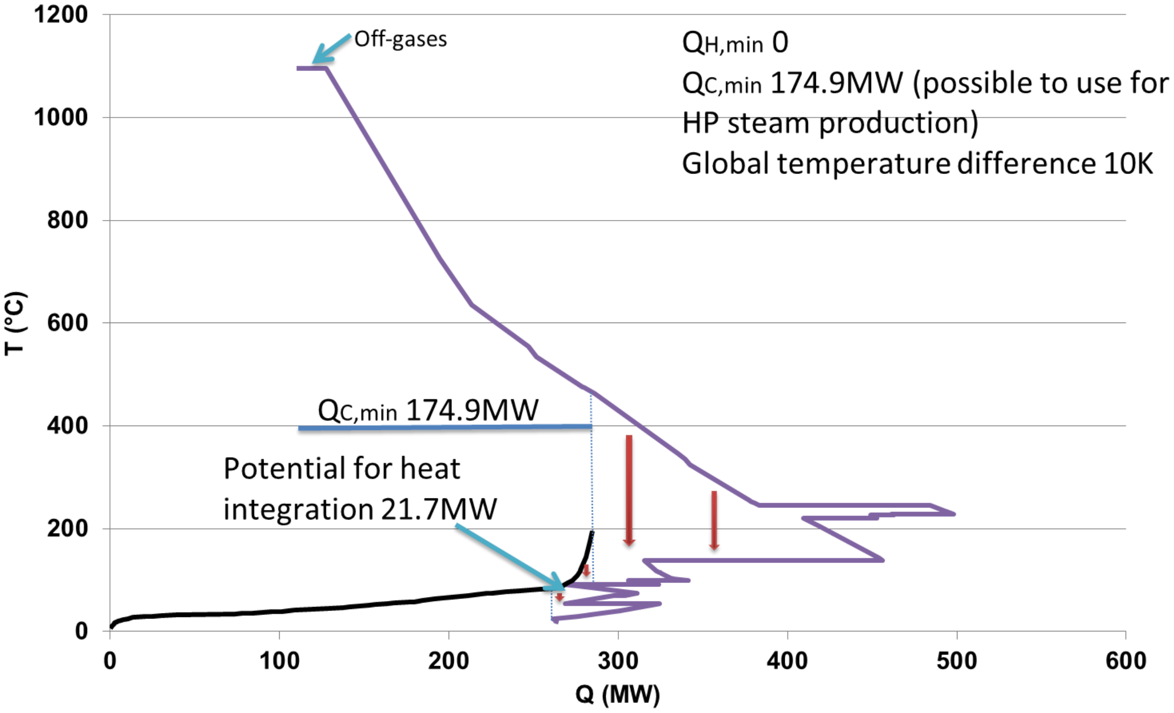


Figure 4-12 Background/Foreground analysis using the Biomass to olefins processes, high ethylene case (purple) and the available hot streams at Borealis, Table 8-24 (black).

From the background/foreground analysis, Figure 4-12, it is possible to see the resulting high temperature excess heat after integration with the steam cracker, which also can be used for the production of HP steam, and is approximately 174.9 MW, when including the off-gases from the methanol synthesis, 17. 7MW. The total process electricity demand for the biomass to olefins processes is 37.2 MW.

4.2.5.2 High propylene case

Doing the same analysis in the high propylene case as in the high ethylene case, i.e. analyzing the maximum potential for steam production, or the high temperature excess heat, from the heat integration with Borealis, Table 8-24, in the processes from biomass to olefins, see Figure 4-13, the maximum potential for heat integration is approximately

22.3 MW. The resulting high temperature excess heat, with the potential for steam production, is approximately 176.9 MW, including the potential for steam production from off-gases. The difference between the two cases is small, which is due to that the biomass to methanol processes is the larger part of the GCC, and the only difference between the two cases is the MTO process.

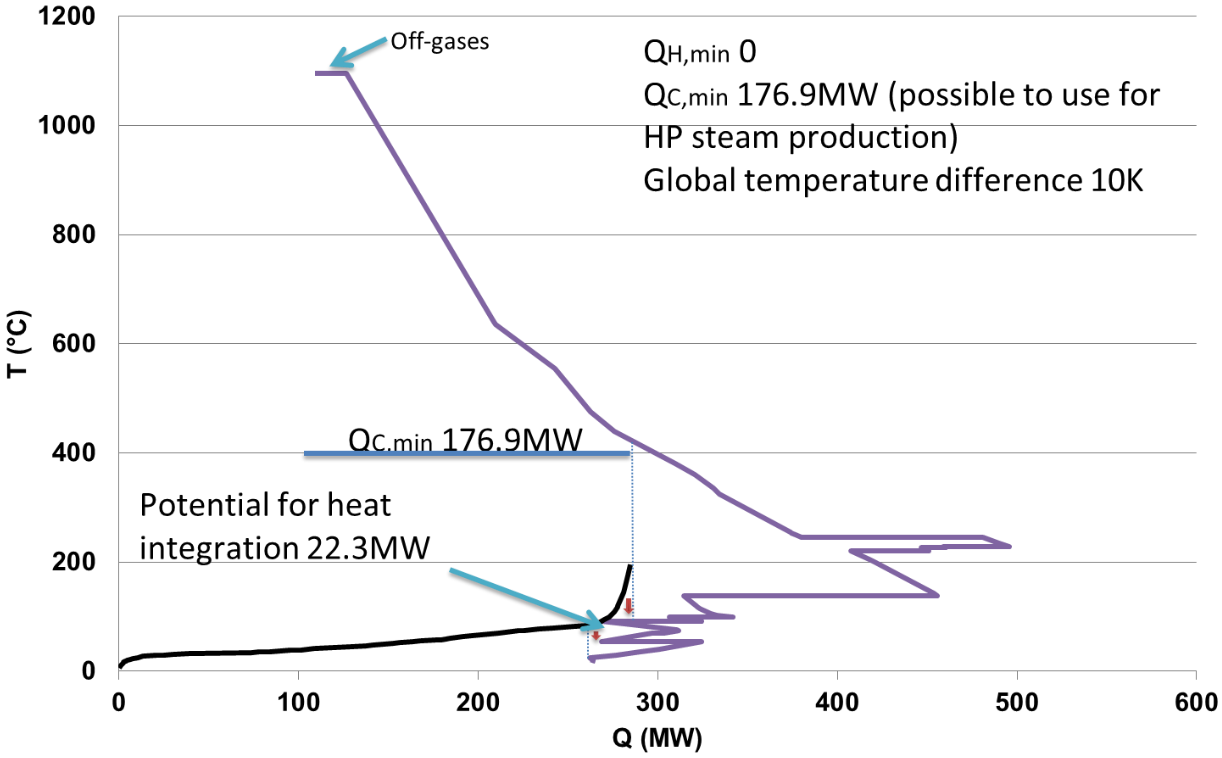


Figure 4-13 Background/Foreground analysis using the Biomass to olefins processes, high propylene case (purple) and the available hot streams at Borealis, Table 8-24 (black).

4.2.5.3 Concluding discussion

Integration between the biomass to olefins processes and the steam cracker results in an increase of the resulting available excess heat at high temperatures. However, most of the heat available in the different streams cannot be used in the biomass to methanol processes and the MTO process, which is due to the heat that is needed at those temperature levels in the processes are also available in the processes.

Referring to the fact that site-wide heat integration often results in excess of LP steam production (Hackl, et al., 2011), it might be possible to utilize LP steam to heat parts of the processes and instead use the high temperature heat to produce more HP steam.

4.3 Concluding discussion

Figure 4-14 presents an overview of the resulting high temperature excess heat that can be used for HP steam production that is available after heat integration with the steam cracker, as well as the process electricity demand.

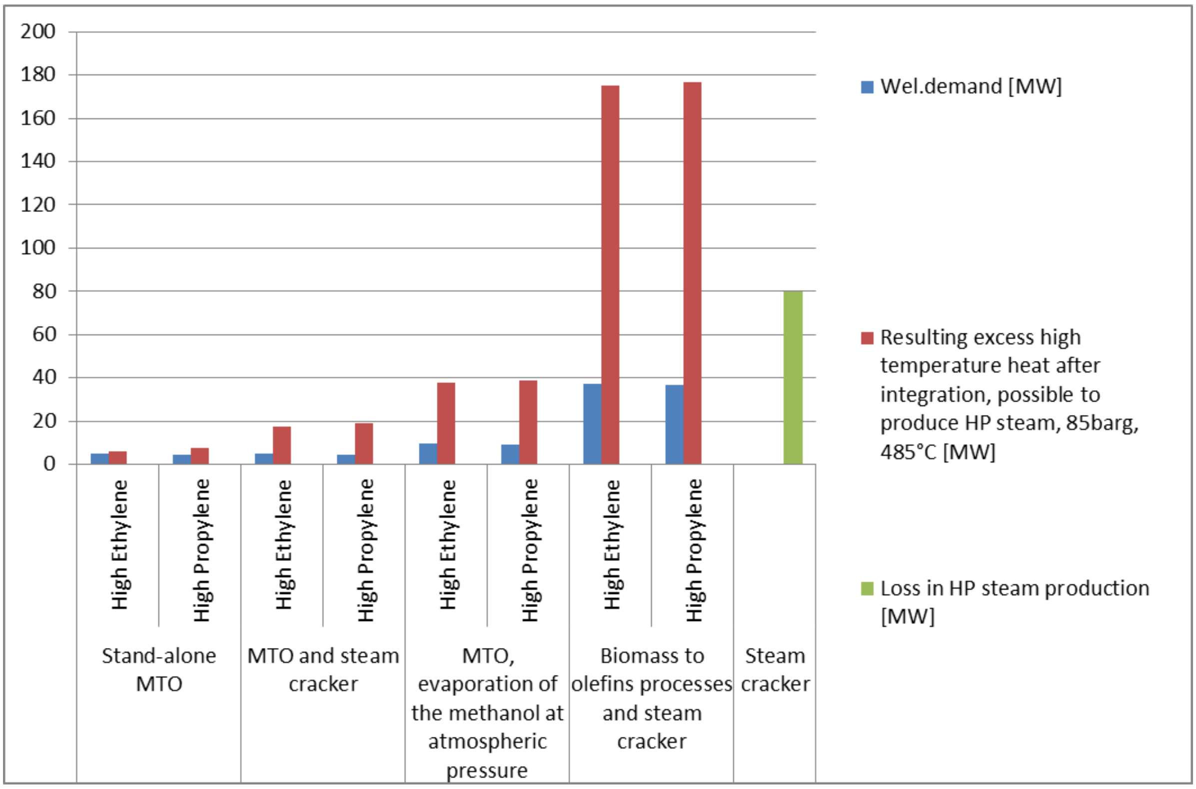


Figure 4-14 Summary of results obtained from integration with the steam cracker, MTO and steam cracker and biomass to olefins processes and the steam cracker.

As shown in Figure 4-14, the resulting available excess heat from the biomass to olefins processes integrated with the steam cracker can cover the loss in HP steam production from the steam cracker. Thus, if a biomass to olefins process were to be located close to the steam cracker plant, the processes could both cover the heat demand of the plant, the electricity demand within the processes, and also deliver HP steam to other chemical plants located in Stenungsund. It would also be possible to produce additional electricity.

In Figure 4-14 is it also possible to see that neither the stand-alone MTO, nor the MTO process integrated with the steam cracker nor the MTO process where the methanol is evaporated at atmospheric pressure can cover the loss in HP steam production from the steam crackers. In the case where the methanol is evaporated at atmospheric pressure, the process can almost cover half of the loss when the steam cracker is reduced, however to remember is also that the process electricity demand is increased in this case, compared to the MTO and steam cracker case, and has therefore to be covered. The COP for the increased production of HP steam compared to work input is however approximately 6.7 in both cases, and thereby would it be supportable to implement this setup. To cover the demand from the processes at the cracker plant it is however possible to produce more HP steam in the boiler available at the plant, with the maximum capacity of 80 MW. Since the boiler currently runs at a minimum capacity of 30.3 MW, it is not possible to cover the entire loss of HP steam production from the steam crackers, 80 MW. The potential for an increased steam production from the boiler is 50 MW, so it would not be possible to cover the loss in HP steam production with the MTO process integrated with the steam cracker, due to that the total sum would be approximately 20 MW plus 50 MW minus work in the form of electricity. It could be possible to cover the loss with the MTO process where the methanol is evaporated at atmospheric pressure, the total sum would approximately be 40 MW plus 50 MW minus work in the form of electricity. If just integrating the MTO process with the steam cracker, it is not possible to cover the loss in HP steam production from the steam cracker.

Since the case where the methanol is evaporated at atmospheric pressure together with the existing boiler at the plant have the possibility to cover loss in HP steam production, this might be a setup worth to consider.

To be noticed is that when doing the analysis a few assumptions were made. One assumption was made regarding the effects when reducing the steam cracker plant capacity and replacing it with the MTO process. This assumption was that all other processes at the plant was unchanged, the process demand for steam, which is likely not the case when for example another feed composition of olefins will be sent to the separation processes than what is done today. This will have an effect on the demand for steam from the processes at the plant, and thereby affect the need for steam production. The fuel gases normally generated from the steam crackers (used for production of steam and used to deliver heat to the endothermic cracking process) will be reduced when the capacity of the steam cracker is reduced, which will have an effect of the energy balance at the plant. Another change in demand that will occur when reducing the steam cracker plant capacity is the dilution steam used in the steam cracking process, which also will have an effect on the overall energy balance at the plant.

Another assumption was made regarding the MTO process, which was that the feed to the MTO reactor only consisted of methanol. Since it is possible, and sometimes advantageous to also have e.g. water in the feed, additional heat compared to a pure methanol feed would be required to also preheat, evaporate and superheat the water in the feed. Additional water in the feed would also have had an effect on downstream processes. Since the water content in the feed for the different found yields was unknown, and given that water in the feed would affect the outcome of the reaction, this could not be investigated. However, if a biomass to methanol process were to be located close to the MTO process, it would not be necessary to separate the methanol from the water produced in the methanol synthesis process. This would be advantageous in an energy perspective since the energy consuming separation towers could be skipped.

5 Conclusion

For the wet biomass to methanol process, the results shown in Figure 4-6 show that it is possible to heat all process streams that require heating by recovering excess heat within the process. Furthermore, the process has a net excess of heat which can be used to supply heat a steam cycle which can produce the electricity needed to cover the process electricity demand. The resulting net electricity production is positive, and it is therefore possible to utilize this electricity where it is needed or sell it. One result from the integration of a steam cycle is that low temperature excess heat will be produced from the condensation of LP steam within the steam cycle, which is possible to utilize somewhere else if needed.

For the stand-alone MTO case, Figure 4-6, similar conclusions can be drawn, i.e. heat recovery from hot streams is sufficient to heat the process cold streams. However, in such a case high temperature heat is used to heat low temperature streams. When integrating a steam cycle with the MTO process, the resulting net production of electricity is positive. However, the downstream gas cleaning processes have been included in the stand-alone MTO case, and it is therefore not possible to draw conclusions regarding the heat and electricity balances of a complete stand-alone MTO process.

Combining the processes, the biomass to olefins case, results in the potential to produce more electricity and excess low temperature heat, than the sum of the two cases, see Figure 4-6. What can be concluded from this is that there are synergy effects that can be achieved by performing heat integration between the two cases, even though one combines two processes with heat in excess. This is because better heat integration possibilities arise when more thermal streams at different temperatures are combined, low temperature heat within the biomass to methanol process can be used for the heating of low temperature streams within the MTO process, and vice versa.

In the case when integrating the MTO process and the steam cracker one integrates two processes with excess of heat. It is also possible to conclude that one can gain from performing this heat integration. When using the excess heat available at Borealis to heat some parts of the MTO process, is it possible to liberate high temperature heat generated within the MTO process that can be used to produce HP steam to cover the losses at the steam cracker plant, see Figure 4-14. However, as can be seen in Figure 4-14, this setup cannot cover the losses of HP steam from the crackers when reducing the capacity, it would not even be possible to cover the losses if the boiler was run at maximum capacity.

It should also be noted that streams having a temperature above 120˚C (starting temperature for the production of steam) in the MTO process only contain 51 MW of heat, which cannot cover the losses at the cracker plant, approximately 80 MW. However, as can be seen in Figure 4-14, it is possible to release more high temperature excess heat if the methanol is evaporated at atmospheric pressure, then it would be possible to produce approximately 40 MW of excess HP steam. This corresponds to approximately half of the reduction of the steam production from the cracker furnaces. It should however be recalled that the electricity demand will be higher, reducing the potential to cover the losses in steam production from the crackers. If combining this setup with the boiler at the cracker plant at maximum capacity, it would be possible to cover the losses in steam production.

Combining all the cases, biomass to olefins and the steam cracker, the configuration with the maximum potential for steam production would have the capacity to cover the losses in steam production at the steam cracker plant, seen in Figure 4-14, where one also would have the potential to produce more electricity than done today at the steam cracker plant or export HP steam. This case results in approximately 175 MW of high temperature excess heat. If using 80 MW to cover the loss from the steam cracker plant, it would be possible to export approximately 95 MW of HP steam.

6 Future work

The product downstream separation processes for the MTO process should be added to the simulation model. This would also result in a more accurate model of a stand-alone MTO case, going from methanol to pure olefin products.

To be able to more accurately evaluate the effects of implementing a MTO process at the steam cracker plant, and thereby reducing the capacity of the steam cracker, a more extensive analysis of the different changes at the plant should be made.

A complete MTO process simulation model and a more accurate energy balance of the steam cracker plant, both before and after the MTO process has been implemented, results in that it is possible to evaluate the effects of having a MTO process integrated with the steam cracker plant versus having a stand-alone MTO process.

It would also be beneficial to create a simulation model based on kinetic expressions. This to be able to model the effect of changing operating parameters (e.g. water content, temperature and pressure) for the MTO process resulting in different product mixes.

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8 Appendix

Appendix A – Biomass to Methanol processes

Calculations of oxygen and steam flow to gasifier

Table 8-1 *BOIE correlations* (Sheng & Azevedo, 2005) *for heating value calculations*

BOIE(i)	**Btu/Ib**
1:Carbon	134.87
2:Hydrogen	301.33
3:Sulfur	13.67
4:Oxygen	13.67
5:Nitrogen	13.67
6	-587.92

For BOIE(i) see Table 8-1 and for ULT, see ULTANAL in Table 3-1 in Section 3.2.1.1.

$$HHV = (BOIE(i) * ULT(i) + BOIE(6)\ ) * 2.326 = 19555.4179\ kJ/kg$$

$$for\ i = 1 - 5$$

$$1\frac{Btu}{Ib} = 2.326\frac{kJ}{kg}$$

1% of the heating value per kg of biomass

$$Q = Biomass\ flow * HHV * 0.01 = 0.85 * 19555.4179 * 0.01 = 166.22kW$$

Resulting oxygen flow per kg of biomass (15% moisture and 2.18% ash) was 0.256033kg, which corresponds to an oxygen flow per kg of dry and ash free biomass of 0.2937 kg.

The steam flow to the gasifier was set so that the steam to oxygen ratio was 1:1, therefore was the input of steam to the gasifier was 0.2937kg per kg of dry and ash free biomass, however the biomass contained 15% moisture, so the total amount of steam in the gasifier was 0.4903kg per kg of biomass.

Table 8-2 *Possible products and inert components in the Gibbs reactor in the gasification simulation model.*

Possible products	**Inert**
C (solid)	CH_4
H_2	C_2H_4
O_2	C_2H_4
N_2	C_2H_6
S	C_3H_8
H_2O	C_6H_6
CO_2	$C_{10}H_8$
CH_4	NH_3
C_2H_4	
C_2H_6	
C_3H_8	
C_6H_6	
$C_{10}H_8$	
NH_3	
H_2S	
Cl_2	
HCl	
CO	

Comparison between the results obtained in Hannula & Kurkela (2012) (left) and the results obtained with the model used in this master thesis (right).

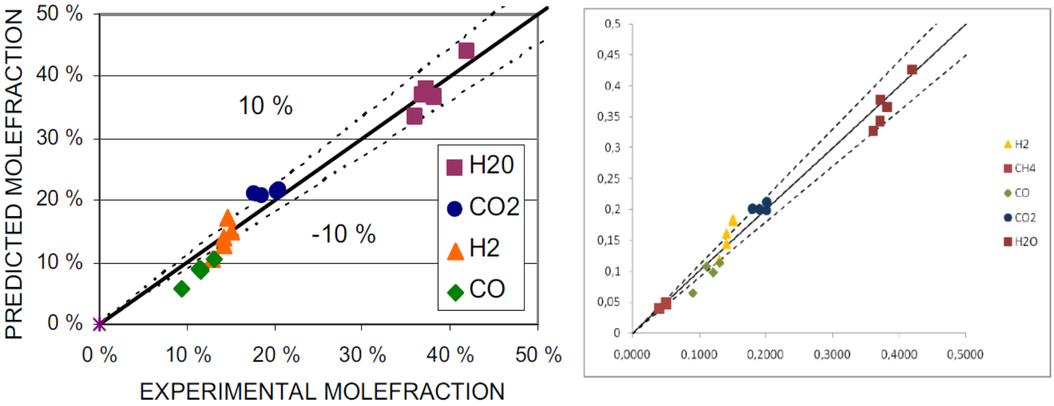

Figure 8-1 *Comparison of measured values with values predicted by the model for the main product gas components in wet gas at the gasifier outlet. Left: Hannula & Kurkela (2012). Right: gasification model used in the master thesis (Heyne, 2012).*

Equilibrium reactions used in the tar cracker

$$\mathrm{CO} + H_2\mathrm{O} \leftrightarrow \mathrm{CO_2} + \mathrm{H_2}$$

$$\mathrm{C}H_4 + H_2\mathrm{O} \leftrightarrow \mathrm{CO} + 3\mathrm{H_2}$$

$$C_2H_4 + 2H_2\mathrm{O} \leftrightarrow 2\mathrm{CO} + 4\mathrm{H_2}$$

$$C_2H_6 + 2H_2\mathrm{O} \leftrightarrow 2\mathrm{CO} + 5\mathrm{H_2}$$

$$C_2H_2 + 2H_2\mathrm{O} \leftrightarrow 2\mathrm{CO} + 3\mathrm{H_2}$$

$$C_6H_6 + 6H_2\mathrm{O} \leftrightarrow 6\mathrm{CO} + 9\mathrm{H_2}$$

$$C_{10}H_8 + 10H_2\mathrm{O} \leftrightarrow 10\mathrm{CO} + 14\mathrm{H_2}$$

$$NH_3 \leftrightarrow 0.5N_2 + 1.5\mathrm{H_2}$$

$$C_3H_8 + 23\mathrm{O} \leftrightarrow 3\mathrm{CO} + 7\mathrm{H_2}$$

Table 8-3 Assumed molar conversion in the tar cracker reactor, for reactions see above.

Component	**Molar conversion (%)**
CH_4	20
C_2H_6	90
C_2H_4	50
C_2H_2	50
C_6H_6	70
$C_{10}H_8$	95
NH_3	70
C_3H_8	90

Table 8-4 Possible products and inert components in the Gibbs reactor in the autothermal reformer simulation model.

Possible products	**Inert**
H_2	N_2
O_2	
N_2	
CO	
H_2O	
CO_2	
CH_4	
C_2H_4	
C_2H_6	
C_6H_6	
H_2S	
HCl	

Table 8-5 Gas composition after respectively process (Gasification to Water-gas-shift), based on 1kg biomass (15% moisture and 2.18% ash) to the gasifier.

	Gasification	**Tar**	**Wet gas**	**ATR**	**WGS**

		cracker	**cleaning**		
Total mole flow mole/s	64.52	72.87	55.10	66.70	84.11
Component	**mole%**	**mole%**	**mole%**	**mole%**	**mole%**
H_2	19.8	33.9	44.9	33.5	34.4
O_2	0	0	0	0	9E-11
N_2	0.2	0.2	0.2	0.2	0.2
S	2.4E-11	2.1E-11	0	0	0
H_2O	32.1	18.5	5.8	24.8	32.6
CO	16.9	20.3	26.0	30.5	16.3
CO_2	22.5	22.2	18.0	11.0	16.5
CH_4	5.7	4.0	4.4	0.05	4E-2
C_2H_2	0.04	0.02	0	0	0
C_2H_4	1.6	0.7	0.5	9E-9	7E-7
C_2H_6	0.4	0.04	0.02	2E-9	1E-7
C_3H_8	0.02	0.002	0	0	0
C_6H_6	0.4	0.09	0.1	2E-20	1E-18
$C_{10}H_8$	0.4	0.02	0	0	0
NH_3	0.05	0.01	0	0	0
H_2S	0.02	0.01	1E-4	8E-7	6E-5
Cl_2	0	0	0	0	0
HCl	0.005	0.005	0	0	0

Table 8-6 Mass balance for the commercial-scale demonstration unit of the LPMEOH^{TM} process (Air Products and Chemicals, Inc, 1998) and simulations of the commercial-scale demonstration unit of the LPMEOH^{TM} process with a temperature approach of 27K.

	Commercial-scale demonstration unit of the LPMEOH^{TM} process		**Simulation of the commercial-scale demonstration unit of the LPMEOH^{TM} process, Temperature approach 27K**	
Component	Reactor feed	Reactor product, mole flow	Reactor feed	Reactor product, mole flow
H_2	4828	2516	4852	2581
CO	9686	7882	9566	7775
CO_2	3681	3936	3775	4212
H_2O	464	14	465	28
N_2	250	250	246	246
CH_3OH	89	1441	104	1458

Table 8-7 Gas composition before and after the methanol synthesis reactor, based on 1kg biomass (15% moisture and 2.18% ash) to the gasifier.

	Before reactor		**After reactor**		
Component	**Mole flow mole/s**	**Mole%**	**Mole flow mole/s**	**Mole%**	**Conversion once through %**
H_2	70.5818	60.52	42.2597	47.67	40.13
O_2	5.71E-9	4.9E-9	5.71E-9	6.45E-9	
N_2	12.7745	10.95	12.7745	14.41	
H_2O	0.3028	0.26	0.6464	7.29E-1	
CO	22.6443	19.42	8.9987	10.15	60.26
CO_2	7.4308	6.37	7.0900	7.99	
CH_4	2.0794	1.78	2.0800	2.35	
C_2H_4	1.67E-5	1.43E-5	1.67E-5	1.88E-5	
C_2H_6	3.13E-6	2.68E-6	3.13E-6	3.53E-6	

Figures of the simulation models for some of the processes from biomass to methanol

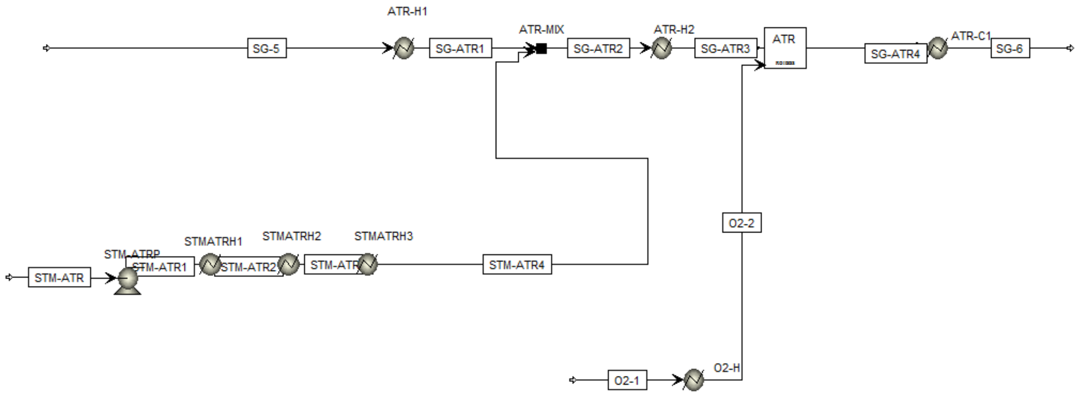

Figure 8-2 Figure of the simulation model for the ATR process.

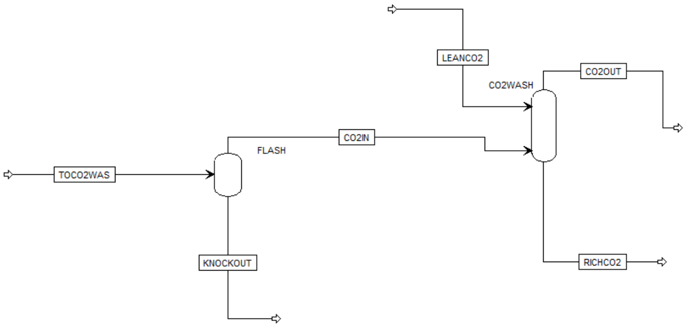

Figure 8-3 Figure of the simulation model for the CO_2 absorption process including flash out of water.

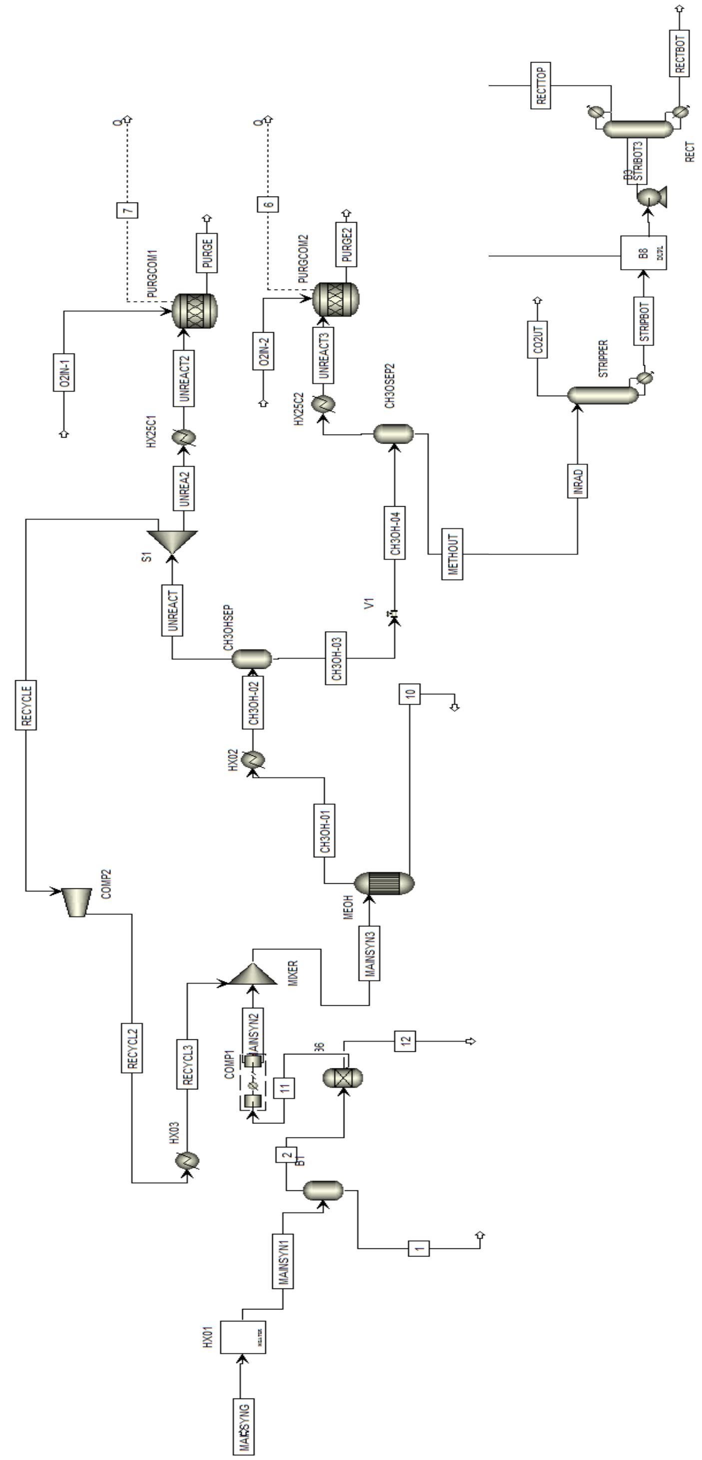

Figure 8-4 Figure of the simulation model for the methanol synthesis process, including flash out of water and separation of CO_2.

Appendix B – Methanol to Olefins

Table 8-8 Components present in the MTO simulation model.

Type	Name	Chemical formula
Conventional	Methanol	CH_3OH
Conventional	Water	H_2O
Conventional	Hydrogen	H2
Conventional	Ethylene	C_2H_4
Conventional	Propylene	C_3H_6
Conventional	1-Butene	C_4H_8
Conventional	1-Pentene	C_5H_{10}
Conventional	Methane	CH_4
Conventional	Ethane	C_2H_6
Conventional	Propane	C_3H_8
Conventional	Carbon-monoxide	CO
Conventional	Carbon-dioxide	CO_2
Conventional	Nitrogen	N_2
Conventional	Oxygen	O_2
Non-conventional	Coke	$CH_{0.8}$
Solid	Aluminum	Al

Table 8-9 Mass yields for the High ethylene case, based on Table 2-2 and Table 2-1.

Component	Mass yield
Ethylene	0.21450
Propylene	0.14008
Butylene	0.04378
Pentene	0.00876
Methane	0.01312
Ethane	0.00236
Propane	0.00173
Water	0.55817
Carbon-monoxide	0.00240
Carbon-dioxide	0.00309
Coke	0.01200
Hydrogen	0.00002
Total	1

Table 8-10 Mass yields for the High propylene case, based on Table 2-2 and Table 2-1.

Component	Mass yield
Ethylene	0.14727

Propylene	0.19578
Butylene	0.05048
Pentene	0.01871
Methane	0.00742
Ethane	0.00416
Propane	0.00267
Water	0.55950
Carbon-monoxide	0.00238
Carbon-dioxide	0.00148
Coke	0.01000
Hydrogen	0.00016
Total	1

Table 8-11 Material and temperature balance for the MTO reactor in the High ethylene case.

	Reactor feed kg/h, ˚C	**Reactor product kg/h, ˚C**	**Catalyst material stream kg/h, ˚C**
Methanol	116600.631		
Ethylene		25011.0007	
Propylene		16333.7155	
Butylene		5104.2849	
Pentene		1020.8572	
Methane		1529.6231	
Ethane		275.0609	
Propane		201.6853	
Water		65082.5071	
Carbon-monoxide		280.3429	
Carbon-dioxide		360.2796	
Coke		1399.2403	
Hydrogen		2.0334	
Catalyst material to reactor			544138.47
Temperature	341	540	469

Table 8-12 Material and temperature balance for the MTO reactor in the High propylene case.

	Reactor feed kg/h, ˚C	**Reactor product kg/h, ˚C**	**Catalyst material stream kg/h, ˚C**
Methanol	116600.631		
Ethylene		17171.5894	
Propylene		22828.5699	
Butylene		5885.4237	
Pentene		2181.0688	

Methane		865.5035	
Ethane		484.6820	
Propane		311.5813	
Water		65237.9231	
Carbon-monoxide		276.9610	
Carbon-dioxide		173.1010	
Coke		1166.0340	
Hydrogen		18.1932	
Catalyst material to reactor			544138.47
Temperature	195	445	366

Calculation of catalyst material fed to the regenerator

High ethylene case

Coke production, see Table 8-11: 1399.2403 kg/h

Average level of coke deposited on the catalyst particle: 4.5wt% of the catalyst particle weight.

Weight of catalyst fed to the regenerator:

$$\frac{1399.2403}{0{,}045} = 31\ 094.23\ kg/h$$

Catalyst weight relative to the methanol feed:

Methanol feed, see Table 8-11: 116 600.631 kg/h

$$\frac{31\ 094.23}{116\ 600.631} = 0.2667$$

Weight of catalyst particles going to regeneration relative to the amount of catalyst particles that are cooled and recycled back to the reactor:

$$\frac{31\ 094.23}{544\ 138.47 - 31\ 094.23} = 0.0606 = 6.06\%$$

High propylene case

Coke production, see Table 8-11: 1166.0340 kg/h

Average level of coke deposited on the catalyst particle: 4.5wt% of the catalyst particle weight.

Weight of catalyst fed to the regenerator:

$$\frac{1166.0340}{0{,}045} = 25\ 911.87\ kg/h$$

Catalyst weight relative to the methanol feed:

Methanol feed, see Table 8-11: 116 600.631 kg/h

$$\frac{25\ 911.87}{116\ 600.631} = 0.2222$$

Weight of catalyst particles going to regeneration relative to the amount of catalyst particles that are cooled and recycled back to the reactor:

$$\frac{25\ 911.87}{544\ 138.47 - 25\ 911.87} = 0.05 = 5.00\%$$

Catalyst weight recirculated without regeneration

High ethylene case

$$544\ 138.47 - 31\ 094.23 = 513\ 044.24 kg/h$$

High propylene case

$$544\ 138.47 - 25\ 911.87 = 518\ 226.60\ kg/h$$

Specifications for the quench towers

High ethylene case

Reactor effluent, prior to first quench tower:

Mass flow: 115 201.391 kg/h

Temperature: 540˚ to 119˚

Heat duty: -30.38 MW

First quench tower:

Number of stages: 3

Top stage pressure: 2 bar

Water, first quench tower:

Mass flow: $0.47 * 115\ 201.391 = 54\ 144.654\ kg/h$

Temperature: 81˚C

Reactor effluent, prior to second quench tower:

Mass flow: 113 235.736 kg/h

Temperature: 110˚ to 79˚

Heat duty: -37.00 MW

Second quench tower:

Number of stage: 6

Top stage pressure: 1.5bar

Water, second quench tower:

*Mass flow: 117 276.*97 kg/h

Temperature: 35˚C

Quench tower bottom outlet:

Mass flow: 178 540.458 kg/h

Mass flow recycled to quench tower 1: ~54 144.654 kg/h

Temperature: 90˚C to 35 ˚C

Heat duty: -5.97 MW

Quench tower top outlet:

Mass flow: 51 972.547 kg/h

Temperature: 45.5˚C

High propylene case

Reactor effluent, prior to first quench tower:

Mass flow: 115 434.597 kg/h

Temperature: 445˚ to 125˚

Heat duty: -22.51 MW

First quench tower:

Number of stages: 3

Top stage pressure: 2 bar

Water, first quench tower:

Mass flow: $0.47 * 115\,434.597 = 54\,254.2606\ kg/h$

Temperature: 77˚C

Reactor effluent, prior to second quench tower:

Mass flow: 113 463.437 kg/h

Temperature: 110˚ to 81˚

Heat duty: -37.00 MW

Second quench tower:

Number of stages: 6

Top stage pressure: 1.5bar

Water, second quench tower:

Mass flow: 112 463.51 kg/h

Temperature: 35˚C

Quench tower bottom outlet:

Mass flow: 173 881.204 kg/h

Mass flow recycled to quench tower 1: ~54 254.26 kg/h

Temperature: 92˚C to 35 ˚C

Heat duty: -7.37 MW

Quench tower top outlet:

Mass flow: 52 045.744 kg/h

Temperature: 47˚C

Product composition after the quench towers

Table 8-13 Product gas composition after reactor and after the quench tower, high ethylene case.

	Reactor feed kg/h	**Reactor product kg/h**	**Left after quenching kg/h**
Methanol	116600.631		
Ethylene		25011.0007	24969.28
Propylene		16333.7155	16302.41
Butylene		5104.2849	5089.625
Pentene		1020.8572	1015.703
Methane		1529.6231	1528.307
Ethane		275.0609	274.6943
Propane		201.6853	201.332
Water		65082.5071	1952.42
Carbon-monoxide		280.3429	279.26
Carbon-dioxide		360.2796	357.0643
Coke		1399.2403	0
Hydrogen		2.0334	2.025

Table 8-14 Product gas composition after reactor and after the quench tower, high propylene case.

	Reactor feed kg/h	**Reactor product kg/h**	**Left after quenching kg/h**
Methanol	116600.631		
Ethylene		17171.5894	17142.00
Propylene		22828.5699	22783.52
Butylene		5885.4237	5868.062
Pentene		2181.0688	2169.793
Methane		865.5035	864.732
Ethane		484.6820	484.017
Propane		311.5813	311.021
Water		65237.9231	1957.101
Carbon-monoxide		276.9610	275.8563
Carbon-dioxide		173.1010	171.5297
Coke		1166.0340	0
Hydrogen		18.1932	18.1178

Appendix C – Process stream data from simulation models

Stream data for the processes from biomass to methanol

Table 8-15 Stream data for the drying process from simulation model.

T_{Start} ˚C	T_{Target} ˚C	Duty kW	Hot/Cold	Specification
19.8	70.0	155 913.53	Cold	Air heating

Table 8-16 Stream data for the gasification process from simulation model.

T_{Start} ˚C	T_{Target} ˚C	Duty kW	Hot/Cold	Specification
-	-	153.402	-	Pump
16.1	223.3	19 723.47	Cold	Water up to bp
223.3	223.3	36 593.20	Cold	Water evaporation
223.3	228.3	211.00	Cold	Steam superheating
15	200	3 378.40	Cold	Oxygen heating

Table 8-17 Stream data for the wet gas cleaning processes from simulation model.

T_{Start} ˚C	T_{Target} ˚C	Duty kW	Hot/Cold	Specification
639.9	148.2	99 083.00	Hot	Syngas cooling
108.0	25.0	48 425.00	Hot	Scrubb water cooling

Table 8-18 Stream data for the ATR process from simulation model.

T_{Start} ˚C	T_{Target} ˚C	Duty kW	Hot/Cold	Specification
108.2	250	19 488.6	Cold	Syngas heating
-	-	66.00	-	Pump
16.6	221.3	6 916.6	Cold	Water to bp
221.3	221.3	13 680.9	Cold	Evaporation of water
221.3	250	474.23	Cold	Superheat of steam
248.7	550	48 322.7	Cold	Steam+syngas heating
15	200	1 868	Cold	Oxygen heating
1100	330	138 924	Hot	ATR product cooling

Table 8-19 Stream data for the water-gas-shift process from simulation model.

T_{Start} °C	T_{Target} °C	Duty kW	Hot/Cold	Specification
480.9	330	18 130	Hot	Cooling of product out of reactor
-	-	157	-	Pump
11.1	215.3	22 833	Cold	Water to bp
215.3	215.3	43 560	Cold	Evaporation of water
215.3	330	6 800.6	Cold	Superheating of steam

Table 8-20 Stream data for the CO_2 absorption and methanol synthesis processe from simulation model.

T_{Start} °C	T_{Target} °C	Duty kW	Hot/Cold	Specification
330	40	146 979	Hot	Syngas cooling before CO_2 abs
133	133	140 962.8	Cold	CO_2 absorption
-	-	19 912.2	-	Multistage compressor
254.8	240	1 436.9	Hot	Compressor cooler
-	-	11 834.7	-	Recycle compressor
113	240	21 270	Cold	Recycle heating
250	250	100 977	Hot	Heat of reaction
250	45	86 807	Hot	Cooling of reactor product
		11 063		Purge 1
		11 065		Purge 2
64.84	64.84	6 181.7	Cold	Reboiler separation column 1
86.37	86.37	55 334.7	Cold	Reboiler separation column 2
58.72	58.72	55 910	Hot	Condenser separation column 2

Stream data for the processes from methanol to a mixture of olefins

Table 8-21 Stream data for the methanol to olefins process, methanol to a mixture of olefins, High ethylene case.

T_{Start} °C	T_{Target} °C	Duty kW	Hot/Cold	Specification
-	-	13.36	-	Methanol pump
20.06	94.26	8 795.38	Cold	Methanol preheating
94.26	94.26	35 693.00	Cold	Methanol evaporation
94.26	341	14 936.1	Cold	Methanol superheating
540	119.23	30 377.5	Hot	Product gas cooling after reactor
109.1	79.17	37 000	Hot	Cooling between quench towers
90.2	35	5 967.53	Hot	Cooling of quench water
540	468	9 327.18	Hot	Catalyst cooler 1, 80% eff.
730.3	480	6 293.39	Hot	Catalyst cooler 2, 80% eff.
730.3	120	4 768.17	Hot	Flue gas cooling
		5 043.44		Product gas compressor

Table 8-22 Stream data for the methanol to olefins process, methanol to a mixture of olefins, High propylene case.

T_{Start} °C	T_{Target} °C	Duty kW	Hot/Cold	Specification
		13.36		Methanol pump
20.06	94.26	8 795.38	Cold	Methanol preheating
94.26	94.26	35 693.00	Cold	Methanol evaporation
94.26	195.42	5 580.78	Cold	Methanol superheating
445	124.95	22 509.6	Hot	Product gas cooling after reactor
109.8	80.77	37 000	Hot	Cooling between quench towers
91.66	35	7 371.18	Hot	Cooling of quench water
445	365	9 944.23	Hot	Catalyst cooler 1, 80% eff.
645.2	385	5 891.03	Hot	Catalyst cooler 2, 80% eff.
645.2	120	3 135.09	Hot	Flue gas cooling
-	-	4 581.03	-	Product gas compressor

Changes to the stream data for the processes from biomass to olefins

Table 8-23 Changes of the work for increasing the pressure of the methanol, and changes of the duty for the increase of the methanol temperature when the methanol is assumed to be delivered directly from the methanol process.

T_{Start} °C	T_{Target} °C	Duty kW	Hot/Cold	Specification
		14.27		Methanol pump
87.41	94.26	855.71	Cold	Methanol preheating

Hot streams from Borealis that can be used to heat the MTO process or biomass to methanol processes

Available hot streams at the existing steam cracker plant can be seen in Table 8-24. Streams no. 1 to 41 was obtained from a pinch analysis made of the existing cracker plant. At the existing steam cracker plant is a hot stream of 300 to 150˚C, 22 410kW, available, but due to that this stream originates from the crackers that is supposed to be replaced with the MTO process, this has been excluded. Streams no. 42 to 48 originates from cooling flue gases from the crackers, and is adapted so that they approximately correspond to streams that are available when replacement of the cracker has occurred. Streams no. 42 to 48 was obtained by simulating the fuel gas put to the different crackers obtained from Petersson (2013). The temperature of the fuel gas was determined from upstream steam production. Streams no.42 to 48 starts to condense at 62˚C.

Table 8-24 Hot stream from the Borealis plant that can be utilized to heat the MTO process and the biomass to methanol processes.

Stream no.	**T_{Start} ˚C**	**T_{Target} ˚C**	**Duty kW**
1	118	21	635
2	75	50	4 582
3	90	40	838
4	65	50	2 697
5	81	18	944
6	52	45	3 150
7	51	41	3 255
8	57	22	2 306
9	63	23	2 468
10	113	105	1 701
11	105	100	1 866
12	100	90	3 876
13	90	80	29 624
14	80	70	18 785
15	70	59	13 353
16	59	35	16 670
17	89	22	12 610
18	64	25	8 550
19	82	32	8 280
20	36	11	4 539
21	56	27	1 210
22	95	81	872
23	87	79	473
24	84	79	279
25	81	27	2 964
26	95	81	796
27	87	79	449
28	84	79	265
29	81	27	2 814
30	91	16	8 320
31	50	46	2 930
32	123	28	1 010

33	68	60	330
34	43	34	3 510
35	40	32	2 910
36	44	32	21 700
37	90	39	9 000
38	39	38	30 000
39	39	27	4 000
40	53	24	1 300
41	180	30	800
42a	200	62	4 876.48
42b	62	40	8 235.2
43a	200	62	4 876.48
43b	62	40	8 235.2
44a	150	62	1793.22
44b	62	40	4776.5
45a	100	62	270.68
45b	62	40	1683.92
46a	150	62	1816
46b	62	40	4837.29
47a	150	62	926.84
47b	62	40	2468.6
48a	125	62	671.99
48b	62	40	2508.8

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