Process Design and Simulation of Propylene and Methanol Production through Direct and Indirect Biomass Gasification

by

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Abstract

As a result of increasing environmental concerns and the depletion of petroleum resources, the search for renewable alternatives is an important global topic. Methanol produced from biomass could be an important intermediate for liquid transportation fuels and value-added chemicals. In this work, the production of methanol and propylene is investigated via process simulation in Aspen Plus. Two gasification routes, namely, direct gasification and indirect gasification, are used for syngas production. The tar produced in the process is converted via catalytic steam reforming. After cleanup and treatment, the syngas is converted to methanol which will be further converted to high value olefins such as ethylene, propylene and butene via the methanol to propylene (MTP) processes. For a given feedstock type and supply/availability, we compare the economics of different conversion routes. A discounted cash flow with 10% of internet rate of return along 20 years of operation is done to calculate the minimum selling price of propylene required which is used as the main indicator of which route is more economic attractive.

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INTRODUCTION

1.1 Background

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 often threatened with depletion of them. The lack of oil affects both the energy security around the world and the availability of feedstock used in the chemical industry. One way to deal with this issue is to replace the non-renewable feedstock with biomass.

Biomass is a biological material derived from living, or recently living organisms. In the context of energy this is often related to plant based materials, however biomass can equally apply to both animal and vegetable derived material such as urban waste and corn stover [1]. It is basically carbon and a mixture of oxygen, nitrogen, hydrogen and also small quantities of other atoms such as alkali, alkaline earth and heavy metals. In addition to being renewable, biomass is considered carbon-neutral. The CO_2 produced during the consumption of biofuels can be absorbed by biomass through photosynthesis during its growth. This implies that there is no extra carbon released into the atmosphere. If the biomass is supplied sustainably, the carbon neutral cycle resolves the environmental challenges of CO_2 emissions derived from fossil fuel and their dangerous effects on the global climate.

Biomass can be converted to biofuels through various pathways. Gasification is considered one of the more promising due to high conversion and energy efficiency. This process consists of partial combustion of biomass to produce a low calorific value gas, synthesis gas or syngas, which is a combination of CO, H_2, CH_4 and CO_2 along with tar (condensable organic compounds) and other contaminants (NH_3, H_2S, etc.). The syngas can be used for power generation by combustion in power plants, upgraded to high carbon compounds (biodiesel and gasoline) through Fischer–Tropsch and methanol synthesis [2].

Methanol has been identified by most experts as the fuel of choice to replace gasoline and diesel because it costs less than other alternative fuels (when it is produced from natural gas); it is an oxygenated fuel, which burns cleaner; it has a higher octane rating, which enhances engine performance; and it is safer (methanol fires are extinguishable with water) [3]. Methanol is currently manufactured worldwide by the conversion of synthesis gas ("syngas") derived from natural gas, refinery off-gas, petroleum, or coal. However, research scientists have identified methanol from biomass as the most cost-effective, near-term, indigenous, and renewable liquid fuel alternative to replace gasoline and diesel fuel for ground transportation [4]. Furthermore methanol is a platform chemical used to produce a range of other chemicals and fuels including olefins, gasoline, dimethyl ether, methyl *tert*-butyl ether, acetic acid, and formaldehyde

Ethylene and propylene, also referred to as light olefins, are important building blocks used for producing e.g. polymers [5]. 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) [6]. 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 [7]. 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 [5].

In this master thesis, the production of methanol and olefins from biomass is investigated via process simulation in Aspen Plus. Two gasification routes, namely, direct gasification and indirect gasification, are used for syngas production. The tar produced in the process is converted via catalytic steam reforming. After cleanup and treatment, the syngas is converted to methanol which will be further converted to high value olefins such as ethylene and propylene via methanol to propylene (MTP) processes.

1.2 Aim and Scope

The aim of this master thesis is to compare two different pathways of gasification regarding the yield and economical effectiveness. The software Aspen Plus was used as a process design and simulation tool responsible for evaluating the energy and mass balance that later on will be applied to scale the process hardware. The heat integration is investigated using Aspen Energy Analyzer and the Pinch Analysis approach is used to design a heat exchanger network. It is important to utilize excess heat within the processes as efficiently as possible to minimize the need of external energy sources. Also the power integration is met by using the excess of heat mainly in the methanol synthesis and fired heat and by burning some of the light gases isolated from the hydrocarbon separation after the MTO process.

The simulation models were created by using built-in models of Aspen Plus. However, 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.

In order to validate the models and gather some important data, a feedstock of 2,000 dry metric tons per day was chosen to match that of the Aden et al. [8] Biochemical process and the Phillips et al. indirect gasification process. [9] With an expected 8,406 operating hours per year (96% operating factor) the annual feedstock requirement is 700,000 dry metric tons per year which is a small portion of the 140 million dry tons per year of forest resources potentially available.

CHAPTER 2

PROCESS DESIGN AND DESCRIPTION

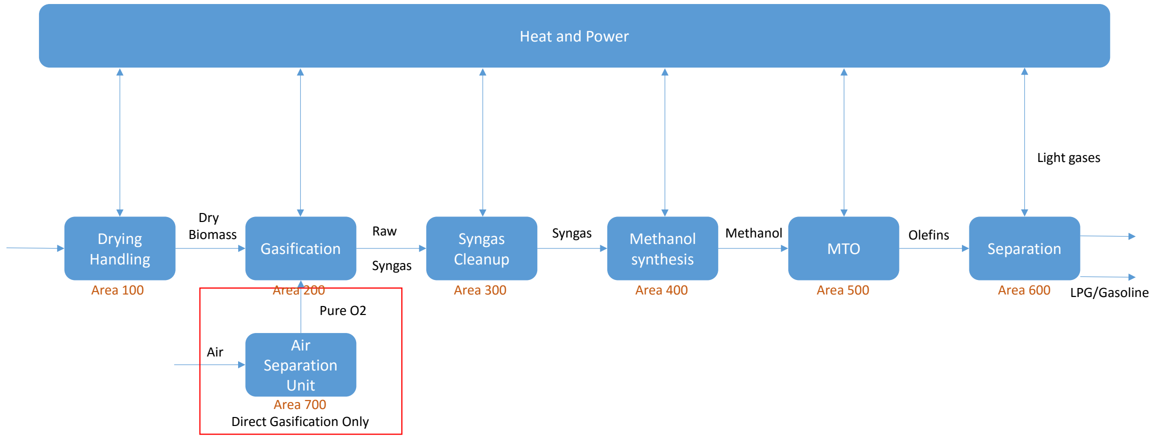


Figure 2-1 - General Flowsheet

The olefins production through biomass gasification can be broken down into seven different areas. All of them are integrated in order to minimize the use of utilities and maximize the power produced by the plant. A process flow diagram for each area and each technology can be seen in the Appendix A and B and they are going to be explained in detail in CHAPTER 3.

2.1 Drying and Handling (Area 100)

This section of the process accommodates the delivery of biomass feedstock, short term on-site storage, and the preparation of the feedstock for processing in the gasifier. Wood chips are delivered to the plant primarily via trucks. Assuming that each truck capacity is about 25 tons this means that if the wood, at a moisture content of 50%, was delivered to the plant via truck transport only, then 176 truck deliveries per day would be required. [10] As the trucks enter the plant they are usually weighed and the wood chips are dumped into a storage pile. From the storage pile, the wood chips are conveyed through a magnetic separator and screened. Particles larger than 2 inches are sent through a grinder for further size reduction.

Drying is accomplished by direct contact of the biomass feed with hot flue gas. The wet wood chips enter each rotary biomass dryer (see Figure 2-2) through a feed screw conveyor. The wood is dried to a moisture content of 5 wt% with flue gas from the gasification. [11] In case the destination is a direct gasifier, the dried biomass is then pressurized with nitrogen available from the Air Separation Unit in a lock hopper. In case it goes to an indirect gasifier, the lock hopper is not necessary since the reactor operates at low pressure.

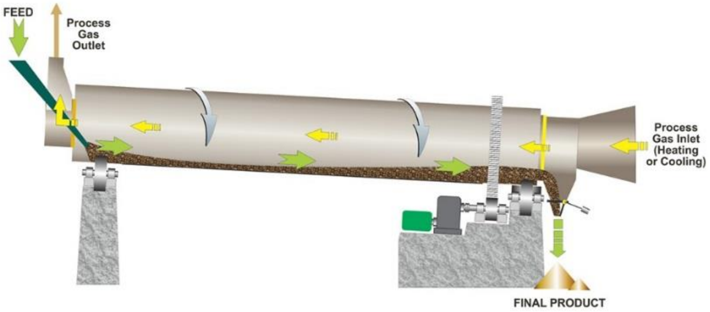


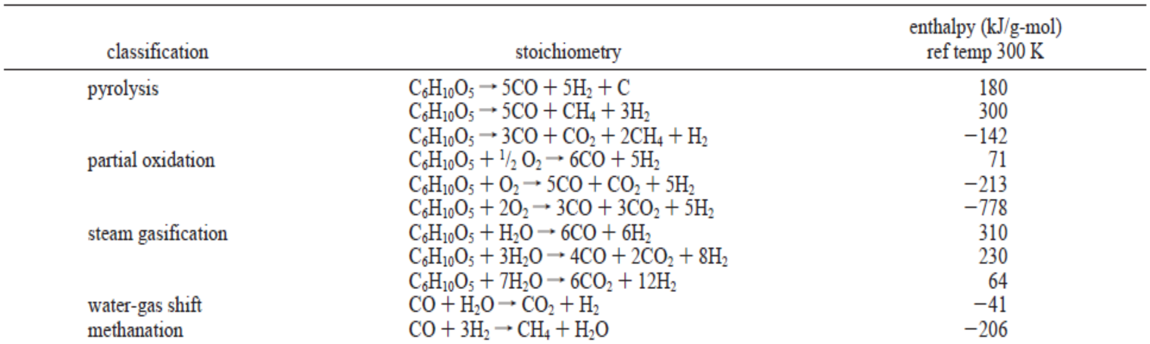
Figure 2-2: Rotary Dryer Scheme

2.2 Gasification (Area 200)

Gasification is a technology which converts any carbon-containing material, coal and/or biomass for example, into synthesis gas. Carbon reacts in the presence of a catalyst, usually olivine [12] with steam and oxygen or air at temperatures typically reaching 1,500 F to produce raw synthesis gas, a mixture composed primarily of carbon monoxide and hydrogen and some minor byproducts. The byproducts are removed to produce a clean syngas that can be used as a fuel to generate electricity or steam, as a basic chemical building block for a large number of uses in the petrochemical and refining industries, and for the production of hydrogen. [13]

The gasification process may be split into steps: pyrolysis, char gasification and combustion (see reactions on Table 2-1). Pyrolysis is the heating of biomass in absence of oxygen producing various condensable and non-condensable gases and char which consist mainly of fixed carbon and ash. It is directly related to the production of tars which inactivates downstream reactions since it is a mixture of heavy hydrocarbons that coats the surface of catalysts. Char gasification is the partial oxidation of char producing the syngas. Combustion is the total oxidation of the carbon and hydrogen to carbon dioxide and water. Although the total oxidation must be avoided in big scale, it is crucial step since provides the energy required for the process. [14] The water-gas shift reaction that occurs linked up with the char gasification uses the oxidation power of the steam to convert the carbon monoxide to carbon dioxide and hydrogen. Therefore the amount of steam inserted in the system is a parameter directly related to the syngas composition.

Table 2-1: Fundamental Reactions and Enthalpy of a Biomass Gasification



classification	stoichiometry	enthalpy (kJ/g-mol) ref temp 300 K
pyrolysis	$C_6H_{10}O_5 \rightarrow 5CO + 5H_2 + C$	180
	$C_6H_{10}O_5 \rightarrow 5CO + CH_4 + 3H_2$	300
	$C_6H_{10}O_5 \rightarrow 3CO + CO_2 + 2CH_4 + H_2$	−142
partial oxidation	$C_6H_{10}O_5 + {}^{1}/_{2}\,O_2 \rightarrow 6CO + 5H_2$	71
	$C_6H_{10}O_5 + O_2 \rightarrow 5CO + CO_2 + 5H_2$	−213
	$C_6H_{10}O_5 + 2O_2 \rightarrow 3CO + 3CO_2 + 5H_2$	−778
steam gasification	$C_6H_{10}O_5 + H_2O \rightarrow 6CO + 6H_2$	310
	$C_6H_{10}O_5 + 3H_2O \rightarrow 4CO + 2CO_2 + 8H_2$	230
	$C_6H_{10}O_5 + 7H_2O \rightarrow 6CO_2 + 12H_2$	64
water-gas shift	$CO + H_2O \rightarrow CO_2 + H_2$	−41
methanation	$CO + 3H_2 \rightarrow CH_4 + H_2O$	−206

Depending on the type of gasifier used, the above reactions can take place in a single reactor vessel or be separated into different vessels. In the case of direct gasifiers, pyrolysis, gasification, and combustion take place in one vessel, while in indirect gasifiers, pyrolysis and gasification occur in one vessel, and combustion in a separate vessel.

2.2.1 Direct Gasification

This type of gasification is operated at pressures higher than 30 bar and temperatures around 1600°F. [13] In this study only O2/steam-blown fluidized-bed gasifier is assumed since is the one which shows the biggest potential in respect of syngas conversion and also for having published data which is extremely important to validate the simulation models. Basically, oxygen and steam are blown in the reactor and therefore are known as the oxidation agents. As mentioned above the direct gasifier is characterized by having each step of the gasification occurring in the same vessel. Excess of nitrogen of the air in the syngas can cause a low heating value gas and oversized hardware which raises the capital cost of the plant. To avoid that high pressure of oxygen is required which is met by installing an air separation unit.

A representation of a standard gasifier is shown on Figure 2-3. Pressurized lock hoppers with screw conveyors are used to push the feed into the high pressure gasifier. The lock hoppers are pressurized using nitrogen from the air separation unit. A cyclone at the exit of the gasifier separate the char, olivine, and ash from the syngas. Then the syngas is sent for cleanup and conditioning.

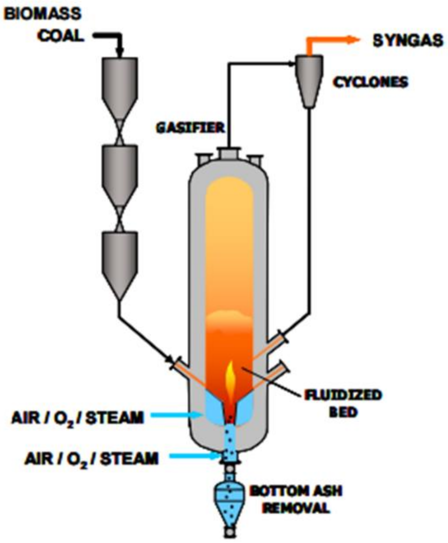


Figure 2-3: Direct Gasifier

However the Direct Gasification produces a syngas with low H2/CO ratio and relatively high tar composition which can inactivate downstream process catalyst and cause operational problem such as clogging. Because the methanol production requires a high H2/CO ratio a water-gas shift reaction is usually necessary and conveniently set after the syngas cleanup. Also a tar cracking unit is usually setup after the gasifier since it is operated under the same conditions of pressure and temperature and utilizes the excess heat coming from the gasification reactor. In spite of that, an addition heat is still necessary to make the endothermic process of tar cracking viable. This extra heat is usually provided by burning a high heating value fuel (e.g. natural gas) in a fired heat device [15].

2.2.2 Indirect Gasification

The Indirect Gasifier is based on the principle that separation of the gasification and combustion zones (GZ and CZ) will avoid N2 dilution of the syngas (due to combustion of fuel with air) and thus a high quality gas will be produced without the need for an expensive air separation unit.

The fundamental idea of this gasification system is to physically separate the gasification and combustion reactions in order to gain a largely N2 free syngas [16]. With reference to Figure 2-4, the biomass fuel enters a bubbling fluidized bed reactor (GZ) where it is pyrolysed and gasified with steam [17]. Residual char produced by the pyrolysis leaves the GZ with bed material through an inclined chute and enters a circulating fluidized bed riser (CZ) where it is combusted with air. After separation from the flue gas in a cyclone, the heated bed material flows back to the GZ via a loop seal [17]. This bed material provides the heat required to drive the endothermic steam gasification reactions which produce the syngas. The gasifier operates at atmospheric pressure and temperature around 1600ºF [18]. The syngas is of high quality and is characterized by low N2 content, high H2 content, low tar levels and high heating value. These favorable characteristics make the syngas suitable for many applications, including gas engines, gas turbines or fuel cells, as an intermediate product for chemical synthesis or for synthetic natural gas production [19].

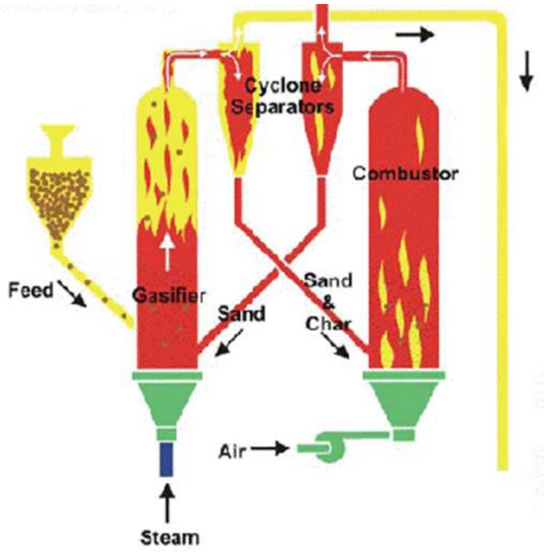


Figure 2-4: Indirect Gasifier Representation

The disadvantage, though, of this technology is that the syngas produced has a high composition of methane which is an inert gas in the methanol synthesis loop. Therefore if this gas is not treated it can lead to oversized hardware such as compressors raising extremely the capital cost of the plant. Consequently a tar reformer is used right after the gasifier since it is operated under same temperature and pressure conditions. The methane is converted by the excess steam into syngas in an endothermic process. An external source of energy is likely required which is met by burning a high heating value fuel. However, the high H2/CO ration of the synthesis gas produced makes the water-gas shift reactor not required [9].

For the lack of a water-gas shit reactor and an air separation unit, the indirect gasifier most likely requires a lower capital investment than the direct gasifier. However, this is not enough to point the low pressure technology as the most effective one since the operation costs also plays a key role in the cost evaluation.

2.3 Syngas Cleanup and Conditioning (Area 300)

The main impurities in the syngas exiting the gasifier that must be removed are char, tars, hydrocarbons, sulfur, and CO2. In addition, trace contaminants such as ammonia, metals, halides, and alkali species were of sufficient concern that equipment was added to remove them as well. Finally, the syngas must also be adjusted to obtain the appropriate H2/CO ratio for the methanol production.

The sulfur poisons the active sites of the catalyst used in the downstream process lowering dramatically its activity. Different catalysts have different levels of sulfur of which the concentration of sulfur starts to be a problem for the system. However it usually as low as 0.1ppmv which is a very low concentration. [20] For that reason, the main goal of the cleanup process is to remove almost completely the sulfur coming from the biomass to the syngas.

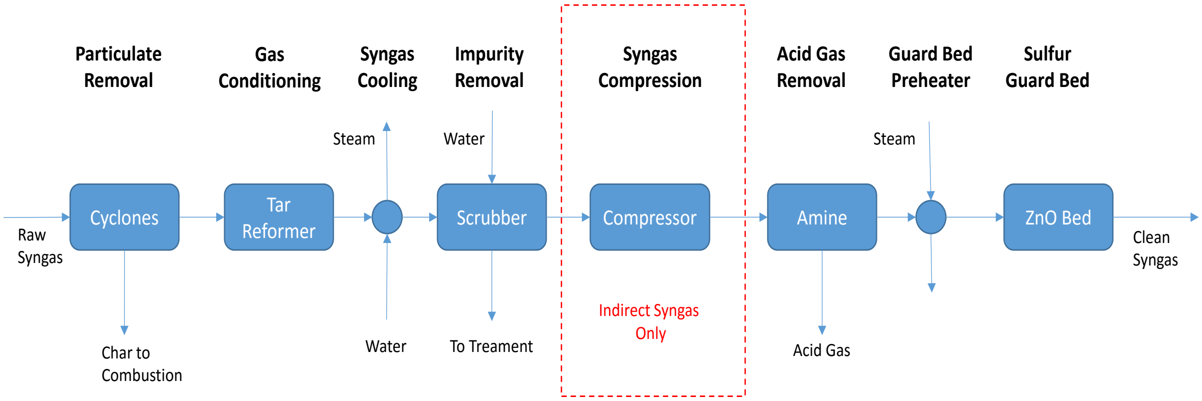


Figure 2-5: Syngas Clean-up process flow

Besides that the CO2 also reduces the catalyst activity by inhibiting methanol synthesis. In spite of this inhibition, a small quantity of CO2 is still required by the kinetics of the reaction which will be discussed in the Methanol Synthesis section. In addition, it is important to remove the H2O from the syngas since doing it shifts the equilibrium reaction towards formation of methanol [21].

A scheme for the process can be seen in Figure 2-5. Both the low and high pressure cases used very similar processes for syngas clean-up: particulate removal with cyclones, tar reforming, cooling and water scrubbing, acid gas removal with amine, and sulfur polishing. The main difference between the cases is the inclusion of a compression step in the low-pressure case. Since the cleaning up process coming from the indirect gasification is more comprehensive it was chose as baseline to detail the overall gas cleanup and conditioning process. In the end of this section, particular details with the high pressure gas process will be highlighted.

2.3.1 Particulate Removal

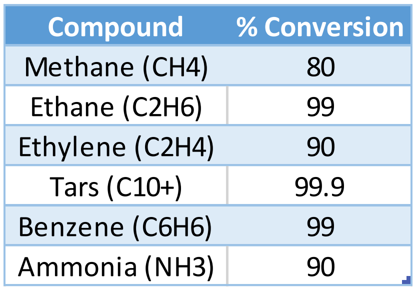
The syngas exiting the gasifier contains impurities that must be removed in order to meet the specifications required for methanol synthesis. Cyclones are used as the initial step in the gas cleanup process to remove the bulk of the char entrained in the syngas stream. This technology is standard in industry due to its low cost and high level of performance for removing particulates. The cyclones is operated at gasification temperature and pressure.

2.3.2 Tar Reforming

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 has the advantage that heat can be recovered at high temperatures [22]. For that reason in addition of having published data on the literature, this type of cracking was chose in this thesis.

Syngas is fed to a tar reformer to remove tars, light hydrocarbons, and ammonia before any additional gas treating or cooling. Reforming must occur prior to cooling the syngas to prevent tar condensation and deposition on downstream equipment. The tar reformer considered was the NREL’s reactor [9]. Table 2-2 shows the reactor conversion rate as provided by NREL. In the tar reformer, tars (mono and polyaromatic compounds) and light hydrocarbons such as methane, ethylene, and ethane are converted to H2 and CO. Ammonia is converted to N2 and H2.

Table 2-2: Tar Reformer Perfomance



Compound	% Conversion
Methane (CH4)	80
Ethane (C2H6)	99
Ethylene (C2H4)	90
Tars (C10+)	99.9
Benzene (C6H6)	99
Ammonia (NH3)	90

Syngas containing catalyst and residual char is taken to another cyclone to separate the solid material from the gas. The catalyst is sent to a burner where char and residual carbon is combusted. The hot, regenerated catalyst is then recycled to the cracking reactor which helps to provide the energy required for the reforming reactions. An external source of heat is met by using a fired heat hardware that provides the heat required by a hot flue gas produced.

2.3.3 Syngas Cooling

The remaining gas treatment steps require the syngas to be at a much lower temperature [23]. Therefore, the gas is cooled in three stages from 1598°F to 225°F prior. The heat recovered from the process is used for steam generation throughout the system. The process design has been optimized as much as possible to use this steam, reducing the plant utility load. Integration was limited to the needs of the clean-up section; broader heat integration with the overall thermochemical platform or biomass refinery may lead to additional efficiency gains.

2.3.4 Wet Scrubber

A wet scrubber operates by introducing the dirty gas stream with a scrubbing liquid – typically water. Particulate or gases are collected in the scrubbing liquid. Wet scrubbers are generally the most appropriate device for collecting both particulate and gas in a single system. A schematic of a Venturi Scrubber (a type of wet scrubber) is shown in Figure 2-6.

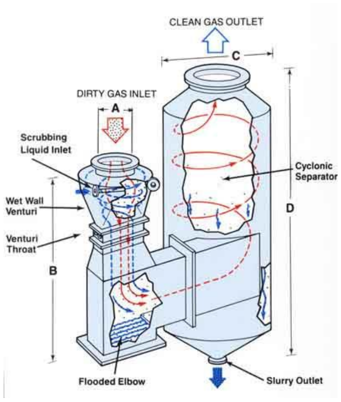


Figure 2-6: Venturi Scrubber Schematic

2.3.5 Compression

The syngas leaving the scrubber has to be compressed using a multi-stage centrifugal compressor with interstage cooling. It was determined by the NREL that for syngas cleaning application the compressing hardware is a horizontally split centrifugal design, with a polytropic efficiency of 78% and 110°F intercoolers. [23] The discharge pressure is designed such that the compressed gas is at the operating pressure range for maximizing the sulfur removal in the amine absorber column and in the ZNO bed.

2.3.6 Amine Absorber

To maximize the production of methanol a certain composition ratio between H2, CO and CO2 has to be met. It will be discussed later in the methanol synthesis section. However, it is important to know that this relation will be accomplished only if a certain amount of CO2 is removed. CO2 removal from the syngas can achieved via amine absorption [24]. The syngas containing CO2 enters the absorber and contacts an aqueous solution of amine that flows counter-currently to the syngas stream. CO2 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 [25]. Furthermore, because H2S has acidic characteristics it can also be removed with amine. With a higher circulation rate sulfur concentration of 2-3 ppmv can be reached. However, because the CO2 is the main component removed it controls the circulation rate being impossible to reach the concentration of sulfur necessary which is less than 0.1ppmv.

2.3.7 ZNO Bed

Consequently a further sulfur removal has to be done to lower its concentration to 0.1ppmv. The ZnO beds are used as a polishing step to reduce the sulfur concentration to the < 0.1 ppmv level required for methanol synthesis. It is basically a fixed bed reactor using zinc oxide that reacts with the H2S as follows:

$$H2S + ZnO \longrightarrow ZnS + H2O \qquad (2\text{-}1)$$

It is operated at 750°F and pressure to enhance the reaction kinetics reducing the ZnO load and increasing its lifespan. [26] Two heat exchangers are used before and after the beds. The one before has the goal to heat up the gas leaving the amine absorber. On the other hand, the after one cools down the clean syngas that finally goes to the methanol synthesis loop.

2.3.8 Direct Gasification particularities

Even though a lot of the clean-up processes are the same for both technologies there are some small differences. First, the syngas originated from the direct gasification does not need to be compressed after the wet scrubber since it is already at high pressure. Second, as mentioned above, the direct gasifier produces a low H2/CO gas ratio. As the methanol requires a H2/CO relatively high, a water-shift gas reaction (see Equation (2-2)) has to be implemented to correct this ratio.

Instead of using a water shift reactor, a steam injection into the tar cracker is sufficient to perform the required correction reducing the overall system cost. [23]

$$H2O + CO \longleftrightarrow CO2 + H2O \tag{2-2}$$

2.4 Methanol Synthesis (Area 400)

The methanol process consists of three parts; synthesis gas preparation, the methanol synthesis and methanol distillation. The first technology, the high-pressure synthesis, was commercialized in 1923. It operated above 300 bar and used a Cr-based catalyst. The low-pressure methanol synthesis replaced the high-pressure methanol synthesis in the 60s [27]. The low-pressure process resulted from the formulation of a new and more active Cu-based catalyst, and the ability to produce a sulfur-free synthesis gas. The low-pressure synthesis operates between 50 and 100 bar. Two low-pressure methanol processes dominate the market; the ICI process uses multi-bed synthesis reactors with feed-gas quench cooling and the Lurgi process uses multitubular synthesis reactors with internal cooling [28]. For this thesis, the Lurgi process was the technology chosen for the methanol production for having reliable data discussed in the literature and also for producing a medium pressure steam which it used to power generation reducing operational costs.

2.4.1 Process Description

Basically, synthesis gas is converted to methanol over a $Cu/Zn/Al_2O_3$ catalyst according to the following highly exothermic reaction and the water-gas shift reaction:

$$H_2O + CO \longleftrightarrow CO_2 + H_2O \tag{2-3}$$

$$CO_2 + 3H_2 \longleftrightarrow CH_3OH + H_2O \tag{2-4}$$

In the Lurgi reactor, the catalyst is packed in vertical tubes surrounded by boiling water. The reaction heat is transferred to the boiling water and steam is produced. Efficient heat transfer gives small temperature gradients along the reactor. Typical operating conditions are 507 °F and 980 psi [29]. The reactor temperature is controlled by the pressure of the boiling water. Because of the quasi-isothermal reaction conditions and high catalyst selectivity, only small amounts of by-products are formed and, therefore, were neglected in this study.

Methanol conversion is limited by equilibrium and unreacted synthesis gas is separated from crude methanol, then compressed and recycled. A portion of recycle gas is purged to remove inerts. In order to minimize the amount of reactants purged, it has been proven that operating this reactor with a stoichiometric number (SN) of 2 tends to maximize its efficiency. The SN is definied as follow [30].

$$SN = \frac{[H2] - [CO2]}{[CO] + [CO2]}$$

The methanol synthesis loop consists of a reactor with a steam drum, an economizer which uses the energy of the effluent to heat up the feed stream, a cooler, flash drums, distillation column and recycle compressors. A flowsheet of the methanol synthesis loop is given in Figure 2-7.

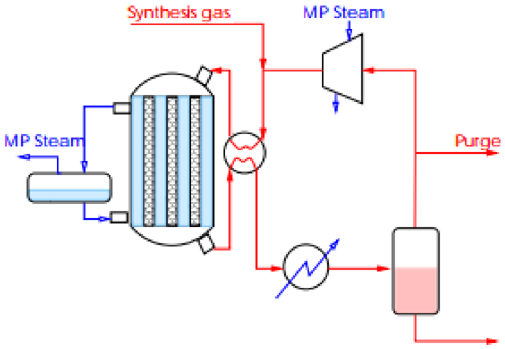


Figure 2-7: Flowsheet of Lurgi's methanol synthesis loop

A high methanol purity is isolated by flash and distillation. Dissolved gases are removed by flashing at low pressure. At last, water and methanol are separated in a distillation column which is operated at atmospheric pressure.

2.4.2 Kinetics Overview

The kinetics used for the simulation and scaling of the methanol production are given by Vanden Bussche and Froment [31] in respect to the reactions showed by Equation (**2-2**) and (**2-3**) and described by LHHW-type equations (Langmuir Hinshelwood-Hougen-Watson) which structure is:

$$R = (\text{kinetic term})\frac{(\text{driving-force term})}{(\text{adsorption term})} \tag{2-5}$$

The reaction rate for the first reaction for the production of methanol from carbon dioxide is given in Equation (**2-6**).

$$R_1 = (k_4 p_{CO_2} p_{H_2}) \frac{\left[1 - \frac{1}{K_{E1}}\left(\frac{p_{CH_3OH}p_{H_2O}}{p_{CO_2}p_{H_2}^3}\right)\right]}{\left[1 + k_3\left(\frac{p_{H_2O}}{p_{H_2}}\right) + k_1\sqrt{p_{H_2}} + k_2 p_{H_2O}\right]^3} \tag{2-6}$$

The reaction rate for the water-shift reaction is given in Equation (**2-7**).

$$R_2 = (k_5 p_{CO_2}) \frac{\left[1 - \frac{1}{K_{E2}}\left(\frac{p_{CO}p_{H_2O}}{p_{CO_2}p_{H_2}}\right)\right]}{\left[1 + k_3\left(\frac{p_{H_2O}}{p_{H_2}}\right) + k_1\sqrt{p_{H_2}} + k_2 p_{H_2O}\right]} \tag{2-7}$$

The kinetic and adsorption parameters entered into the Aspen LHHW reaction model to implement these kinetics can be seen in the Appendixes C

Since the reactions are exothermic, the chemical equilibrium constants decrease with increasing temperature. Therefore, low reactor temperatures should improve conversion, provided they are not so low that the specific reaction rates are too small. For a given reactor size and a desired conversion, the recycle flow rate increases as reactor temperatures are lowered, which means higher compressor work.

2.5 Methanol to Olefins (MTO) synthesis (Area 500)

The major MTO technologies include the UOP/Hydro MTO process and the Lurgi process. They are very similar except for the ratio of ethylene and propylene produced. Basically 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 [32].

The UOP/HYDRO MTO process is based on the development of a new catalyst which is highly selective for conversion of methanol to ethylene and propylene. On the other hand, Lurgi process is based on an efficient combination of the most suitable fixed-bed reactor system and a very selective and stable zeolite-based catalyst. The main points are the ease of scale-up of the fixed-bed reactor and the significantly lower investment cost in respect to a fluidized bed reactor which is used by the UOP/HYDRO technology.

Since one of the main objectives of this thesis is to prioritize propylene over ethylene production with the minimum capital and operational cost, the Lurgi process was chosen as an approach to olefins production which will be discussed in the following section.

2.5.1 Process Description

Methanol is used as feed to the process. The methanol feed is vaporized, superheated and fed to the DME Reactor which is a single stage adiabatic reactor. The high activity and selectivity of the catalyst achieve an almost thermodynamic equilibrium. The reaction (see Equation (2-8)) is exothermic and its equilibrium does not depends on the reactor operation pressure [33].

$$2\ CH3OH \longleftrightarrow CH3OCH3 + H2O \qquad (2\text{-}8)$$

The product of the DME Reactor is sent to the MTP reactor which contains in general 6 beds. These bed are extremely necessary since the propylene and ethylene ratio depends of the temperature control. Therefore a cooler is set in between each bed.

In the MTP reactor the DME and methanol mixture is converted to olefins through the reaction showed below:

$$n\ CH3OCH3 \longleftrightarrow 2\ CnH2n + n\ H2O \qquad (2\text{-}9)$$

Where N ranges from 2 to 8 since about 85% of the carbon is converted from C2 to C8, although the propylene is the most representative.

The above mentioned high selectivity of propylene requires temperature around 842 °F and a pressure of 22 psi [34]. Naphthenes, paraffins and aromatics tend to be the side products with water originated by the oxygen from the methanol.

In-between each bed the stream is cooled and mixed with additional fresh DME/Methanol reactant. The amount of fresh reactant required is set to maintain an adiabatic temperature rise in each bed. This guarantees similar reaction conditions resulting in better selectivity of propylene.

Process steam is also injected in the feed of the first MTP catalyst bed in other to minimize coke formation since small amounts of heavy carbons coats the actives catalyst surface. The vapor also serves as heat sink for the exothermic reactions supporting the temperature control within the bed.

The hydrocarbon recycle to the first reaction stage increases the propylene yield by conversion of olefins other than propylene to the same product rang as the DME feed. In addition, the hydrocarbons serve as a heat sink for the exothermic reaction, supporting temperature control over the catalyst bed [34].

The hot effluent from the reaction section is cooled down and taken to a separation section responsible for extracting the relevant components from heavy carbons, olefins and light ends.

2.5.2 Water Quench

The MTP reactor effluent is cooled in a heat recovery system and by quench where the hydrocarbon product is separated from the bulk of water. The hydrocarbons leave the quench system as vapor while water condenses. The water may contain methanol and DME which can be further recovered in a Methanol Recovery Column and the fed to the DME reactor. The stripped water containing traces of methanol is finally treated for use as process water [35].

2.5.3 Compression

The Hydrocarbon vapor product from the quench is compressed by a multi stage centrifugal compressor. The product is cooled and partially condensed between each stage. The condensed water is recycled to the quench while the hydrocarbon liquid and vapor are sent to the purification section.

2.6 Separation (Area 600)

A simplified schematic is shown in Figure 2-8 [34] .

The Debutanizer separates light boiling components from C4+ hydrocarbons. The bottom product is fed to a Dehexanizer distillation column where C7+ forms the MTP-Gasoline product. The rest is sent back to MTP reaction to maximize the propylene yield.

The compressed hydrocarbon vapors including light olefins and DME and the vapor produced by the Debutanizer are fed to the DME Removal System. There C3- hydrocarbons are separated from C4+ hydrocarbons and oxygenates.

The C4 hydrocarbon fraction is recycled to the MTP reaction system for further propylene production. A smaller portion is purged of the loop forming the C4 component in the MTP-LPG Product

The C3- product, which is free of DME and any other oxygenates, is fed to the Deethanizer. From it, a C2- stream is recovered as top product. One part of the C2- stream is recycled to the MTP Reactor, the rest is sent to the ethylene purification unit.

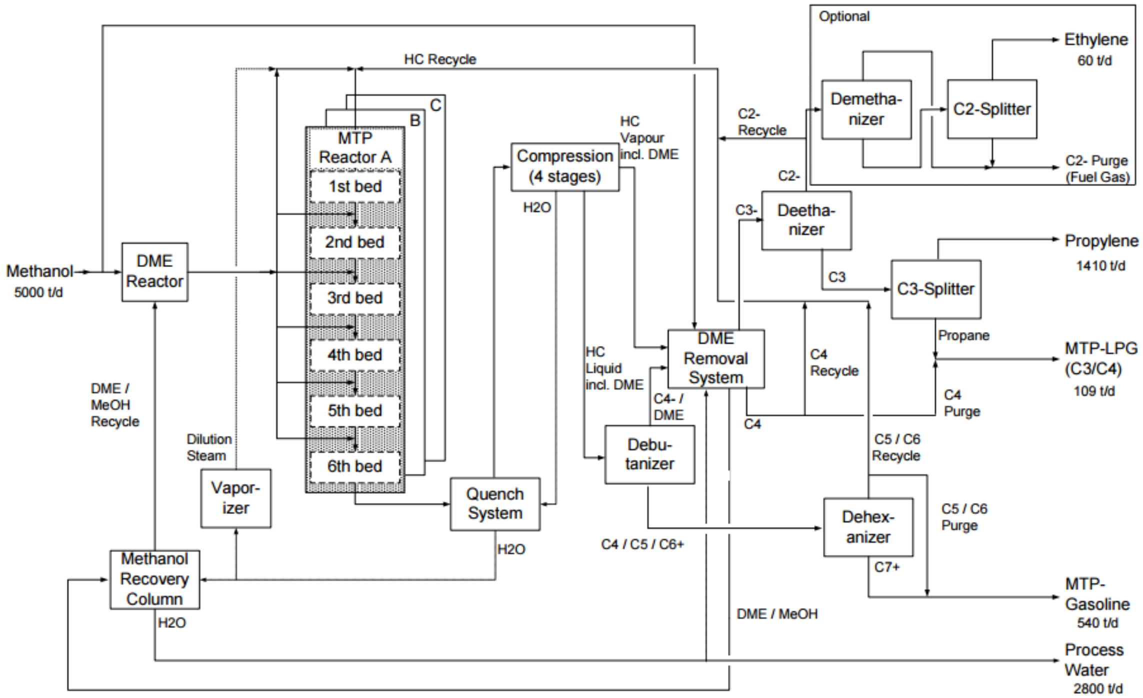


Figure 2-8: Simplified MTP process Flow sheet

The C3 bottom product, containing propylene and propane flows through a bed of activated alumina to the C3-splitter which separates propane from the polymer grade propylene product. The propane forms the C3 component in the MTP- LPG Product.

The ethylene purification is achieved in a two column system, the demethanizer and the C2-Splitter column. The vapors from the Demethanizer contain C1, hydrogen and inert material, while the bottom product C2 is heated up and sent to the C2-Splitter. The C2 stream is split and rectified to polymer grade ethylene on the top of the column. The ethane stream is mixed with the stream of the Demethanizer and is used internally as fuel gas for heater firing.

2.7 Air Separation Unit (Area 700)

The O2/N2/AR could be separated by different technologies. However, the cryogenic air separation process is one of the most popular air separation process, used frequently in medium to large scale plants. It is the most preferred technology for producing nitrogen, oxygen, and argon as gases and/ or liquid products and supposed to be the most cost effective technology for high production rate plants. In today's market scenario, all liquefied industrial gas production plants make use of cryogenic technology to produce liquid products [36].

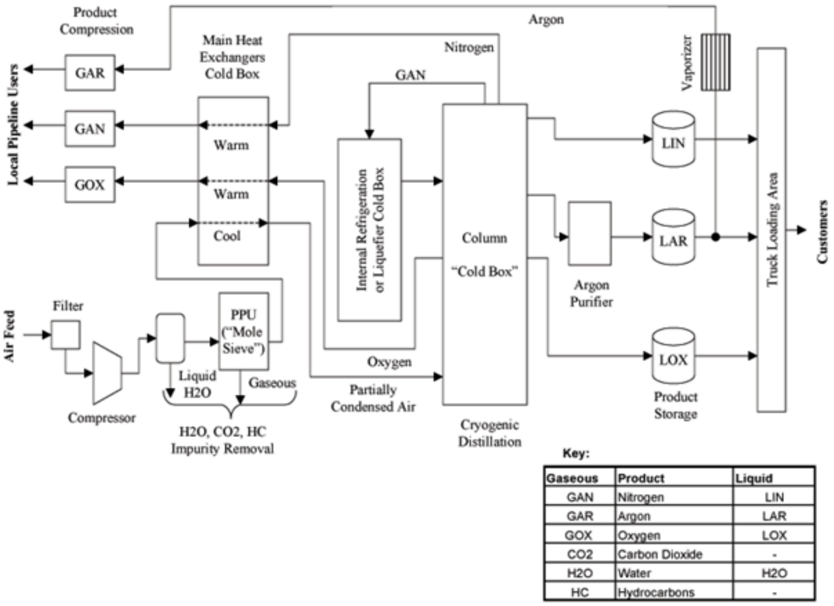
The first step in any cryogenic air separation plant is filtering and compressing air. After filtration the compressed air is cooled to reach approximately ambient temperature by passing through air-cooled or water-cooled heat exchangers. This leads to a better impurity removal, and also minimizing power consumption, causing less variation in plant performance due to changes in atmospheric temperature seasonally. After each stage of cooling and compression, condensed water is removed from the air.

The second step is removing the remaining carbon dioxide and water vapor, which must always be removed to satisfy product quality specifications. They are to be removed before the air enters the distillation portion of the plant. The portion is that where the very low temperature can make the water and carbon dioxide to freeze which can be deposited on the surfaces within the process equipment. There are two basic methods to get rid of water vapor and carbon dioxide - molecular sieve units and reversing exchangers.

The third step in the cryogenic air separation is the transfer of additional heat against product and waste gas so as to bring the air feed to cryogenic temperature. The cooling is usually done in brazed aluminum heat exchangers. They let the heat exchange between the incoming air feed and cold product and waste gas streams leave the air separation process. The very cold temperatures required for distillation of cryogenic products are formed by a refrigeration process comprising expansion of one or more elevated pressure process streams.

This step involves the use of distillation columns to separate the air into desired products. For example, the distillation system for oxygen has both "high" and "low" pressure. Oxygen leaves from the bottom of the distillation column, nitrogen leaves from the top. Argon has a boiling point similar to that of oxygen and it stays with oxygen. If however high purity oxygen is needed, it is necessary that at an intermediate point argon must be removed from the distillation system. Impure oxygen produced in the higher pressure distillation column is further purified in the lower pressure column. Plants which produce high purity oxygen, nitrogen or other cryogenic gases require more distillation stages [37].

The cryogenic air separation flow diagram given below does not represent any particular plant and shows in a general way many of the important steps involved in producing oxygen, nitrogen, and argon as both gas and liquid products.



Gaseous	Product	Liquid
GAN	Nitrogen	LIN
GAR	Argon	LAR
GOX	Oxygen	LOX
CO2	Carbon Dioxide	-
H2O	Water	H2O
HC	Hydrocarbons	-

Figure 2-8: Air Separation Unit Flowsheet

2.8 Heat and Power 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 [38].

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 ΔTmin (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 that curve is also possibly to identify the minimum hot (QH,min) and cold utilities (QC,min) needed at a specific ΔTmin.

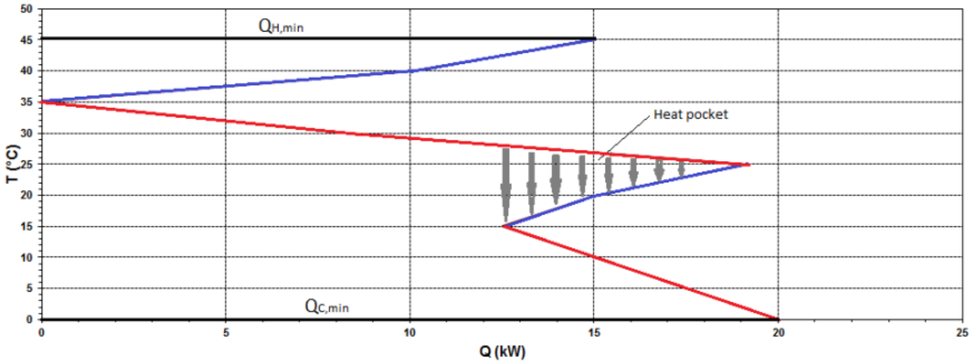


Figure 2-9: Grand Composite Curve example

The pinchpoint 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 35 deficit above the pinch, which requires external heating (QH,min), and it has an overall heat excess below the pinch, which is requires external cooling (QC,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 [38]:

- 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 result in increased energy consumption

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 Aspen Plus Energy Analyzer. In this program it is possible, among other things, to construct Composite, Grand Composite Curves. 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.

2.9 Process Economics

The process economics are based on a "nth" plant which neglects the uncertainty costs a first time plant may have (such as longer start-ups, losses of wrong operation).

The capital costs were based on different sources. For some hardware that use well known technology (for instance, amine treatment, acid gas removal, air separation unit), an overall cost for the package unit was used. Many of the common equipment items (tanks, pumps, simple heat exchangers) were costed using the Aspen Icarus Process Evaluator® software. Other more specific unit operations (gasifier, dryer, tar cracker) used cost estimates from other studies. The installed capital costs were developed using general plant-wide factors. The installation costs incorporated cost contributions not only for the actual installation of the purchased equipment but also for instrumentation and controls, piping, electrical systems, buildings, yard improvements, etc. These are also described in more detail in Chapter 4.

The sizes of the equipment needed in the process were often different than the ones used as reference. In order to correct this difference, an exponential scaling expression was used to adjust the base equipment costs:

$$New\ Cost = Base\ Cost * \left(\frac{New\ Capacity}{Base\ Capacity}\right)^n \qquad (2\text{-}10)$$

where ranges from 0.6 – 0.8 and it is called as characteristic scaling exponent. The capacity is assumed to be a production variable such as mass of inlet stream or heat duty. The value of n is obtained from the literature.

Since a variety of sources were used, the equipment costs were derived based upon different cost years. Therefore, all capital costs were adjusted with the Chemical Engineering (CE) magazine's Plant Cost Index [39] to a common basis year of 2015.

Table 2-3: Chemical Engineering Magazine's Plant Cost Indices

YEAR	INDEX
1999	390.6
2000	394.1
2001	394.3
2002	395.6
2003	402
2004	444.2
2005	468.2
2006	507.2
2007	525.4
2008	575.4
2009	521.9
2010	550.8
2011	585.7
2012	584.6
2013	567.3
2014	576.1
2015	570.6

Once the scaled, installed equipment costs were determined, overhead and contingency factors were applied to determine a total plant investment cost. That cost (developed by the Aspen Plus model, Heat and Power Integration), was used in a discounted cash flow analysis to determine the minimum cost of propylene production using a specific discount rate. The minimum price was used as main indicator of economic performance and so as a comparison bases between the direct and the indirect gasification cases.

CHAPTER 3

PROCESS MODELLING

A simulation model was created in Aspen Plus to establish mass and energy balances. Input data for the model was obtained from the literature. Stream data from the simulation 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 work performed at NREL [22] with additional developments and improvements, based on findings in the literature. Special attention for modeling and simulation development was focused on the gasification, Tar cracking, methanol synthesis loop and propylene synthesis.

Since the Lurgi MTP process is a novel technology there is not enough data in literature or even discussions regarding the range of products and the operation conditions. Therefore some simplifications were assumed in this model which will be discussed later on. Data for the MTP process was taken from articles which investigate the performance in a lab scale of different catalysts for the production of olefins from syngas. The conversions, range of products and operation conditions were assumed to be the same as these experiments, although it is known that big scale process have usually different performance even if similar lab conditions are held.

3.2 Simulation Basis

Aspen Plus is a comprehensive chemical process modeling tool used to design and improve process plants [40] .It is a software package designed to allow the user to build and run a process simulation model based on the complete layout of the engineering system. The layout includes flowsheet, chemical components and operating conditions. The flowsheet presented on APPENDIX A and B 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. These values depend on the thermodynamic model and operating conditions chosen.

3.2.1 Simulation basic assumptions

For that study the following assumptions were taken into account:

- No pressure drop
- The system behaves in according to RK thermodynamic model
- For the water cycle, the Steam Table was assumed.
- No particle size distribution was assumed
- Char is assumed 100% Carbon
- Component key of tar is $C_{10}H_8$

Although pressure drop occurs in a real life application, it is a good approach in a simulation level in which the main goal is to compare two different pathways than obtaining an absolute number. On the other hand, the RK model describes with a good accuracy the syngas behavior under high pressure and temperature conditions as well as the equilibrium reactions in the methanol synthesis and so it was chosen as baseline equation of state for the simulation. The STEAM Table was assumed due to its accuracy with the thermodynamics calculations for water.

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 that will be discussed in the Results Sections.

3.2.2 Biomass and Feedstock

The processes from biomass to methanol and methanol to propylene 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. Since the raw material used is biomass which is basically a mixture of molecules, a nonconventional component approach was assumed.

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 [18] input to the dryer and to the gasifier, can be seen in Table 3-1.

Table 3-1: Biomass composition

Ultimate Analysis (dry basis)	wt.%
Carbon	51.19
Hydrogen	6.08
Oxygen	41.3
Nitrogen	0.2
Sulphur	0.02
Clorine	0.05
Ash	1.16
Proximate Analysis (dry basis)	wt.%
Volatile matter	80
Fixed Carbon	18.84
Ash	1.16
Moisture	20

The design plant size of 2,000 dry metric tonnes per day was chosen to match that of the Aden et al. [8] biochemical process3 and the Phillips et al. [9] indirect gasification process. With an expected 8,406 operating hours per year (96% operating factor) the annual feedstock requirement is 700,000 dry metric tonnes per year.

3.3 Drying and Handling

As mentioned in the process outline, the biomass is delivered by trucks to the plant site and, prior drying, it is treated to reduce the particle size in a grinder enhancing the heat and material transfer. Also, screw conveyors is usually the mechanism chosen to move the reduced biomass particles. These hardware were not simulated in Aspen Plus, however they were taken into account for the economics evaluation that will be discussed in the next section.

After this pretreatment the biomass is fed to the dryer at 60F. To reach a moisture content of 5% within the biomass, the process flue gas is blown into the dryer which evaporates the excess of water due to its excess of energy. The dried biomass leaves the dryer at 219°F and it is feed to the gasifier by a screw conveyor mechanism. The exhaust gas leaving the dryer is cooled and sent to stack to be emitted to the atmosphere. The stack temperature of the flue gas is set at 62°F above the dew point of the gas in order to avoid process problems such as corrosion by the condensation of acid gases [41]. The excess heat of the exhaust gas is used within the process to heat up others process that will be discussed in the heat integration later on.

The Aspen Plus simulation flowsheet can be seen in the APPENDIX A and B in the section 100-200 as well as the main characteristics of the income and outcome streams (temperature, pressure, mass flow of each component and so on).

3.4 Gasification

Because the biomass was modeled as a non-conventional material, the Aspen Plus software cannot calculate some thermodynamics parameters and so the RYield block was set to convert it to a conventional material. Basically the biomass is broken down in conventional compounds such as carbon, hydrogen, oxygen, nitrogen and sulfur based on the ultimate analysis, ash and char (considered as 100% Carbon). The mass yields for that block are determined and set through a calculator block. The outlet stream is named 'COMP' which are the same for both pathways. This hypothetical reaction is extremely endothermic and so a heat stream 'HX' from the RYield block for the gasifier reaction block has to be set to conserve energy of a hypothetical step.

From that part on the direct and indirect gasifier are modeled differently and son are split into two subsections.

3.4.1 Direct

The 'COMP' stream enters the gasifier. The gasifier pressure is 438 psia and 1600°F. Oxygen feed 'O2' coming from the ASU is compressed and then heat up to 370°F and 438psi. Also steam is injected as the fluidization medium in a steam-to-feed ratio of 0.2lb of steam per lb of dried biomass at 769°F and 438psi [41]. Adding more steam or increasing the target temperature increases the amount of combustion, which depletes the amount of syngas that can be used for methanol and propylene synthesis.

To calculate the outlet syngas composition the gasifier was modeled using correlations based on data form the Gas Technology Institute (GTI) 12 tonne per day test facility [42]. These correlations and some important considerations are presented in the Appendix E. In the simulation prospective, the calculation was done linking the Aspen Plus software with Excel worksheet where the equations as well as the atomic balance were held.

The outlet stream 'C-SYNG-1' is feed into a cyclone where the char and ash is separated from the produced syngas. The stream 'Char' is taken to a burner in other to burn the unconverted carbon producing a high heat value flue gas that it is used by other process as heat source. The exhaust gas outlet 'C-SYNG-2 flows to the gas cleanup section.

3.4.2 Indirect

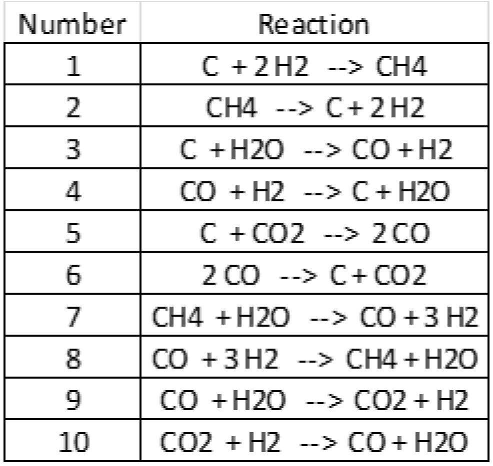
The outlet stream 'COMP' is fed to a separator block 'CHARSEP' whose purpose is to separate out a portion of the char (assumed 100% C) and all of the ash. The char split fraction is set using a design specification; the block split fraction is varied until the gasification temperature of 1562°F is achieved [43]. The char and ash are directed to the gasifier combustion zone, simulated by an RStoic reactor titled 'COMBUSTOR'.

The air stream 'O2COLD' is heated up and fed to this block. The mole fraction of the air was specified as 0.79 N2 and 0.21 O2 and its temperature was set to 842 °F [44]. The air mass flow rate is computed and set using a calculator block. Air mass flow rate equals biomass mass flow rate multiplied by an assumed air-fuel ratio of 1.12. The air and char react to produce the heat required for gasification, represented by the heat stream 'QGASIF' connecting the block 'COMB' to 'GASIF'. No chemical reactions were specified; the generate combustion reactions option was selected. The combustion temperature is set by a calculator block. It was assumed to be 55 °C above the gasification temperature [17]. The chosen air-fuel ratio ensures complete combustion of the char; therefore, the stream 'ASHSEP' contains only CO2, O2, N2 and ash

The main fuel stream is fed to the gasification zone 'GA-REAC' simulated using an RGibbs reactor. The other feed stream is the steam needed to gasify the biomass and fluidise the bed. The steam temperature was set to 842°F and its mass flow rate depends on the gasifier steam to biomass ratio (STBR). STBR is defined as the mass flow rate of biomass moisture plus the injected steam divided by the dry biomass mass flow rate. The injected steam mass flow rate is set by a calculator specification block employing the wet biomass mass flow rate, the specified moisture content and a STBR of 0.75 in its calculations [17].

The gasifier reactor named "GA-REACT" is a RGibbs, where evaluates the amount of products based on the minimization of free Gibbs energy. It assumed that all the nitrogen and sulfur content was converted into NH3 and H2S. The following gasification reactions was set into this block:

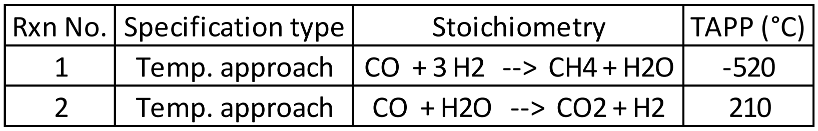
Table 3-2: Gasification Reactions



Number	Reaction
1	C + 2 H2 --> CH4
2	CH4 --> C + 2 H2
3	C + H2O --> CO + H2
4	CO + H2 --> C + H2O
5	C + CO2 --> 2 CO
6	2 CO --> C + CO2
7	CH4 + H2O --> CO + 3 H2
8	CO + 3 H2 --> CH4 + H2O
9	CO + H2O --> CO2 + H2
10	CO2 + H2 --> CO + H2O

However, the reactions does not reach the equilibrium proposed by this block and so the results does not match with the data published in the literature. To solve this problem, the outlet stream enters a new RGibbs reactor called “CALIBRA”. In this block two reactions was set with different temperature approaches. The temperature approaches was chosen based on minimization of error with the published data by trial and error (see Table 3-3).

Table 3-3: Calibration reactions and parameters



Rxn No.	Specification type	Stoichiometry	TAPP (°C)
1	Temp. approach	CO + 3 H2 --> CH4 + H2O	-520
2	Temp. approach	CO + H2O --> CO2 + H2	210

The outlet syngas ‘C-SYNG-2’ enters the syngas cleanup zone. The simulation flowsheet is presented in the APPENDIX B.

3.5 Syngas Cleanup

The units modelled in the thesis are tar cracking, venture scrubber, multi-stage compressor (only for the indirect gasification), amine absorber and at last ZnO beds. Heat exchangers are used throughout the process to reach the required temperature condition for a good process operation and efficiency.

3.5.1 Tar reformer

For design proposes the tar reformer is used in both pathways for different reasons. In the direct gasification technology the tar content is relatively high and the H2/CO ratio is low. Thus the tar cracking process is employed to crackdown the tar and increases the H2/CO ratio through water-gas shift reaction (see Equation (2-3)). However, for the indirect technology, the tar content is so small that is usually neglected. In spite of that, the cracking reactor is extremely important since it also reforms the high methane content present in the syngas produced. The methane as an inert gas can rapidly increase the equipment size and so the capital cost of the plant.

The syngas stream 'C-SYNG-2' is sent to the catalytic tar bubbling fluidized bed reactor where hydrocarbons are converted to CO and H2 while NH3 is converted do N2 and H2. In the Aspen simulation, the conversion of each compound is defined by target values defined by research efforts of NREL [41] as follows:

Table 3-4: Target conversions for low pressure operation

Compound	Target Conversion
Methane (CH4)	80%
Ethane (C2H6)	99%
Ethylene (C2H4)	90%
Tars (C10H8)	99.9%
Benzene (C6H6)	99%
Ammonia (NH3)	90%

The values are assumed for the tar cracking of the syngas originated for the high and low pressure case. The target conversion may not be valid at the higher pressure of 438 psi. However, the effects of pressure on the equilibrium reactions were neglected since there are not data available on the literature that shows how the conversions are affected.

Because the H2/CO ratio in the high pressure syngas is low, steam is inserted in order to drive the Water-gas shift reaction to convert the excess of CO into H2 [23].

In the Aspen simulation the tar reformer operates isothermally at the same temperature of the gasifier. A Rstoic block models the Tar reformer with the decompositions reactions (see Equation X to Y) and the water-gas shift reaction (just for the high pressure operation). Then, the conversions showed on Table 3-4 are set for each correspondent reaction. The outlet syngas 'SYNGAS' is at last sent to the next cleanup steps.

Moreover, the cracking reactions require energy which is offered by combustion of natural gas. This process was modeled feeding a methane (natural gas) and air streams into a Rstoic block which works as a burner. A heat stream 'HTRQUIRE' is set from the burner to the cracker to simulate the duty necessary for the endothermic reactions. The amount of natural gas burned is set based on the outlet gas temperature of 1800°F [23] .The flue is then used as heat source in the plant that will be discussed in the pinch analysis section.

3.5.2 Venture Scrubber

Prior to the scrubber, the syngas is cooled to the dew point. The syngas is scrubbed with water at a temperature of 25˚C. The scrubber is simulated as a separator in Aspen plus. The separator block is set to remove completely ethylene, benzene and tar which were not converted in the tar reformer.

3.5.3 Compression

The syngas coming from the indirect gasifier is nearly at atmospheric pressure. Because the efficiency of the amine absorption tower and the ZnO bed are dependent of pressure, a compression stage is required in other to build up the gas pressure.

Following the work done by NREL [9] the pressure of 442psi was set as goal to the compression. The model uses a 4 stages compression block in ASPEN with intercoolers set to 110˚F.

Each compressor was modeled such that each section has a polytropic efficiency of 78% [23]. The interstage cold stream are air heat exchangers.

3.5.4 Amine Absorber

CO2 has to be removed to get a balanced feed gas (fresh feed plus recycled gas) to the methanol synthesis, (H2-CO)/(CO2+CO)=2.1, to get as high overall methanol yield as possible, and to purge as little unreacted gas as possible.

The acid gas scrubber was simulated using a simplified model of SEP blocks. To specify the amount of CO2 that needs to be removed to meet the above mentioned specification, a design block is set. The amount of H2S eliminated by this process is defined to be 8ppmv which it is in agreement with this technology [8]. Because the percentage of syngas lost in this process is considered zero for this study. The amine system heating and cooling duties were calculated using information (see Table 3-5) taken from section 21 of the GPSA Data Handbook [45]. This method gave a heat duty of 2,364 Btu per pound of CO2 removed, with a similar magnitude cooling duty provided by forced-air cooling fans. These values are extremely important for the heat integration methodology discussed later on.

Table 3-5: Acid Gas Removal Parameters

Acid Gas Removal	Value
Amine Used	Monoethanolamine (MEA)
Amine Concentration	35wt%
Absorber Temperature	110
Abosorber Pressure	445psi
Duty per Pound CO2 removed*	2364 BTU/lb
Duty per Pound CO2 inserted	2364 BTU/lb

*removed by forced air

At last the stream 'DRYSYNG' leaves the block and goes to the next cleanup process: The ZnO beds

3.5.5 ZnO beds

Because the methanol reaction catalyst based on cooper loses activity rapidly for concentrations above 0.1ppm, the 'DRYSYNG' stream has to be taken for a further sulfur separation [46]. To increase efficiency which lower the load of catalyst required, the stream is heat to 750˚F with the flue gas coming from the fired heat device. The block is modeled with a SEP block. For this thesis, an assumption is made that the separation efficiency is 100% resulting in a sulfur free syngas.

After the reactor, a cooler is used to cool down the syngas to 110˚F and the stream 'CLN-SYNG' is finally taken to the methanol synthesis section

3.6 Methanol Synthesis

In this section, the syngas is converted to methanol in a fixed bed reactor. The heat of reaction is used to produce steam which, after a superheater, is taken to produce power. The unreacted syngas in recycled in two different moments: after the reaction and in the methanol separation from the water. However, the syngas enters this area at relatively low pressure and so it has to be compressed since the catalytic activity is directly proportional to the components partial pressures.

3.6.1 Compression

Synthesis gas at 445 psi is compressed in a two-stage compression system to 980psi considering the same polytropic efficiency of 78% [23]. Three recycle gas streams are added, and the total gas stream enters a feed-effluent heat exchanger (FEHE). The gas is then heated to 302 °F in a preheater (HX3) and enters the reactor.

3.6.2 Reactor

The reactor is modeled assuming a RPlug block. In this block the reactions and the kinetics parameters (described on Appendix C) were set. This highly exothermic reaction generates high pressure steam in order to get rid of the excess of heat produced. This is modeled by a heat stream "RX-HEAT" going from the reactor to the exchanger block located in the section WORKPROD1 of the Appendix A and B. The high-pressure steam produced through this reactor is usually at 42 bar and the effluent leaves the reactor at 980 °F [47].

3.6.3 Separator, Recycle and Vent

After the reactor effluent is cooled to 174 °C in the FEHE, it is further cooled to 38 °C and partially condensed in a water-cooled heat exchanger. The vapor phase is separated by flash in the tank 'X'. A small fraction of this vapor

(0.022) is vented off to avoid the built in of inerts in the process such as methane and nitrogen [47].

3.6.4 Flash and Distillation

The liquid from the separator contains significant amounts of light components because of the high pressure in the separator. If this stream were fed directly into the distillation column, these inert components would build up in the condenser and blanket the condenser. Either a high pressure or a low temperature would be needed in the condenser, which may require the use of expensive refrigeration. Therefore, a flash tank is used to remove most of the light components before feeding into the column. The flash tank is operated at 29psi. The light gases are compressed to 110 bar and recycled to the reactor [48].

The liquid from the flash tank is pumped into a 42-stage distillation column on stage 27. The column operates at 15psi, and a reflux-drum temperature of 50 °C is used so that cooling water can be used in the condenser. A small vapor stream from the top of the reflux drum recycles the small amount of inert components entering the column. This small vapor is compressed back up to 980 psi and recycled to the reactor. The liquid phase is recycle to the column with a ratio of 0.407 [47].

The stream 'METHANOL' leaves the distillation column and enters the methanol to propylene section.

3.7 Methanol to Propylene

3.7.1 Overview

The Methanol coming from the previous section is partially converted into dimethyl ether (DME). The DME is an intermediate in the MTP process and so a mixture of methanol/DME enhances the efficiency of the upgrade reactions. This mixture is pressurized and heated to the reactor entrance temperature, 500 °F. The feed is separated into four feed streams in order to minimize reactant partial pressure in each reactor and reduce the exothermic heat of reaction which increases the selectivity of propylene [49]. Bigger amounts of the feed stream are sent to the later reactor as there is more product to absorb the heat produced. The first DME feed stream is mixed with the recycle stream rich in C4+ compounds and then diluted with steam, which also serves as heat sink. The DME/methanol/Steam enters the first of the four adiabatic, fixed-bed reactors. In this reactor propylene and several other byproducts are produced. The temperature increase of the stream is used to produce high pressure steam before being mixed with another fraction of the feed and then it goes to the second reactor. The second, third and fourth reactor are operated with the same conditions and procedure: mixing with a fraction of feed, feed to reactor and high pressure steam production [50]. No more steam and recycle steam are added in the reaction train.

The hydrocarbons produced by these reactions ranges from methane to C8+ compounds with presence of some oxygenate. However, for the propose of this study and lack of published data the key components taken into account were: ethylene, propylene, butene, pentene, hexane and heptene.

3.7.2 Reactor design

Each reactor is assumed to convert completely methanol/DME. The reactors were designed in order to provide 100% DME/methanol conversion.

Operating at smaller conversions has the benefit of decreased reactor size and the presence of additional recycled feed to absorb the heat produced, but requires an additional DME separation column in order to separate and recycle the unreacted feed. These columns require significant volumes of water to recover the DME/methanol and subsequent distillation sections to remove the DME/methanol from the water [51]. Any DME that is not recovered also ends up in the final ethylene/propylene separation, reducing the grades of one or both feeds. Since 100% conversion was tested and found feasible at long run times, the high conversion was pursued.

Additionally, further optimization of the reactor conversion and propylene product selectivity could be done by making slight variations in the catalyst across each sequential reactor. Finally, if it were desired to increase the propylene production beyond the conversion ratio specified in this problem, there has been some success recycling C4+ back through the reactor as described by the Lurgi technology [34].

Finally, the conversion assumed for each reactor was based on the study of Tian-Sheng Zhao et all [52] as follows:

Table 3-6 - Conversion MTP reactions

Product	Conversion
Methane	0.77%
Ethylene	4.63%
Propylene	45.44%
Butene	25.40%
Pentene	15.00%
Hexene	5.23%
Heptene	3.53%

The Butene is seen as the liquefied petroleum gas (LPG) byproduct and the mixture of pentene/hexane/heptene is seen as the gasoline produced by the process. However, the separation of the LPG and Gasoline is not modeled in this study.

3.7.3 Modelling

The reactions taking place within the reactor are complicated and not well known. Some kinetic models exist for the methanol-to-olefin process, but these are extremely complicated and do not lend themselves for use in a preliminary design [53]. Another difficulty is that the majority of papers regarding the DME-to-olefin process only show the mole fractions of hydrocarbon or olefin products. An RSTOIC block was used to calculate the outlet product distribution base on the conversion showed on Table 3-6.

Regarding the amount of hydrocarbon that returns to the reactor, Lurgi's process address that 31% of the methanol mass is converted to propylene. Therefore, a design block was set which calculates the amount of hydrocarbon that has to return in order to meet this target yield.

3.8 Separation

The separation model consists of a water quench, compression section, debutanizer and deethanizer .

3.8.1 Water quench

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 [54].

In Aspen Plus, this operation is simulated via an separator block where 97% of water is separated from the raw product stream [55].

3.8.2 Compression

The olefin stream is compressed in 4 stages compressor to 530psi. Between every stage there is an intercooler and then a flash tank. The flash tank separates the gas phase which goes to the next stage compressor from the liquid phase which flows to a pump. This design is assumed in order to reduce size and power required of the compressor section. After the fourth compressor, all streams are mixed and sent to the distillation column.

In Aspen, the block MComp was used with intercoolers designed to reach an outlet stream temperature of 110 ˚C

3.8.3 Debutanizer and Deethanizer

A pressure of 530 psi was chosen for this distillation block in order to make physically viable the use of cold water and low pressure steam as utilities [50]. The column and modeled using a DSTWU block with a recovery key of 99.99% propylene and 0.01% of butene in the distillate.

Propylene and ethylene are removed from the top of the column while the heavier byproducts are separated off of the bottom. The light olefins are further pressurized to 580 psi in a pump and sent to the deethanizer column. The DSTWU block with a recovery key of 99.99% ethylene and 0.01% of propylene in the distillate was assumed.

The ethylene and propylene outlet stream are expanded and used in the deethanizer column condenser in order to minimize the amount of refrigerant utility required. On the other hand, the heavy hydrocarbons leaving the debutanizer are partially recycled to the reactor train and part is assumed as by-product LPG/Gasoline.

Both distillations columns were designed at as high pressure as possible, without approaching the critical pressure of the components and subsequently increasing column diameter in order to minimize the amount of refrigerant required.

3.9 Air Separation Unit

A process flow diagram of cryogenic air separation system is shown in Appendix A. Separation of over 99% of the O2 in the air feed is carried out in two distillation columns thermally linked by a dual-function heat exchanger called as reboiler/condenser. This heat exchanger serves as a reboilers for the HP column and as a condenser for LP column. The LP column operates at low pressure as 1.2 bars which are close to ambient pressure to minimize energy use. The HP column operates at pressure 4 bar [56].

Filtered air is first compressed to 4.2 bars and cooled to 45oC temperature by water cooled heat exchanger. The compressed air then enters a main heat exchanger and is further cooled and partially liquefied by countercurrent heat exchanger with cold nitrogen and oxygen streams from the columns. Partially liquefied air at 4.2 bars pressure enters the HP column [57]. The separated N2 gas condenses to provide reflux to the HP column and enters to the LP column after sub cooling in the sub-cooler. Up to 30% of the air is further compressed to a pressure of 50 bars which gives a positive temperature difference. The refrigeration balance on the plant is provided by expanding a portion of the high pressure air stream in a turbine. The discharge air stream from expander is feed to LP column. The O2 rich liquid stream and a high pressure fraction of the air which has been liquefied are the feed streams to the LP column. The distillation separates N2 gas stream from top of LP column and a liquid O2 stream from bottom of LP column are supplied to main heat exchanger and heated to ambient temperature, which cools and partially liquefies the air feed streams.

3.10 Water issues

Water is required as a reactant, a fluidizing agent, and a cooling medium in this process. As a reactant, it participates in reforming and in water gas shift reactions. In the gasification and MTP process, it also acts as the fluidizing agent in the form of steam.

Water usage is becoming an increasingly important aspect of plant design, specifically with regard to today's environment concerns. Many plants are experiencing significant water supply concerns [58]. For several years, significant areas of water stress have been reported during the growing season, while livestock and irrigation operations also compete for the available resources.

Therefore, a primary design consideration for this process was the minimization of fresh water requirements, which therefore meant minimizing the cooling water demands and recycling process water as much as possible. Air-cooling was used in several areas of the process in place of cooling water (e.g., distillation condensers, compressor interstage cooling).

The following scheme shows the recycling of water modeled in this study. The main ones are in the Gasification and MTP section. The water removed from the flash-drums between each compressor stage are taken to a deaerator in order to get rid of soluble gases. In the meantime, the quench in the MTP process separates a lot of water. Part of it is heated to 707C and introduced into the first propylene reactor. Another fraction is heated up and mixed with the water separated from the flash drums in order to meet the amount of steam required.

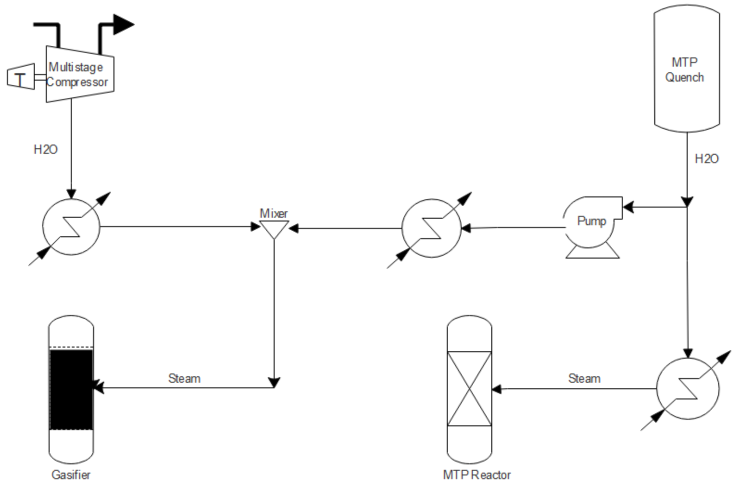


Figure 3-1: Water recycle scheme

3.11 Heat and Power

The power and heat integration were elaborated with the following objectives:

- Zero heating required
- Zero power required

The heat integration was done for the propylene and methanol obtained via direct and indirect gasification. In both integrations, the main goal was to achieve a requirement of zero hot utilities. Since the Tar cracking requires the burning of natural gas, the flue gas produced can be used throughout the plant as a heat source. This excess of heat is then used to produce superheated steam which produces powers in a steam turbine. On the other hand, the cooling utilities calculated by the pinch analysis approach are assumed as the cooling met and are not simulated in the process.

The power production happens in two different sections. The heat released in the formation of methanol produces steam which associated with the flue gas from the fired heater produces superheated steam. This steam at 750˚F and 42 bar runs a steam turbine. The exhaust steam at 140psi is reheated and sent to another turbine. The exhaust steam at 16psi is then cooled in a cooling tower and the condensate is pumped to 42psi and sent to the methanol reactor, starting over the steam cycle.

The second section responsible of producing power uses the purge stream of the methanol synthesis loop and the ethylene produced in the MTP section. The two streams are mixed and sent to a burner at 200psi. The air is also compressed to 200psi. The burning produces superheated steam at 1798psi and 1000 ˚F. The flue gas runs a gas turbine and the steam runs a steam turbine. The exhaust steam at 464psi is reheat by the flue gas to 911 ˚F and sent to the second turbine. The exhaust steam at 10psi is then cooled on a cooling tower and pumped to 1798psi. Before going to the combustor the liquid water exchanges heat with the flue gas coming from the second steam superheater in order to increase the efficiency of the process.

The design goal is to produce a plant with no power requirement. For that reason, if the power produced after the power integration is not equal to the power required, natural gas is burned in other to meet the power necessary.

CHAPTER 4

SIMULATION RESULTS

In this chapter the results of the three main sections will be presented. This data will be confronted with the literature data in order to validate each model. The heat and power integration is also going to be discussed as well as the natural gas requirement and overall yield of methanol and propylene.

The yield calculation is based in a processing of 2,000 dry metric tonnes per day of wet biomass. As the biomass has 20% of moisture, 2,400 metric tonnes are grinded and sent to the drier before taken to the gasification area.

4.1 Direct Gasification

The direct gasification values are obtained directly from a correlation issued by the NREL research lab (see appendix E).

Like it was predicted the syngas produced has a H2/CO ratio quite low for the methanol synthesis. Besides, the tar and methane concentration is quite high reinsuring the necessity of having a tar cracking reactor that is going to breakdown these compounds into H2 and CO as well as the injection of steam that corrects the H2/CO ratio through water-gas shift reaction.

Table 4-1: Syngas composition by Direct Gasification

Gasifier outlet gas composition	mol% (wet)	mol% (dry)
H2	17.62%	22.70%
CO2	29.08%	37.48%
CO	14.98%	19.31%
H2O	22.41%	-
CH4	13.66%	17.61%
C2H6	0.65%	0.84%
C6H6	1.03%	1.33%
TAR	0.32%	0.41%
NH3	0.24%	0.31%
H2S	0.01%	0.01%
N2	0.00%	0.00%
AR	0.00%	0.00%
H2/CO	1.18	1.18
GASIFIER EFFICIENCY	65% HHV 63% LHV	

4.2 Indirect Gasification

The literature data comes from a study done for Proll T. et all for the fast internally circulating fluidized bed (FICFB) reactor [44]. The Table 4-2 shows the comparison of the Literature and model results.

Table 4-2: Syngas composition by Indirect Gasification

Temperature	1562˚F	
Pressure	15.7 PSI	
Gasifier outlet gas composition	**Literature**	**mol% (dry)**
H2	45.80%	45.83%
CO2	21.20%	21.17%
CO	21.60%	21.56%
CH4	10.00%	9.88%
C2H6	-	-
C6H6	-	-
TAR	-	-
NH3 (ppmv dry)	1100-1700	1497
H2S (ppmv dry)	21.5 - 170	101
N2	1.40%	1.40%
H2/CO	2.12	2.13
Syngas LHV MJ/cum (dry at 0˚C and 1 atm)	11.3	11.23
GASIFIER EFFICIENCY (LHV and mass basis)	71.5 - 78.4%	76.7%

As can be seen, the model results are in very good agreement with the literature data. The indirect gasification produces a high H2/CO ratio syngas which is suitable for the methanol synthesis. However, the concentration of 10% of methane still need to be decreased in order to avoid the buildup of inerts in the methanol loop which rapidly increases the capital cost since more power is required as well as bigger equipment. Therefore, the tar cracking is also applied to this syngas which converts 80% of methane into H2 and CO.

Table 4-3: Amount of syngas produced via different gasification methods

Gasifier outlet gas composition (lbmol/h)	Direct	Indirect
H2	2,968.54	8,301.17
CO2	4,900.29	3,833.45
CO	2,524.41	3,905.19
H2O	3,775.40	10,928.30
CH4	2,302.47	1,789.36
C2H6	109.87	0.00
C6H6	173.68	0.00
TAR	53.30	0.00
NH3	40.56	27.12
H2S	1.68	1.83
H2/CO	1.18	2.13
Total Molar flow	16,850.20	28,786.42

The Table 4-3 shows quantitative values from both gasification technologies. The indirect produces a higher amount of syngas in a better ratio for the downstream process. In addition, the tar presented in the direct gasification can generate some operation problems such as clogging. The operation of the indirect is also easier since it is under atmospheric pressure while the Direct operates in a pressure of 480psi. Undoubtedly, the indirect gasification produces a much better syngas for methanol production. However, it has the disadvantage of being a new technology and so all problems and applications are not fully predicted and understood. Having it said, it is still necessary to evaluate both pathways economically since a new technology, although better, could be way more expensive than a less efficient but long used one. Furthermore, the low pressure syngas has to be compressed in a multistage compressor which can be a key factor for the economic viability of this pathway.

4.3 Tar Cracking

The low and high pressure syngas leaving the gasifier are taken to the tar cracking. Steam is added to the reactor in the high pressure case for, once again, correct the ratio of H2/CO. The required energy for these processes is different and so the amount of natural gas burned in order to provide it.

As we can see on the table X, more natural gas is burned to the direct pathway. This might looks disadvantageous in a first sight but it is important to remember that the excess of heat is used to generate power. Again, an economic analysis associated with a power and heat integration has to be done in order to answer if the amount of power generated compensates the higher amount of natural gas burned. Furthermore, in the indirect case natural gas in also burned with the purge/ethylene purge in order to generate the power required by the biomass-propylene process.

Table 4-4: Outlet syngas composition after Tar Cracking and amount of Natural Gas Required

Tar outlet gas composition (lbmol/h)	Direct	Indirect
H_2	11,841.71	12,612.10
CO_2	5,496.67	3,856.18
CO	5,457.88	5,336.22
H_2O	499.17	9,535.80
CH_4	460.49	348.43
C_2H_6	1.10	0.00
C_6H_6	17.37	0.00
TAR	0.05	0.00
NH_3	4.06	2.73
H_2S	1.68	1.83
H_2/CO	2.17	2.36
Natural Gas burned	1,419.33	696.08

Also the H2/CO ratio of the direct syngas was correct to 2.17 which suitable for the methanol reaction. The next cleaning up and conditioning will pressurize the syngas and get rid of the excess water and CO2. The amount of CO2 separated is calculated based on the stoichiometric number.

4.4 Methanol synthesis

The model calculation is confronted with the work of William L. Lyuben from Lehigh University [47].

Table 4-5: Methanol synthesis validation

Pressure of Steam produced	609psi	
Reactor Pressure	980 psi	
Per pass conversion	LITERATURE	Model
CO	64%	62%
CO2	17%	18.5%
Overall		
H2	98.6%	98.13%
CO+CO2	96%	98.27%

These high conversions of reactants indicate that the design has achieved only small losses of the valuable reactants, despite the need to purge out the inert components in the fresh feed (methane and nitrogen). This purge stream contains H2, CO and CH4 which are combustibles gases. Thus, they are later expanded and inserted into a burner which produces superheated stream and then power.

Since the amount of H2/CO/CO2 in the syngas produce via direct gasifier is lower than in the indirect case and the conversion are the same as showed on the table above, it is expected that the direct gasification scenario produces fewer methanol. Consequently, the duty required in the distillation column for the condenser and reboiler and the power required for the compressors should be lower as showed below.

Table 4-6: Methanol production and energy requirement

	Direct	Indirect
Methanol Produced (lb/mol)	5521.62	5852.96
Heat duty - Condenser (Btu/lb)	-1.47E+08	-1.59E+08
Heat duty - Reboiler (Btu/lb)	1.57E+08	1.70E+08
Power to Compressors (HP)	11699.24	12215.89

4.5 MTP

The MTP process is set based on the conversion presented on Table 3-6. Because the process is modeled the same way for the indirect and direct pathways, it is predicted that more olefins and heavier hydrocarbon are produced for the low pressure case since it produces more methanol. Consequently, more energy is required in the reboiler and condenser of the debutanizer and deethanizer column.

The ethylene produced is used as refrigerant and then sent to a burner to produce power. The butene, pentene, hexene and heptene are partially recycled to the reactor train. The other fraction is sold as by-product where butene relates to LPG and mixture pentene/hexene/heptene refers to gasoline as described in chapter two. The propylene produced has 99.99% percent of purity which is crucial for its application in the polymeric industry.

The results are showed below for the two scenarios of syngas production.

Table 4-7: Propylene production and energy requirement

Propylene	1303.46478	1381.74035
Butene	144.165368	152.907444
Pentene	85.10249	90.26307
Hexene	29.6724	31.47172
Heptene	20.02745	21.24191
Dethanizer- Condenser duty (BTU/H)	3.20E+06	3.40E+06

4.6 Heat and Power Integration

After the completion of the model including the water integration, Aspen Energy Analyzer was used to calculate the minimum energy requirement for both designs. The grand composite curve was chosen to show the results since it is immediately possible to identify if heating or cooling is required. However, the heating required for both process is zero since natural gas is burned in the fired heater associated with the tar cracking reactor. The excess of each is used in the model to produce power and so no visible excess heat is show in the grand composite curve.

The two cases will be presented separately and another section is going to compare directly the results obtained.

4.6.1 Direct gasification scenario

It is already known that this technology requires a high pressure of oxygen which is obtained through an air separation unit. This separation is conducted under very low temperature of 200C and so very low temperature refrigerant is required. The refrigerant plant is not modeled in this study and so it is assumed that this refrigerant is purchasable.

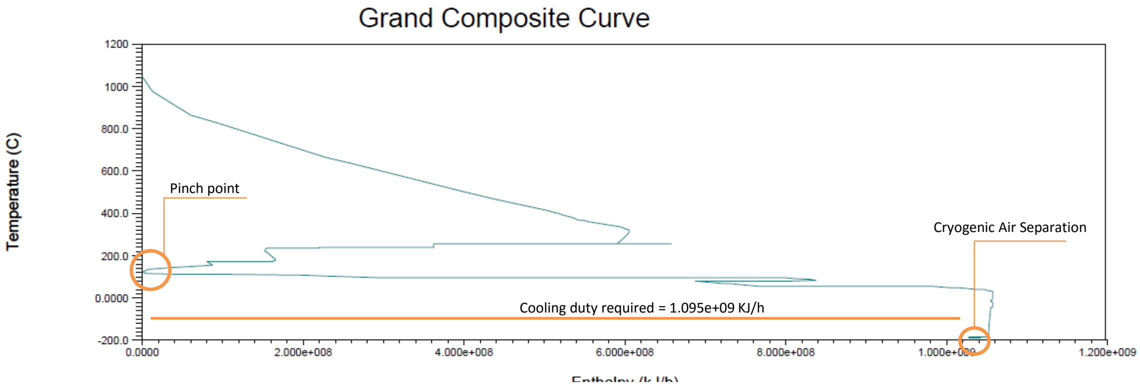


Figure 4-1: Grand Composite Curve for the Direct Gasification case

Considering an temperature approach of 10C the pinch point is showed in the figure. Its value is 129C for the hot stream and so 119C for the cold stream.The pinch analysis method calculated an heat duty of 1.095e+09 that is going to be met with cooling water, air and refrigerant.

4.6.2 Indirect Gasification scenario.

The indirect gasifier does not require a high pressure of air and so it does not require a very low temperature refrigerant. However, a refrigerant still required since the ethylene/propylene column uses low temperatures in order to condense the propylene/ethylene mixture.

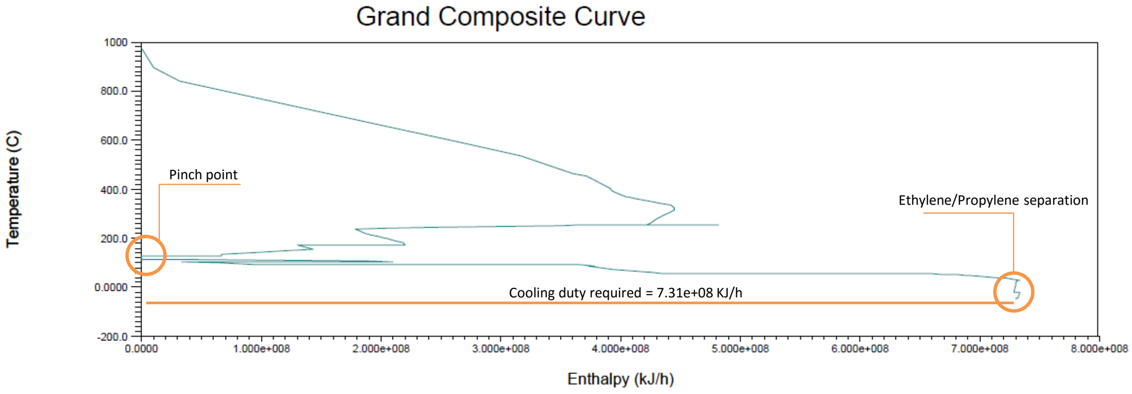


Figure 4-2: Gran Composite Curve for the Indirect Gasification case

The pinch point is at 129.9/119.9C and the indirect requires 7.31e+08 KJ/h which is met with air and refrigerant.

There can be various designs for the heat exchanger network based on design objectives. One particular design was used for this study and can be seen on the Appendix D. It is designed particularly for the indirect case, however as the processes are very similar it can be used for the direct as well. The streams in the direct that does not exist in the indirect as assumed to be satisfied directly by a utility. This might not be the best design for the direct gasifier, but aspen plus energy shows that is near the optimum.

4.7 Overall comparison

The Table below show the overall yield of dry biomass to methanol and propylene process. The lb/lb express the mass of the product per mass of biomass fed to the system. Carbon/Carbon express the amount of biomass carbon is converted into the desired product and the MW_{HHV} express how much the heating value is passed into the product and so it works as an energy efficiency indicator.

$$\boldsymbol{MW_{HHV} = \frac{m_{prod} * HHV_{prod}}{m_{biomass} * HHV_{biomass}}} \qquad \textbf{(4-1)}$$

The lb/lb and carbon/carbon yields indicates that the indirect gasification leads to a bigger production of methanol and propylene. The MW_{HHV} in association with the CH4 required show that the low pressure technology also conserves more energy throughout the process.

Table 4-8: Overall process yield

Process	**Dry Biomass to Methanol**		**Biomass to Propylene**	
Yield	Direct	Indirect	Direct	Indirect
lb/lb	57.18%	60.61%	17.73%	18.79%
Carbon/Carbon	44.07%	46.72%	31.21%	33.09%
MW_{HHV}/MW_{HHV}	32.74%	71.80%	3.15%	64.09%

Technology	**Direct**	**Indirect**
CH4 burned (lbmol/h)	1,419.33	839.8278
Net power (HP)	-21,141.39	-1,005.01

The Direct gasification requires 40% more natural gas then the indirect gasifier. However, it produces almost 20 times more energy. For that reason, although the indirect gasifier looks more promising pathway for this study. It is still necessary to evaluate economically in order to check if the high production of power compensates extra costs that in the indirect does not exist such as the air separation unit and the extra natural gas burned.

After the heat integration, the mass flow amounts required of air and refrigerant are as follows:

Table 4-9: Utilities Required

Mass flow (kg/h)	**Direct**	**Indirect**
Air	2.08E+08	1.45E+08
Refrigerant	-	2.90E+05

The direct gasification does not required a refrigerant because the cryogenic air separation produces O2 at very low temperature that can be used in the condenser of the deethanizer column. The Appendix E reveals more details of the pinch analysis and the heat exchanger network design.

CHAPTER 5

ECONOMIC ANALYSIS

This section describes the cost areas and the assumptions made to complete the discounted cash flow analysis. Basically the total project investment (based on total equipment cost), as well as variable and fixed operating costs, were developed first. With these costs, a discounted cash flow analysis was used to determine the production cost of propylene

5.1 Capital Costs

This section discusses the methods and sources for determining the capital cost of each piece of equipment within the plant. A summary of the individual equipment costs can be found in Appendix X.

The handling and gasification area capital cost estimates are based on previous NREL reports [41] [59]. The others areas estimates were primarily from Icarus. The capital costs of heat exchangers from pinch analysis were also obtained from Aspen Icarus Process Evaluator. Since the equipment costs are from similar sources, it puts both technologies on a similar cost basis for comparison purposes.

Using the estimated equipment costs, the purchased cost of the equipment for the specific size of the plant and the cost year was calculated. Cost factors were then used to determine the installed equipment cost. The factors used in determining the total installed cost (TIC) of each piece of equipment are the same used in the NREL reports mentioned above. They are showed in the table below.

Table 5-1: Cost factors to determine TIC

Total Purchased Equipment Cost (TPEC)	100
Purchased equipment installation	39
Instrumentation and controls	26
Piping	31
Electrical systems	10
Buildings (including services)	29
Yard improvements	12
Total Installed Cost (TIC)	247

The indirect costs (non-manufacturing fixed-capital investment costs) were estimated using the same cost factors as in the NREL reports. The factors are shown in Table 5-2: Indirect cost factors

and have been put as percentages in terms of total installed cost (TIC).

Table 5-2: Indirect cost factors

Indirect Costs	**% TIC**
Engineering	13
Construction	14
Legal and contractors fees	9
Project contingency	3
Total Indirect Costs	**39**

Because the main goal of this work is to compare rather than develop an rigorous economic evaluation, only the main equipment for each area were costed and they can be seen on Appendix F. Furthermore, in order to maintain consistency and so be able to compare, the sizing approach and consideration were the same for both pathways.

The costs of reactors, heat exchangers, compressors, blowers, and pumps were estimated using Aspen Icarus Process Evaluator (IPE). The capital cost for the Air Separation Unit was obtained from literature [60] . Installed cost provided was converted to equipment cost using a factor of 2.47, which is the average installation factor for this study.

5.2 Operation Costs

There are many variable operating costs accounted for in this analysis. The variables, information about them, and costs associated with each variable are shown in Table 5-3.

Table 5-3: Variable Operation Costs

Variable	Information and Operating Cost
Dry Feedstock	Price:\$0.02/lb [59]
Tar Reformer Catalyst	Amount of Catalyst set to be equal of the report of Phillips et all [9]. Price: \$4.65/lb
Methanol Catalyst	Calculated using the catalyst density, bed voidage and reactor volume conform Lyben [47]. Refilled each 5 years. Price:\$4.54/lb
MTP Catalyst	Calculated based on WSHV of 1.5h^{-1}. [51] Refilled each 5 years Price:\$6.80/lb [61]
Electricity	Price:\$0.05/KWh [59]
Sand/ash Purge	Disposal Price: \$0.0111/lb [59]
Air utility	Price: \$1.00E-09/KWh (Icarus)
Refrigerant	Price: \$2.74E-06 /KWh (Icarus)
Natural Gas	Price: \$0.08/KWh [59]

The air utility and refrigerant does not only for the purchase of the utilities but also for the equipment necessary for their application such as blowers, vents and so on. Note also that the Methanol and MTP catalyst are refilled each 5 years.

The fixed operating costs (salaries, overhead, maintenance, etc.) used here are identical to those in the study by Phillips et al [41].

The fixed operating costs used in this analysis are shown in Table 5-4: Fixed Operation Costsand are also base in the Philips et all report [41]. They are shown in 2002 U.S. dollars. The same process based on Table 2-3 was used to correct these values to US dollars of 2015.

Table 5-4: Fixed Operation Costs

Fixed Operating Costs	**Labors**	**Value**
Plant Manager	1	110000
Plant Engineer	1	65000
Maintenance Supervisor	1	60000
Lab Manager	1	50000
Shift Supervisor	5	45000
Lab Technician	2	35000
Maintenance Technician	8	40000
Shift operators	20	40000
Yard employees	12	25000
Clerks & secretaries	3	25000
Overhead/Maint	-	95% labor
Maintenance	-	2%TPI
Insurance & Taxes	-	2%TPI

5.3 Value of Co-Products

The MTP process not only produces propylene but also gasoline and liquefied petroleum gas (LPG). These components present relatively high economic values and so are sold as byproducts.

The components produced by the model are ethylene, propylene, butene, pentene, hexene and heptene. The ethylene is fully used to produce power and so has no value as co-product. The butene produced is assumed to be the amount of LPG produced. Moreover, the mixture of pentene/hexene/heptene is also assumed as the amount of gasoline produced.

The price assumed for the LPG is \$0.45/gal [62] and for gasoline the price is \$2/gal [63] obtained by an average price throughout USA.

5.4 Minimum Propylene Price

Once the capital and operating costs were determined, a minimum propylene selling price was calculated using a discounted cash flow rate of return analysis. The methodology used is identical to that used in Phillips et al.2 [41] .The value is the selling price of ethanol that makes the net present value of the process equal to zero with a 10% discounted cash flow rate of return over a 20 year plant life. The base case economic parameters used in this analysis are given in Table 5-5: Economic Assumptions

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Table 5-5: Economic Assumptions

Assumption	Value
Internal Rate of return	10%
Plant Life	20 years
General Plant depreciation	200% DDB
Startup time	Neglected
Working Capital	5% of TCI

5.5 Economic Results

At last the two pathways of syngas production were compared regarding the capital cost necessary, operation costs and the minimum price of propylene required. The figure below show the difference of capital required to buy and install the equipment as well as the pipes, instrumentations and other.

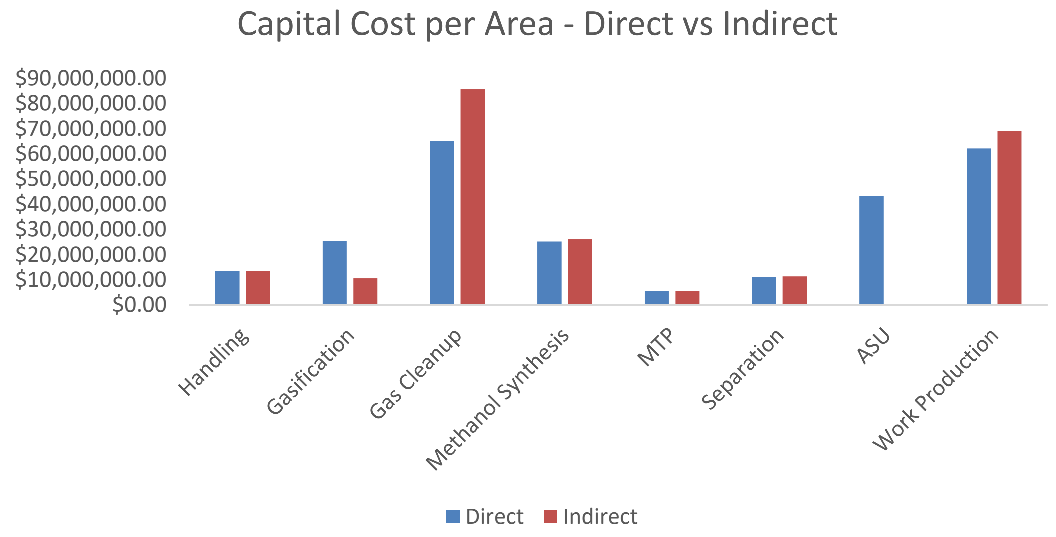


Figure 5-1: Capital Cost per Area

For the handling area the capital required is the same since the same amount of biomass is processed. The Direct gasifier shows a higher cost regarding the indirect gasifier due to the high operation pressure required. After that area, the indirect case requires a bigger investment since it produces more syngas which, consequently, increase the size required for the hardware. Also because of the higher amount of syngas, the work production area is more expensive since more purge from the methanol synthesis is sent to the steam cycle. The total capital cost required is roughly MM$262 for the direct case and MM$232 for the indirect case. The difference of capital cost is mainly resulted of the ASU since it requires an extra MM$43 while it is not a requirement for the other gasifier.

As showed in the pinch analysis, the direct pathway generates a big amount of electricity. However, Figure 5-2: Operation Costs shows that the indirect pathway still cheaper regarding the operation costs with MM$27/year against MM$29/year of the high pressure case. What compensates the income produced by selling electricity is the fixed cost as maintenance, insurance and taxes that are a function of capital cost. The bigger amount of hardware required increase the price of maintenance which compensates the income made by selling electricity, making the overall operation cost more expensive.

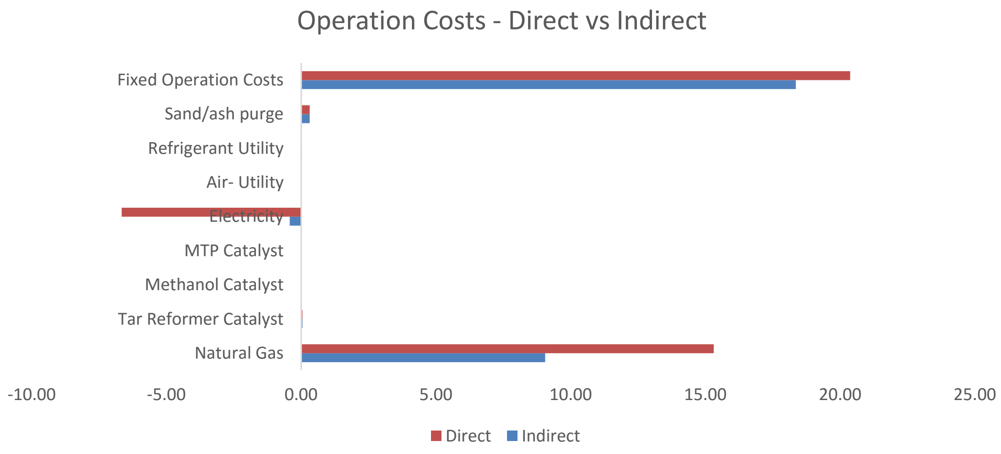


Figure 5-2: Operation Costs

After a discounted cash flow (see Appendix G) with the economic assumptions listed on Table 5-5: Economic Assumptions

, the minimum price of propylene is $424.86/ton and $336.50/ton respectively. Both values are lower than the price of propylene nowadays, $786/ton [64]. The economic analysis was not done rigorously in order to compare the price calculated with a real price. However, it indicates that the indirect technology has potential to produce propylene in a competitive price and so a future work would be trying to design and optimize more rigorously the low pressure case.

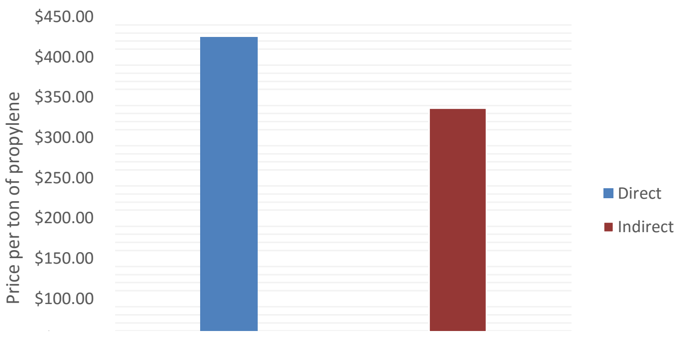


Figure 5-3: Minimum Price Required

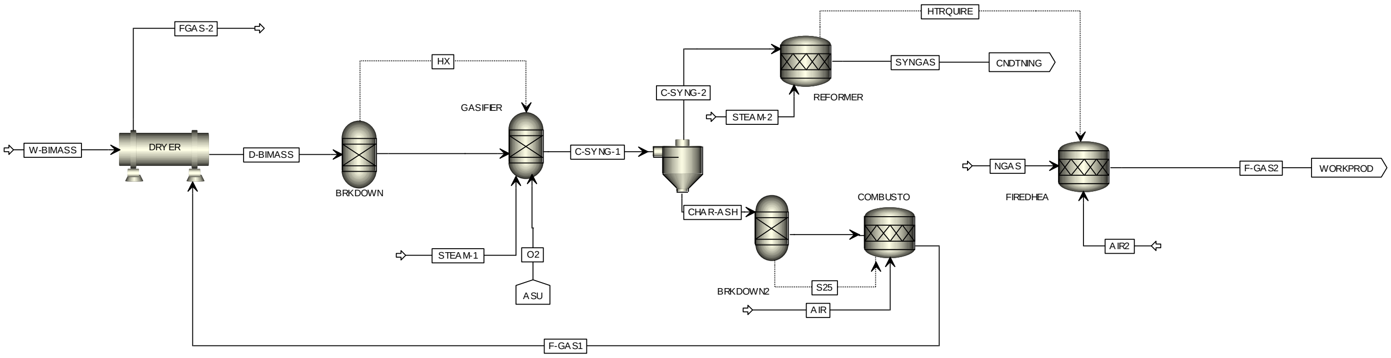
CONCLUSION

After modeling, validations, water recycle, heat integration and power integration, both models were evaluated economically. The indirect gasification showed better yield of propylene as well as lower total project investment, operation costs and finally a better economic performance ratified by a lower minimum price of propylene.

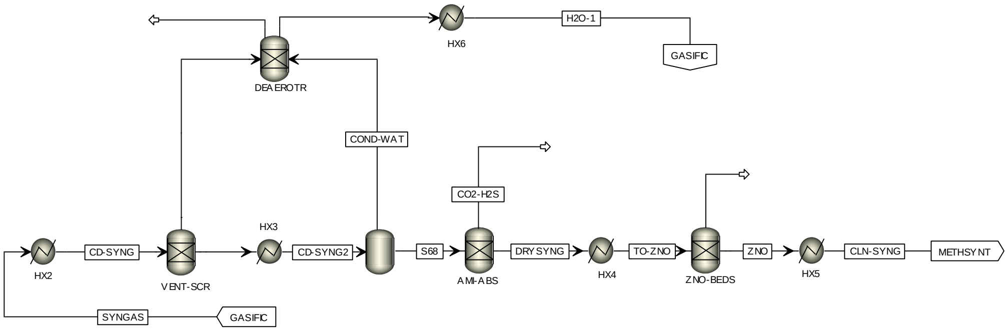
For a future study, the indirect gasification should be the technology of choice to be focused on improving the design, optimization and the economic assumptions as it is showed in this study as the most promising technology.

APPENDIX A

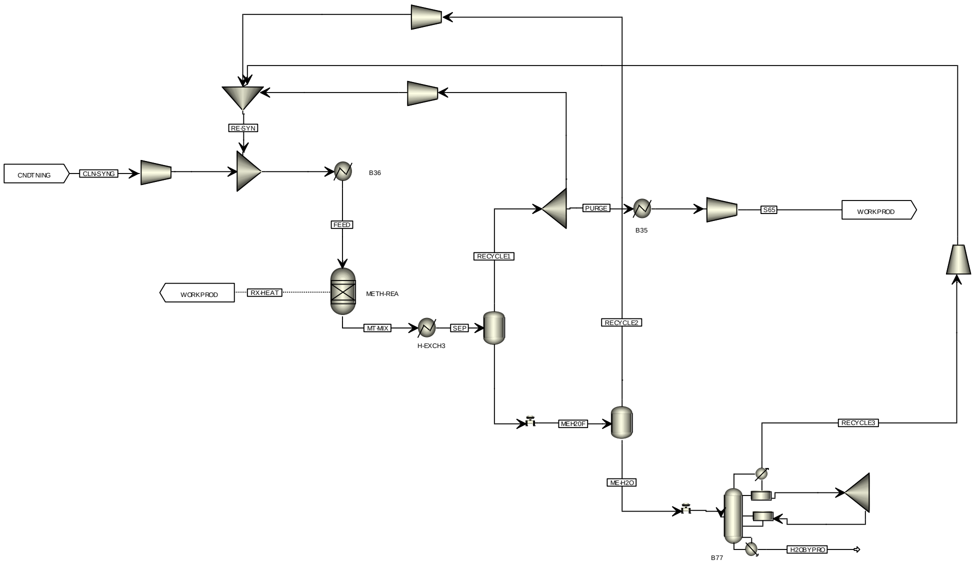
Simulation flowsheet for direct gasification case



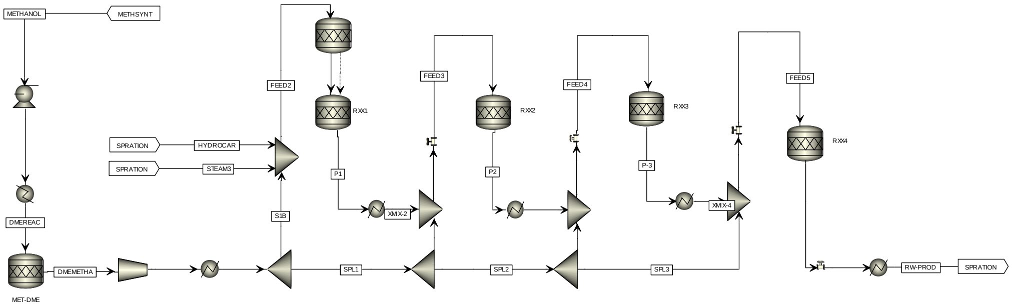
Mole Flow lbmol/hr	W-BIMASS	D-BIMASS	STEAM-1	O2	CHAR-ASH	AIR	F-GAS1	C-SYNG-1	C-SYNG-2	STEAM-2	SYNGAS	NGAS	AIR2	F-GAS2	
H2	0	-	0	0	0	0	0	2968.54	2968.54	0	11841.71	0	0	0	
H2O	0	0	3435.091	0	0	0	757.2073	3775.395	3775.395	850	499.1665	0	0	2838.774	
CO	0	0	0	0	0	0	0	2524.41	2524.41	0	5457.879	0	0	0	
CO2	0	0	0	0	0	0	1005.931	4900.293	4900.293	0	5496.673	0	0	1419.387	
N2	0	0	0	8.93E-15	0	5245.41	5246.115	0	0	0	18.25304	0	10892.78	10892.78	
NH3	0	0	0	0	0	0	0	40.56231	40.56231	0	4.056231	0	0	0	
H2S	0	0	0	0	0	0	0	1.678481	1.678481	0	1.678481	0	0	0	
O2	0	0	0	2112.842	0	1412.226	31.04349	0	0	0	0	0	2895.55	56.77549	
AR	0	0	0	0	0	67.24884	67.24884	0	0	0	0	0	0	0	
CH4	0	0	0	0	0	0	0	2302.473	2302.473	0	460.4947	1419.325	0	0	
C2H6	0	0	0	0	0	0	0	109.8652	109.8652	0	1.098652	0	0	0	
C6H6	0	0	0	0	0	0	0	173.6804	173.6804	0	17.36804	0	0	0	
C10H8	0	0	0	0	0	0	0	53.2996	53.2996	0	0.0532996	0	0	0	
Total Flow lbmol/hr	0	0	3435.091	2112.842	0	6724.884	7107.701	16850.2	16850.2	850	23798.43	1419.325	13788.33	15207.72	
Temperature	60	200	769	370		150	3876.188	1600	1600	769	1600	61	90	1800.047	
Pressure psia	15.7	15.7	438	438	438	430	16	438	438	438	438	15	15	15	
Vapor Frac	0	0	1	1		1	1	1	1	1	1	1	1	1	**Area(s) : 100 - 200**
BIOMASS (lb/h)	367437	309421	0	0	0	0	0	0	0	0	0	0	0	0	**Scenario:Direct Gasification**
CHAR (lb/h)	0	0	0	0	17155.46	0	0	17155.46	0	0	0	0	0	0	**Project: Master Thesis**
ASH (lb/h)	0	0	0	0	0	0	3409.815	0	0	0	0	0	0	0	**Author: Bernardo Lousada**



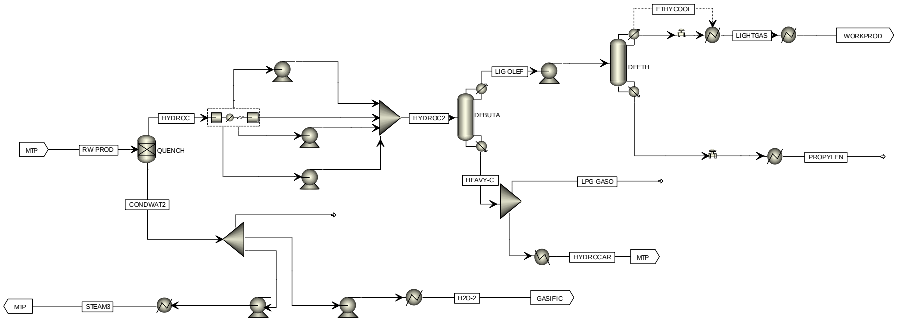
Mole Flow lbmol/hr	**SYNGAS**	**CD-SYNG**	**COND-WAT**	**CD-SYNG2**	**H2O-1**	**CO2-H2S**	**DRYSYNG**	**TO-ZNO**	**ZNO**	**CLN-SYNG**	
H2	11841.71	11841.71	0.00195235	11841.71	0	0	11841.71	11841.71	11841.71	11841.71	
H2O	499.1665	499.1665	425.1593	494.1748	430.151	66.9834	2.032116	2.032116	2.032116	2.032116	
CO	5457.879	5457.879	0.00045906	5457.879	0	0	5457.878	5457.878	5457.878	5457.878	
CO2	5496.673	5496.673	0.044318	5496.673	0	5203.33	293.2981	293.2981	293.2981	293.2981	
N2	18.25304	18.25304	1.92E-06	18.25304	0	0	18.25304	18.25304	18.25304	18.25304	
NH3	4.056231	4.056231	0.7456884	4.056231	0	0	3.310543	3.310543	3.310543	3.310543	
H2S	1.678481	1.678481	0.000372858	1.678481	0	0.1678108	1.510297	1.510297	0	0	
CH4	460.4947	460.4947	0.000385463	460.4947	0	0	460.4943	460.4943	460.4943	460.4943	
C2H6	1.098652	1.098652	9.52E-07	1.098652	0	0	0	0	0	0	
C6H6	17.36804	17.36804	0.000164773	17.36804	0	0	0	0	0	0	
C10H8	0.0532996	0.0532996	1.20E-07	0.0532996	0	0	0	0	0	0	
Temperature F	1600	360	110	110	769	130	110	750	750	110	**Area(s) : 300**
Pressure psia	438	438	438	438	438	19.6	438	438	438	438	**Scenario:Direct Gasification**
Vapor Frac	1	1	0	0.9820979	1	1	1	1	1	1	**Project: Master Thesis**
Total Flow lbmol/hr	23798.43	23798.43	425.9526	23793.44	430.151	5270.482	18097	18097	18095.49	18095.49	**Author: Bernardo Lousada**



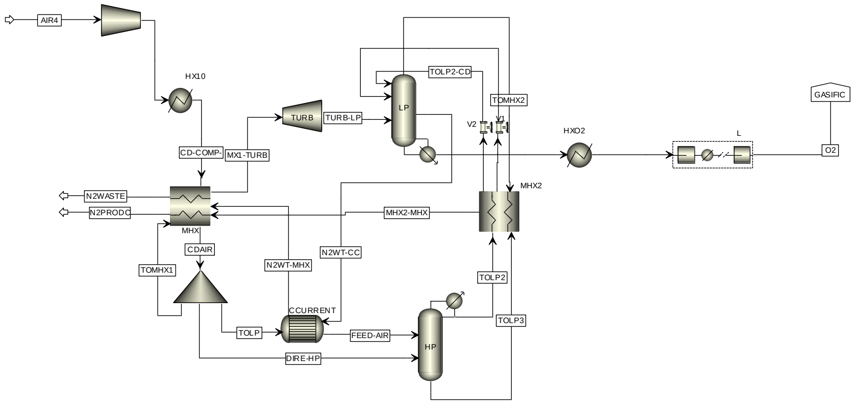
Mole Flow lbmol/hr	**CLN-SYNG**	**RE-SYN**	**FEED**	**MT-MIX**	**SEP**	**RECYCLE1**	**PURGE**	**S65**	**MEH2OF**	**RECYCLE2**	**ME-H2O**	**RECYCLE3**	**METHANOL**	
H2	11841.71	10602.55	22444.25	10841.41	10841.41	10834.65	238.3622	238.3622	6.760696	6.745162	0.0155343	0.0154945	3.98E-05	
H2O	2.032116	4.833459	6.865574	279.1564	279.1564	4.348699	0.0956713	0.0956713	274.8077	0.5553268	274.2523	0.0254516	2.780922	
CO	5457.878	2879.386	8337.264	2944.278	2944.278	2939.805	64.6757	64.6757	4.472939	4.444887	0.0280518	0.0278694	0.000182401	
CO2	309.8495	1613.392	1923.242	1650.951	1650.951	1563.245	34.39138	34.39138	87.70625	67.68125	20.02499	16.8796	3.145407	
N2	18.25304	813.6173	831.8703	831.8703	831.8703	828.9813	18.23759	18.23759	2.889037	2.846855	0.0421825	0.0416004	0.000582171	
NH3	3.309625	14.20324	17.51287	17.51287	17.51287	10.92317	0.2403097	0.2403097	6.589702	1.413878	5.175824	2.10664	3.069184	
CH4	460.4943	20596.66	21057.16	21057.16	21057.16	20908.16	459.9796	459.9796	148.9937	144.211	4.782674	4.646423	0.1362504	
CH3OH	0	506.8739	506.8739	6172.151	6172.151	330.7454	7.2764	7.2764	5841.405	38.90007	5802.505	144.5229	5521.621	
Total Flow lbmol/hr	18093.52	37031.52	55125.04	43794.49	43794.49	37420.86	823.2589	823.2589	6373.625	266.7984	6106.827	168.2659	5530.753	**Area(s) : 400**
Temperature F	110	118.4732	302	507.2	100.4	99.58005	99.58005	223.7405	98.29563	98.29564	98.29564	140	140	**Scenario:Direct Gasification**
Pressure psia	438	980	980	980	980	929.2368	929.2368	220	29.00755	29.00755	29.00755	14.50377	14.50377	**Project: Master Thesis**
Vapor Frac	1	1	1	1	0.8541898	1	1	1	0.0418598	1	0	1	0	**Author: Bernardo Lousada**



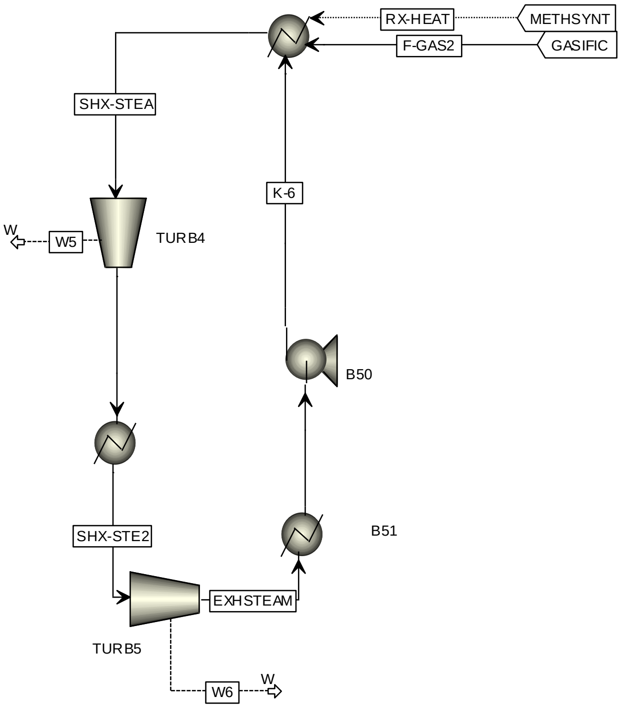
Mole Flow lbmol/hr	**METHANOL**	**DMEREAC**	**DMEMETHA**	**HYDROCAR**	**STEAM3**	**S1B**	**FEED2**	**SPL1**	**P1**	**SPL2**	**FEED3**	**P2**	**SPL3**	**FEED4**	**P3**	**FEED5**	**RW-PROD**	
H2	TRACE	TRACE	TRACE	TRACE	TRACE	TRACE	TRACE	TRACE	TRACE	TRACE	TRACE	TRACE	TRACE	TRACE	TRACE	TRACE	TRACE	
H2O	2.780922	2.780922	2211.429	365.3749	9300	398.0572	10063.43	1813.372	10655.15	1326.861	11141.66	11869.44	552.857	12643.44	13801.49	14354.34	15181.52	
CO	0.000182401	0.000182401	0.000182401	5.83E-30	0	3.28E-05	3.28E-05	0.000149569	4.619815	0.000109441	4.619855	5.691006	4.56E-05	5.69107	7.191684	7.19173	8.26102	
CO2	3.145407	3.145407	3.145407	1.33E-16	0	0.5661733	0.5661733	2.579234	0.5661733	1.88725	1.258158	1.258158	0.7863514	2.359056	2.359056	3.145407	3.145407	
N2	TRACE	TRACE	TRACE	TRACE	TRACE	TRACE	TRACE	TRACE	TRACE	TRACE	TRACE	TRACE	TRACE	TRACE	TRACE	TRACE	TRACE	
NH3	3.069184	3.069184	3.069184	2.77E-06	0	0.5524531	0.5524559	2.516731	0.5524559	1.841515	1.227671	1.227671	0.7672956	2.301891	2.301891	3.069187	3.069187	
CH4	0.1362504	0.1362504	0.1362504	2.22E-22	0	0.024525	0.024525	0.1117253	9.264089	0.0817504	9.294064	11.43637	0.0340625	11.48405	14.48528	14.51934	16.65793	
CH3OH	5521.621	5521.621	1104.324	0	0	198.7783	198.7783	905.5458	0	662.5963	242.9495	0	276.0809	386.5154	0	276.0809	0	
DME	0	0	2208.648	0	0	397.5567	397.5567	1811.092	0	1325.193	485.8989	0	552.1618	773.0308	0	552.1618	0	
ETHY	0	0	0	1.50E-12	0	0	1.50E-12	0	77.54126	0	77.54126	92.37036	0	92.37036	115.9699	115.9699	132.8267	
PROPYL	0	0	0	0.1045875	0	0	0.1045875	0	761.1143	0	761.1143	906.6508	0	906.6508	1138.262	1138.262	1303.699	
BUTENE	0	0	0	584.5166	0	0	584.5166	0	425.3884	0	425.3884	506.7402	0	506.7402	636.2062	636.2062	728.6819	
PENTENE	0	0	0	345.2215	0	0	345.2215	0	251.2136	0	251.2136	299.256	0	299.256	375.7123	375.7123	430.324	
HEXENE	0	0	0	120.3672	0	0	120.3672	0	87.58981	0	87.58981	104.3406	0	104.3406	130.9984	130.9984	150.0396	
HEPTENE	0	0	0	81.24212	0	0	81.24212	0	59.11893	0	59.11893	70.42492	0	70.42492	88.41763	88.41763	101.2696	
Total Flow lbmol/hr	5530.753	5530.753	5530.753	1496.827	9300	995.5356	11792.36	4535.218	12332.12	3318.461	13548.87	13868.83	1382.688	15804.61	16313.39	17696.08	18059.49	**Area(s) : 500**
Temperature F	140	500	712.4565	707	707	707	705.3386	707	721.2695	707	619.1876	703.1519	707	649.7119	761.233	636.5632	114	**Scenario:Direct Gasification**
Pressure psia	14.50377	174.0453	174.0453	530	450	450	450	450	450	450	370	370	450	260	260	35	35	**Project: Master Thesis**
Vapor Frac	0	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	0.1651829	**Author: Bernardo Lousada**



Mole Flow lbmol/hr	**RW-PROD**	**HYDROC**	**CONDWAT2**	**STEAM3**	**H2O-2**	**HYDROC2**	**HEAVY-C**	**LPG-GASO**	**HYDROCAR**	**LIG-OLE**	**LIGHTGAS**	**PROPYLEN**	
H2	TRACE	TRACE	TRACE	TRACE	TRACE	TRACE	TRACE	TRACE	TRACE	TRACE	TRACE	TRACE	
H2O	15181.52	455.4455	14726.07	9300	3859.827	455.4455	455.4455	90.07061	365.3749	0	0	0	
CO	8.26102	8.26102	0	0	0	8.26102	7.27E-30	1.44E-30	5.83E-30	8.26102	8.26102	2.60E-16	
CO2	3.145407	3.145407	0	0	0	3.145407	1.66E-16	3.28E-17	1.33E-16	3.145407	3.145401	6.51E-06	
N2	TRACE	TRACE	TRACE	TRACE	TRACE	TRACE	TRACE	TRACE	TRACE	TRACE	TRACE	TRACE	
NH3	TRACE	TRACE	TRACE	TRACE	TRACE	TRACE	TRACE	TRACE	TRACE	TRACE	TRACE	TRACE	
CH4	16.65793	16.65793	0	0	0	16.65793	2.76E-22	5.47E-23	2.22E-22	16.65793	16.65793	4.55E-11	
ETHY	132.8267	132.8267	0	0	0	132.8267	1.87E-12	3.69E-13	1.50E-12	132.8267	132.8134	0.0132826	
PROPYL	1303.699	1303.699	0	0	0	1303.699	0.1303699	0.0257824	0.1045875	1303.569	0.1303569	1303.439	
BUTENE	728.6819	728.6819	0	0	0	728.6819	728.6091	144.0925	584.5166	0.0728681	0	0.0728681	
PENTENE	430.324	430.324	0	0	0	430.324	430.324	85.10249	345.2215	0	0	0	
HEXENE	150.0396	150.0396	0	0	0	150.0396	150.0396	29.6724	120.3672	0	0	0	
HEPTENE	101.2696	101.2696	0	0	0	101.2696	101.2696	20.02745	81.24212	0	0	0	
Total Flow lbmol/hr	18059.49	3333.421	14726.07	9300	3859.827	3333.421	1865.818	368.9912	1496.827	1467.603	161.0729	1306.53	**Area(s) : 600**
Temperature F	114	114.0622	114	707	769	117.3368	336.5448	336.5448	707	144.676	77	77	**Scenario:Direct Gasification**
Pressure psia	35	35	35	450	438	530	530	530	530	530	200	16	**Project: Master Thesis**
Vapor Frac	0.1651829	1	0	1	1	0	0	0	1	0	1	1	**Author: Bernardo Lousada**



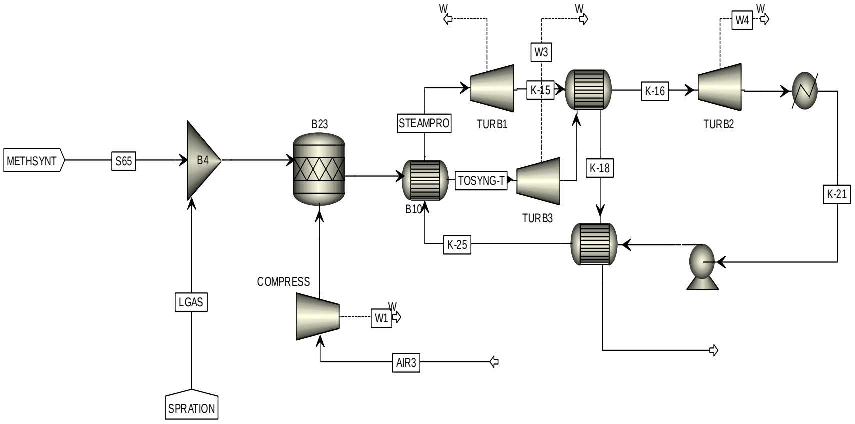
Mole Flow lbmol/hr	**AIR4**	**CD-COMP-**	**CDAIR**	**TOMHX1**	**DIRE-HP**	**TOLP**	**FEED-AIR**	**MX1-TURB**	**TURB-LP**	**N2WT-MHX**	**N2WT-CC**	**MHX2-MHX**	**TOLP3**	**TOLP2**	**TOLP2-CD**	**TOMHX2**	**O2**	**N2WASTE**	**N2PRODC**	
N2	14153.2	14153.2	14153.2	9694.941	707.6599	3750.597	3750.597	9694.941	9694.941	0.0643666	0.0643666	14153.2	1301.163	3157.094	3157.094	14153.2	8.93E-15	0.0643666	14153.2	
O2	3762.242	3762.242	3762.242	2577.136	188.1121	996.9943	996.9943	2577.136	2577.136	0.0679107	0.0679107	1649.4	1063.503	121.6036	121.6036	1649.4	2112.842	0.0679107	1649.4	
Total Flow lbmol/hr	17915.44	17915.44	17915.44	12272.08	895.772	4747.592	4747.592	12272.08	12272.08	0.1322773	0.1322773	15802.6	2364.666	3278.698	3278.698	15802.6	2112.842	0.1322773	15802.6	**Area(s) : 600**
Temperature F	77	113	-207.67	-207.67	-207.67	-207.67	-207.6777	-188.716	-321.057	-216.67	-321.4429	-324.6336	-288.0716	-295.4598	-328.3324	-324.6336	370	77	75.28677	**Scenario:Direct Gasification**
Pressure psia	14.50377	440.8785	440.8785	440.8785	440.8785	440.8785	440.8785	440.8785	8.817569	8.412189	8.412189	8.122113	55.84461	55.84461	8.082772	8.122113	438	8.412189	8.122113	**Project: Master Thesis**
Vapor Frac	1	1	1	1	1	1	1	1	0.9089388	1	0	1	5.46E-06	0	0.1584841	1	1	1	1	**Author: Bernardo Lousada**



Mole Flow lbmol/hr	**SHX-STEA**	**SHX-STE2**	**EXHSTEAM**	**K-6**
H2O	27350.85	27350.85	27350.85	27350.85
Temperature F	750	610	249.2749	247.737
Pressure psia	609.1585	110	16	609.1585
Vapor Frac	1	1	1	0

ENERGY	**W18**	**W19**
POWER hp	-28,038.73	-32,104.83

Area(s) : WORD PRODUCTION 1
Scenario:Direct Gasification
Project: Master Thesis
Author: Bernardo Lousada



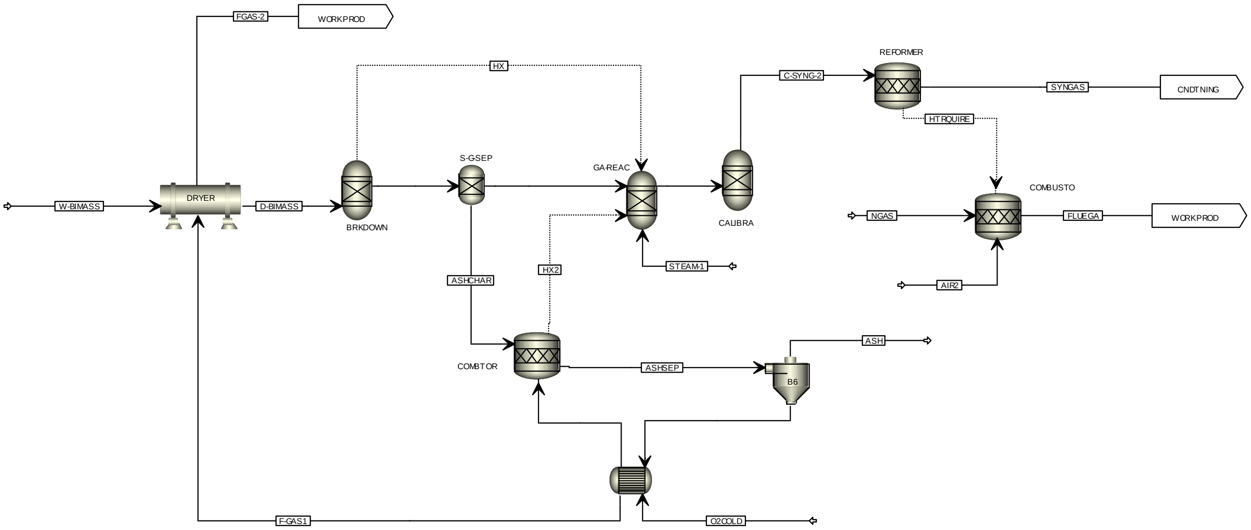
Mole Flow lbmol/hr	**S65**	**LGAS**	**AIR3**	**K-25**	**STEAMPRO**	**K-15**	**K-16**	**K-18**	**K-21**
H2	238.3622	3.98E-05	0	0	0	0	0	0	0
H2O	0.0956713	0	0	8488.759	8488.759	8488.759	8488.759	1472.304	8488.759
CO	64.6757	8.26102	0	0	0	0	0	0	0
CO2	34.39138	3.145401	0	0	0	0	0	860.4053	0
N2	18.23759	0.000582171	5999.521	0	0	0	0	6017.759	0
NH3	0.2403097	0.0642019	0	0	0	0	0	0.3045117	0
O2	0	0	1594.809	0	0	0	0	75.9433	0
CH4	459.9796	16.65793	0	0	0	0	0	0	0
CH3OH	7.2764	0	0	0	0	0	0	0	0
ETHY	0	132.8134	0	0	0	0	0	0	0
PROPYL	0	0.1303569	0	0	0	0	0	0	0
Total Flow lbmol/hr	823.2589	161.0729	7594.33	8488.759	8488.759	8488.759	8488.759	8426.716	8488.759
Temperature F	223.7405	77	68	352.9033	999.9835	617.9313	911	649.9939	197.6834
Pressure psia	220	200	15.7	1798.468	1798.468	464.1208	464.1208	14.69595	10.15264
Vapor Frac	1	1	1	0	1	1	1	1	0

ENERGY	**W7**	**W8**	**W9**	**W10**
POWER hp	13,648.48	-9,364.64	-28,519.35	-20,873.70

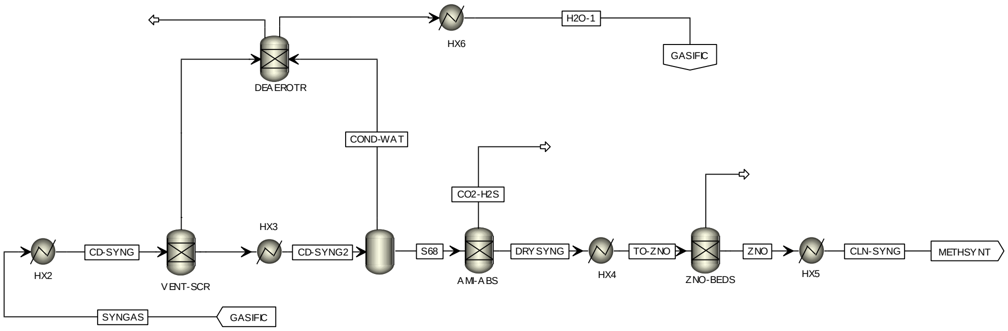
Area(s) : WORD PRODUCTION 2
Scenario:Direct Gasification
Project: Master Thesis
Author: Bernardo Lousada

APPENDIX B

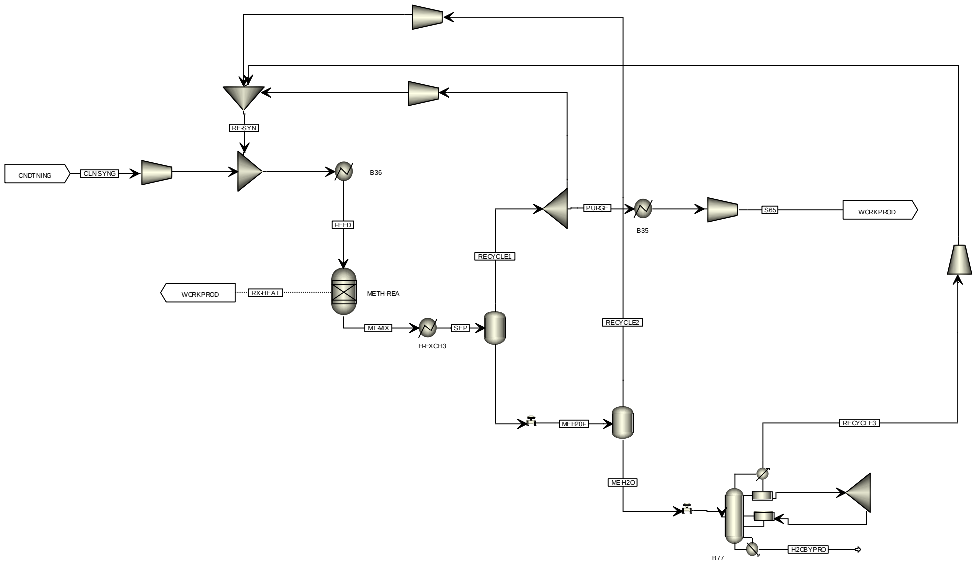
Simulation flowsheet for indirect gasification case



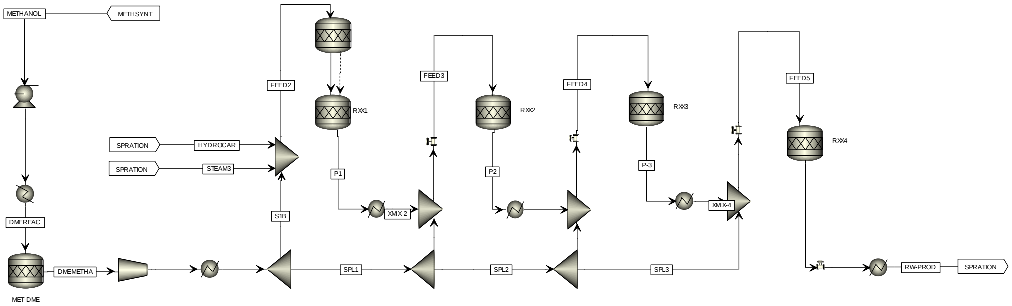
Mole Flow lbmol/hr	**W-BIMASS**	**D-BIMASS**	**F-GAS1**	**F-GAS-2**	**ASHCHAR**	**O2COLD**	**ASHSEP**	**STEAM-1**	**C-SYNG-2**	**NGAS**	**AIR2**	**SYNGAS**	**FLUEGA**	
H2	0	0	0	0	0	0	0	0	8300.358	0	0	12632.41	0	
H2O	0	0	0	3220.398	0	0	0	13053.35	10928.3	0	0	9496.484	1440.033	
CO	0	0	0	0	0	0	0	0	3904.867	0	0	5336.68	0	
CO2	0	0	3000.031	3000.031	0	0	3499.876	0	3833.252	0	0	3833.252	720.0166	
O2	0	0	69.99753	69.99753	0	3486.62	69.99753	0	0	0	1468.834	0	28.80066	
N2	0	0	13183.81	13183.81	0	13116.3	13429.53	0	253.1377	0	5525.613	265.3425	5525.613	
H2S	0	0	0	0	0	0	0	0	1.833404	0	0	1.833404	0	
NH3	0	0	0	0	0	0	0	0	27.12184	0	0	2.712184	0	
CH4	0	0	0	0	0	0	0	0	1789.766	720.0166	0	357.9531	0	
Total Flow lbmol/hr	0	0	16253.84	19474.24	0	16602.92	16999.4	13053.35	29038.63	720.0166	6994.447	31926.67	7714.464	
Temperature	60	219	1011.505	320.503	1661	68	1661	842	1561.874	61	90	1562	1800.019	
Pressure psia	15.7	15.7	15.7	15.7	15.7	15.7	15.7	15.7	15.7	15	15	15.7	15	**Area(s) : 100 - 200**
Vapor Frac	0	0	1	1	0	1	1	1	1	1	1	1	1	**Scenario:Indirect Gasification**
BIOMASS lb/hr	367437	309421	0	0	0	0	0	0	0	0	0	0	0	**Project: Master Thesis**
ASH lb/hr	0	0	0	0	3409.815	0	3409.815	0	0	0	0	0	0	**Author: Bernardo Lousada**



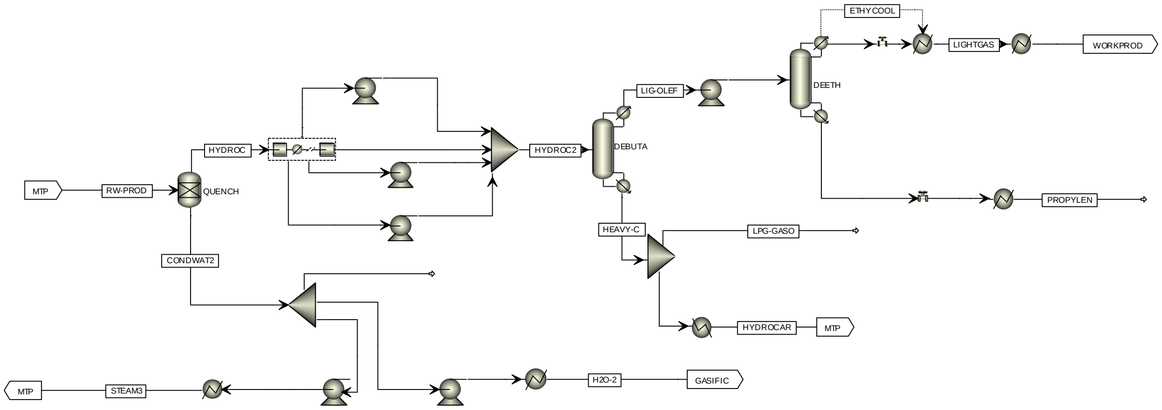
Mole Flow lbmol/hr	**SYNGAS**	**CD-SYNG**	**CD-SYNG2**	**S68**	**COND-WAT**	**CO2-H2S**	**H2O-1**	**DRYSYNG**	**TO-ZNO**	**ZNO**	**CLN-SYNG**	
H2	12632.41	12632.41	12632.41	12632.41	0.00378921	0	0	12632.41	12632.41	12632.41	12632.41	
H2O	9496.484	9496.484	8473.713	64.36405	8409.348	0	9432.12	64.36405	64.36405	64.36405	64.36405	
CO	5336.68	5336.68	5336.68	5336.679	0.000848146	0	0	5336.679	5336.679	5336.679	5336.679	
CO2	3833.252	3833.252	3832.102	3832.04	0.0621775	3177.382	0	654.658	654.658	654.658	654.658	
N2	265.3425	265.3425	265.3425	265.3425	5.28E-05	0	0	265.3425	265.3425	265.3425	265.3425	
H2S	1.833404	1.833404	1.833404	1.832574	0.000829395	1.642228	0	0.1903464	0.1903464	0	0	
NH3	2.712184	2.712184	2.130963	1.395808	0.7351551	0	0	1.395808	1.395808	1.395808	1.395808	
CH4	357.9531	357.9531	357.9531	357.9525	0.000580356	0	0	357.9525	357.9525	357.9525	357.9525	
Total Flow lbmol/hr	31926.67	31926.67	30902.16	22492.01	8410.152	3179.024	9432.12	19312.99	19312.99	19312.8	19312.8	**Area(s) : 300**
Temperature F	1562	225	160.2598	110	110.0629	130	842	115	750	750	110	**Scenario:Indirect Gasification**
Pressure psia	15.7	15.7	15.7	445	15.7	19.6	15.7	445	445	445	445	**Project: Master Thesis**
Vapor Frac	1	1	1	1	8.24E-07	1	1	0.9998584	1	1	0.9994229	**Author: Bernardo Lousada**



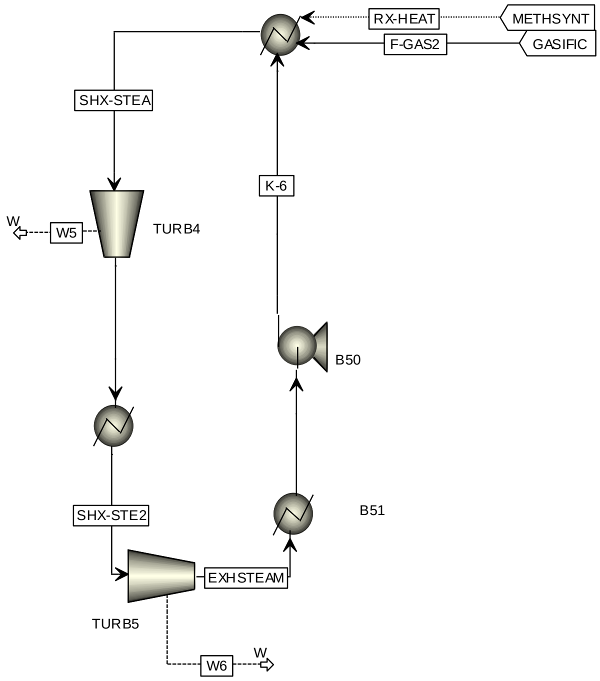
Mole Flow lbmol/hr	CLN-SYNG	RE-SYN	FEED	MT-MIX	SEP	RECYCLE1	PURGE	S65	MEH2OF	RECYCLE2	ME-H2O	RECYCLE3	METHANOL	
H2	12632.41	14232.55	26864.95	14552.78	14552.78	14546.43	320.0214	320.0214	6.358038	6.342515	0.0155221	0.0154835	3.86E-05	
H2O	64.36405	13.19814	77.56219	666.0992	666.0992	11.45515	0.2520132	0.2520132	654.644	1.072442	653.5716	0.9231324	102.3719	
CO	5336.679	2817.607	8154.285	2881.007	2881.007	2877.997	63.31594	63.31594	3.009733	2.990328	0.0194048	0.0192835	0.000121302	
CO2	654.658	2864.136	3518.794	2930.257	2930.257	2815.995	61.95189	61.95189	114.2619	87.12429	27.13758	22.98446	4.153128	
CH3OH	0	574.0882	574.0882	6435.904	6435.904	397.4458	8.743808	8.743808	6038.458	33.43295	6005.025	151.9655	5853.062	
N2	265.3425	11822.19	12087.54	12087.54	12087.54	12059.02	265.2984	265.2984	28.51496	28.09432	0.4206345	0.4150716	0.00556292	
NH3	1.395808	5.89562	7.291427	7.291427	7.291427	4.676499	0.102883	0.102883	2.614929	0.4555431	2.159385	0.8664903	1.292897	
CH4	357.9525	15984.99	16342.95	16342.95	16342.95	16260.33	357.7272	357.7272	82.62071	79.84227	2.77844	2.701792	0.0766474	
Total Flow lbmol/hr	19312.8	48314.66	67627.45	55903.82	55903.82	48973.34	1077.414	1077.414	6930.482	239.3547	6691.127	179.8912	5960.962	**Area(s) : 400**
Temperature F	110	115.6126	302	507.2	100.4	99.65201	99.65201	208.4578	98.7603	98.76032	98.76032	140	140	**Scenario:Indirect Gasification**
Pressure psia	445	980	980	980	980	929.2368	929.2368	220	29.00755	29.00755	29.00755	14.50377	14.50377	**Project: Master Thesis**
Vapor Frac	0.9994229	1	1	1	0.8758054	1	1	1	0.0345367	1	0	1	0	**Author: Bernardo Lousada**



Mole Flow lbmol/hr	**METHANOL**	**DMEREAC**	**DMEMETHA**	**HYDROCAR**	**STEAM3**	**S1B**	**FEED2**	**SPL1**	**P1**	**SPL2**	**FEED3**	**P2**	**SPL3**	**FEED4**	**P3**	**FEED5**	**RW-PROD**	
H2	TRACE	TRACE	TRACE	TRACE	TRACE	TRACE	TRACE	TRACE	TRACE	TRACE	TRACE	TRACE	TRACE	TRACE	TRACE	TRACE	TRACE	
H2O	102.3719	102.3719	2443.597	375.9536	9300	439.8474	10115.8	2003.749	10743.19	1466.162	11280.78	12052.29	610.8989	12907.55	14135.12	14746.02	15622.9	
CO	0.000121302	0.000121302	0.000121302	6.24E-30	0	2.18E-05	2.18E-05	9.95E-05	4.736927	7.28E-05	4.736954	5.829704	3.03E-05	5.829746	7.410576	7.410607	8.489517	
CO2	4.153128	4.153128	4.153128	1.77E-16	0	0.747563	0.747563	3.405565	0.747563	2.491884	1.661244	1.661244	1.038281	3.114846	3.114846	4.153128	4.153128	
CH3OH	5853.062	5853.062	1170.612	0	0	210.7102	210.7102	959.9021	0	702.3694	257.5328	0	292.6529	409.7164	0	292.6529	0	
DME	0	0	2341.225	0	0	421.4204	421.4204	1919.804	0	1404.739	515.0655	0	585.3059	819.4328	0	585.3059	0	
N2	TRACE	TRACE	TRACE	TRACE	TRACE	TRACE	TRACE	TRACE	TRACE	TRACE	TRACE	TRACE	TRACE	TRACE	TRACE	TRACE	TRACE	
NH3	1.292897	1.292897	1.292897	1.08E-06	0	0.2327215	0.2327226	1.060176	0.2327226	0.7757404	0.5171578	0.5171578	0.3232241	0.9696741	0.9696741	1.292898	1.292898	
CH4	0.0766474	0.0766474	0.0766474	2.32E-22	0	0.0137965	0.0137965	0.0628509	9.487607	0.0459886	9.504469	11.68997	0.0191618	11.7168	14.87846	14.89762	17.05544	
ETHY	0	0	0	1.60E-12	0	0	1.60E-12	0	82.1952	0	82.1952	97.916	0	97.916	122.9325	122.9325	140.8031	
PROPYL	0	0	0	0.1108552	0	0	0.1108552	0	806.7955	0	806.7955	961.0834	0	961.0834	1206.601	1206.601	1381.988	
BUTENE	0	0	0	619.5454	0	0	619.5454	0	450.9197	0	450.9197	537.1634	0	537.1634	674.4027	674.4027	772.4404	
PENTENE	0	0	0	365.9099	0	0	365.9099	0	266.2912	0	266.2912	317.2225	0	317.2225	398.2693	398.2693	456.1656	
HEXENE	0	0	0	127.5806	0	0	127.5806	0	92.84685	0	92.84685	110.6049	0	110.6049	138.8632	138.8632	159.0497	
HEPTENE	0	0	0	86.11079	0	0	86.11079	0	62.66719	0	62.66719	74.65302	0	74.65302	93.72604	93.72604	107.351	
Total Flow lbmol/hr	5960.962	5960.962	5960.962	1575.211	9300	1072.973	11948.18	4887.989	12520.12	3576.587	13831.52	14170.63	1490.24	16256.98	16796.29	18286.53	18671.69	**Area(s) : 500**
Temperature F	140	500	710.6593	707	707	707	705.2886	707	721.7179	707	619.662	705.8293	707	650.0326	763.7813	636.808	114	**Scenario:Indirect Gasification**
Pressure psia	14.50377	174.0453	174.0453	530	450	450	450	450	450	450	370	370	450	260	260	35	35	**Project: Master Thesis**
Vapor Frac	0	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	0.1693421	**Author: Bernardo Lousada**



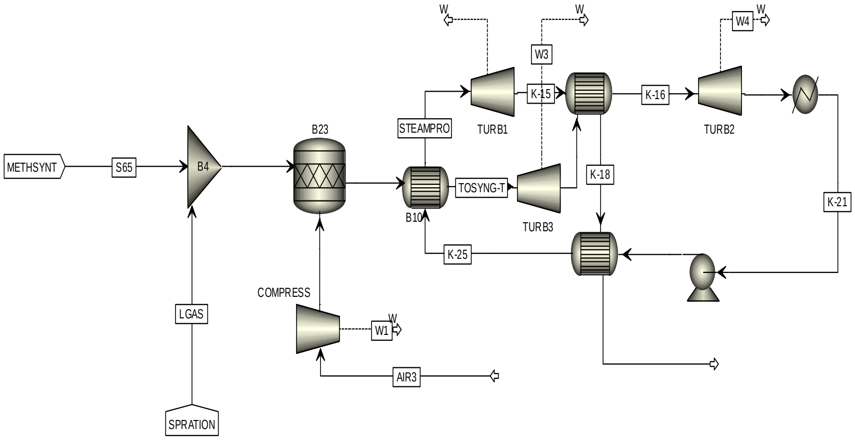
Mole Flow lbmol/hr	**RW-PROD**	**HYDROC**	**CONDWAT2**	**STEAM3**	**H2O-2**	**HYDROC2**	**HEAVY-C**	**LPG-GASO**	**HYDROCAR**	**LIG-OLE**	**LIGHTGAS**	**PROPYLEN**	
H2	TRACE	TRACE	TRACE	TRACE	TRACE	TRACE	TRACE	TRACE	TRACE	TRACE	TRACE	TRACE	
H2O	15622.9	468.6869	15154.21	1	3636.071	468.6867	468.6867	92.73311	375.9536	0	0	0	
CO	8.489517	8.489517	0	0	0	8.489517	7.78E-30	1.54E-30	6.24E-30	8.489517	8.489517	2.66E-16	
CO2	4.153128	4.153128	0	0	0	4.153128	2.20E-16	4.36E-17	1.77E-16	4.153128	4.153119	8.62E-06	
N2	TRACE	TRACE	TRACE	TRACE	TRACE	TRACE	TRACE	TRACE	TRACE	TRACE	TRACE	TRACE	
NH3	1.292898	1.292898	0	0	0	1.292898	1.34E-06	2.65E-07	1.08E-06	1.292897	0.0271417	1.265755	
CH4	17.05544	17.05544	0	0	0	17.05544	2.89E-22	5.72E-23	2.32E-22	17.05544	17.05544	4.64E-11	
ETHY	140.8031	140.8031	0	0	0	140.8031	1.99E-12	3.95E-13	1.60E-12	140.8031	140.789	0.0140803	
PROPYL	1381.988	1381.988	0	0	0	1381.988	0.1381988	0.0273436	0.1108552	1381.85	0.138185	1381.712	
BUTENE	772.4404	772.4404	0	0	0	772.4404	772.3631	152.8177	619.5454	0.077244	0	0.077244	
PENTENE	456.1656	456.1656	0	0	0	456.1656	456.1656	90.25571	365.9099	0	0	0	
HEXENE	159.0497	159.0497	0	0	0	159.0497	159.0497	31.46916	127.5806	0	0	0	
HEPTENE	107.351	107.351	0	0	0	107.351	107.351	21.24018	86.11079	0	0	0	
Total Flow lbmol/hr	18671.69	3517.482	15154.21	1	3636.071	3517.481	1963.754	388.5432	1575.211	1553.727	170.658	1383.069	**Area(s) : 600**
Temperature F	114	114.0974	114	707	842	117.2704	336.6672	336.6672	707	144.9632	77	77	**Scenario:Indirect Gasification**
Pressure psia	35	35	35	450	35	530	530	530	530	530	200	16	**Project: Master Thesis**
Vapor Frac	0.1693421	1	0	1	1	0	0	0	1	0	1	1	**Author: Bernardo Lousada**



Mole Flow lbmol/hr	**SHX-STEA**	**SHX-STE2**	**EXHSTEAM**	**K-6**
H2O	14011.95	14011.95	14011.95	14011.95
Temperature F	750	610	249.2749	247.9056
Pressure psia	609.1585	110	16	609.1585
Vapor Frac	1	1	1	0

Energy	**W18**	**W19**
POWER hp	-14364.4	-16447.44

Area(s) : Work Production 1
Scenario:Indirect Gasification
Project: Master Thesis
Author: Bernardo Lousada



Mole Flow lbmol/hr	**S65**	**LGAS**	**AIR3**	**K-25**	**STEAMPRO**	**K-15**	**K-16**	**K-18**	**K-21**
H2	320.0214	3.86E-05	0	0	0	0	0	0	0
H2O	0.2520132	0	0	9013.652	9013.652	9013.652	9013.652	1608.566	9013.652
CO	63.31594	8.489517	0	0	0	0	0	0	0
CO2	61.95189	4.153119	0	0	0	0	0	923.053	0
CH3OH	8.743808	0	0	0	0	0	0	0	0
O2	0	0	1701.872	0	0	0	0	81.04151	0
N2	265.2984	0.00556292	6402.28	0	0	0	0	6667.584	0
NH3	0.102883	0.0271417	0	0	0	0	0	0.1300247	0
CH4	357.7272	17.05544	0	0	0	0	0	0	0
ETHY	0	140.789	0	0	0	0	0	0	0
PROPYL	0	0.138185	0	0	0	0	0	0	0
Total Flow lbmol/hr	1077.414	170.658	8104.151	9013.652	9013.652	9013.652	9013.652	9280.374	9013.652
Temperature F	208.4578	77	68	362.1073	1000	617.9456	911	660.6102	197.6834
Pressure psia	220	200	15.7	1798.468	1798.468	464.1208	464.1208	14.69595	10.15264
Vapor Frac	1	1	1	0	1	1	1	1	0

Energy	**W7**	**W8**	**W9**	**W10**
POWER hp	14564.73	-9943.86	-31391.784	-22164.4

Area(s) : Work Production 2
Scenario:Indirect Gasification
Project: Master Thesis
Author: Bernardo Lousada

APPENDIX C

Methanol synthesis kinetics parameters

R_1 ($CO_2 + 3H_2 \rightarrow CH_3OH + H_2O$)	
kinetic factor	$k = 1.07 \times 10^{-3}$ $E = 36\,696$ kJ/kmol
driving-force expressions	
term 1	
conc. exponents for reactants:	$CO_2 = 1$; $H_2 = 1$
conc. exponents for products:	$CH_3OH = 0$; $H_2O = 0$
coefficients:	$A = -23.02581$; $B = C = D = 0$
term 2	
conc. exponents for reactants:	$CO_2 = 0$; $H_2 = -2$
conc. exponents for products:	$CH_3OH = 1$; $H_2O = 1$
coefficients:	$A = 24.388981$; $B = -7059.7258$; $C = D = 0$
adsorption expression	
adsorption term exponent:	3
concentration exponents:	
term 1:	$H_2 = 0$; $H_2O = 0$
term 2:	$H_2 = -1$; $H_2O = 1$
adsorption constants:	
term 1:	$A = 0$, $B = 0$, $C = 0$, $D = 0$
term 2:	$A = 8.1471087$, $B = 0$, $C = 0$, $D = 0$

R_2 ($CO_2 + H_2 \rightarrow CO + H_2O$)	
kinetic factor	$k = 1.22 \times 10^{9}$ $E = 94765$ kJ/kmol
driving-force expressions	
term 1	
conc. exponents for reactants:	$CO_2 = 1$; $H_2 = 0$
conc. exponents for products:	$CO = 0$; $H_2O = 0$
coefficients:	$A = -11.512952$; $B = C = D = 0$
term 2	
conc. exponents for reactants:	$CO_2 = 0$; $H_2 = -1$
conc. exponents for products:	$CO = 1$; $H_2O = 1$
coefficients:	$A = -16.184871$; $B = 4773.2589$; $C = D = 0$
adsorption expression	
adsorption term exponent:	1
concentration exponents:	
term 1:	$H_2 = 0$; $H_2O = 0$
term 2:	$H_2 = -1$; $H_2O = 1$
adsorption constants:	
term 1:	$A = 0$, $B = 0$, $C = 0$, $D = 0$
term 2:	$A = 8.1471087$, $B = 0$, $C = 0$, $D = 0$

APPENDIX D

Pinch Analysis

For the heat exchanger network design, a few considerations must be highlighted:

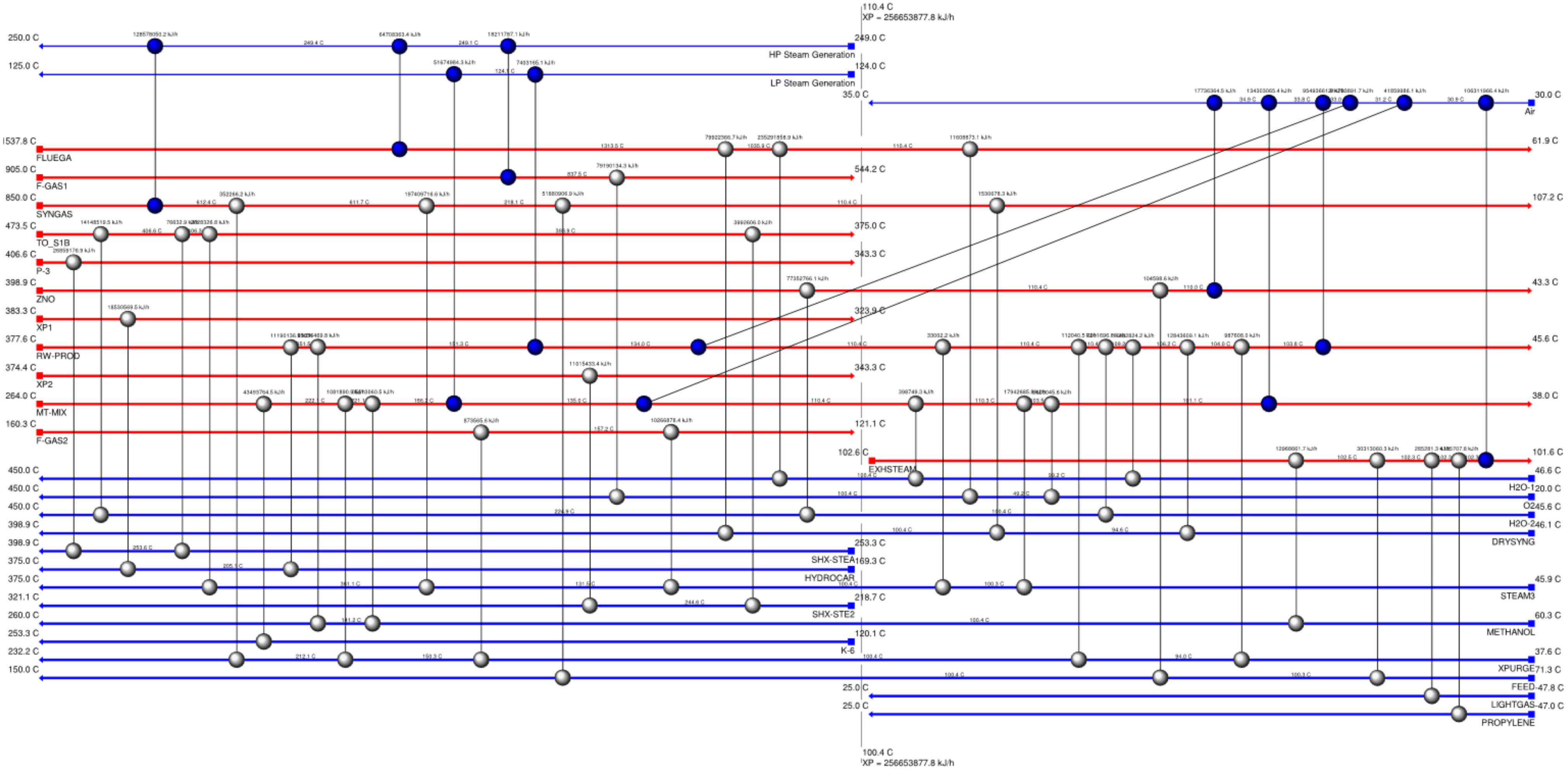
- The condensers of the distillation columns are directly satisfied by air as cold utility. With exception of the condenser of the propylene/ethylene separation that a refrigerant was used.
- The ASU was not taken into account on this design. However the energy requirement can be met by air as cold utility.
- The reboilers are directly satisfied for the HP steam produced showed in the design below.

Aspen Energy Analyzer targets what would be the optimum operational and capital cost. The design achieved good relative values regarding the ones forecasted by the software. However these values are just used for comparison proposes and not for the economics analysis since lack of thermodynamics parameters from the simulation streams in the software (such as heat transfer coefficients) results in an inaccurate calculation of area and, consequently, of cost.

Network Perfomance	**Value**	**% of Target**
Heating (KJ/h)	0	0
Cooling (KJ/h)	8.81E+08	100
Capital (Cost/s)	5.55E+07	81.3
Total Cost (Cost/s)	0.3894	117.2

The proposed design meets completely the cooling duty exceeding the total cost of the target by 17.2%. For the proposed of this study, which is comparing two different pathways this design will be assumed.

For a comprehensive integration, the columns and ASU were incorporated and are showed in the section 4.6 of this work.


110.4 C
XP = 256653877.8 kJ/h
250.0 C
249.0 C
HP Steam Generation
125.0 C
124.0 C
LP Steam Generation
35.0 C
30.0 C
Air
1537.8 C
FLUEGA
61.9 C
905.0 C
F-GAS1
544.2 C
850.0 C
SYNGAS
107.2 C
473.5 C
TO_S1B
375.0 C
406.6 C
P-3
343.3 C
398.9 C
ZNO
43.3 C
383.3 C
XP1
323.9 C
377.6 C
RW-PROD
45.6 C
374.4 C
XP2
343.3 C
264.0 C
MT-MIX
38.0 C
160.3 C
F-GAS2
121.1 C
102.6 C
EXHSTEAM
101.6 C
450.0 C
H2O-1
46.6 C
450.0 C
O2
120.0 C
450.0 C
H2O-2
45.6 C
398.9 C
DRYSYNG
46.1 C
398.9 C
SHX-STEA
253.3 C
375.0 C
HYDROCAR
169.3 C
375.0 C
STEAM3
45.9 C
321.1 C
SHX-STE2
218.7 C
260.0 C
METHANOL
60.3 C
253.3 C
K-6
120.1 C
232.2 C
XPURGE
37.6 C
150.0 C
FEED
71.3 C
25.0 C
LIGHTGAS
-47.8 C
25.0 C
PROPYLENE
-47.0 C
100.4 C
XP = 256653877.8 kJ/h

APPENDIX E

Direct Dasification NREL correlations

Eq.	Form	A	B	C	D	E	R^2
1	$H_2/Feed\ H = A + B*P + C*T + D*(\frac{O_2}{Feed\ C}) + E*(\frac{H_2O}{Feed\ C})$	-3.830761E-01	1.894350E-04	2.666675E-04	1.060088E-01	7.880955E-02	0.7828
2	$CO/Feed\ \ C = A + B*P + C*T + D*(\frac{O_2}{Feed\ C}) + E*(\frac{H_2O}{Feed\ C})$	-8.130017E-02	-3.340050E-04	2.614482E-04	1.495730E-01	-5.268367E-02	0.7984
3	$CO_2/Feed\ C = A + B*P + C*T + D*(\frac{O_2}{Feed\ C}) + E*(\frac{H_2O}{Feed\ C})$	7.157172E-02	3.843454E-04	1.286060E-05	6.124545E-01	9.980868E-02	0.9080
4	$CH_4/Feed\ C = A + B*P + C*T + D*(\frac{O_2}{Feed\ C}) + E*(\frac{H_2O}{Feed\ C})$	1.093589E-02	1.388446E-04	8.812765E-05	-2.274854E-01	3.427825E-02	0.6243
5	$C_2H_4/Feed\ C = A + B*P + C*T + D*(\frac{O_2}{Feed\ C}) + E*(\frac{H_2O}{Feed\ C})$	5.301812E-02	-6.740399E-05	-1.372749E-05	-9.076286E-03	-4.854082E-03	0.8910
6	$C_2H_6/Feed\ C = A + B*P + C*T + D*(\frac{O_2}{Feed\ C}) + E*(\frac{H_2O}{Feed\ C})$	1.029750E-01	-5.440777E-06	-5.350103E-05	-3.377091E-02	-1.915339E-03	0.7451
7	$C_6H_6/Feed\ C = A + B*P + C*T + D*(\frac{O_2}{Feed\ C}) + E*(\frac{H_2O}{Feed\ C})$	4.676833E-02	-1.937444E-05	-1.270868E-05	-1.046762E-02	-8.459647E-03	0.3242
8	$C_{10}H_8/Feed\ C = A + B*P + C*T + D*(\frac{O_2}{Feed\ C}) + E*(\frac{H_2O}{Feed\ C})$	1.827359E-02	-2.328921E-06	-5.951746E-06	-1.936385E-02	-7.678310E-04	0.4726
9	$\%\ Feed\ N\ in\ Char = A$	3.360000E+00					
10	$\%\ Feed\ S\ in\ Char = A$	8.450000E+00					
11	$\%\ Feed\ O\ in\ Char = A + B*P + C*T + D*(\frac{O_2}{Feed\ C}) + E*(\frac{H_2O}{Feed\ C})$	1.512040E+00	1.582010E-04	-6.972612E-04	1.573581E-01	-1.420915E-01	0.3332

[a] All ratios are on a molar basis, pressure in psia, temperature in °F

The following general procedure is used for the gasifier production:

- Gasifier temperature T, pressure P, supplied O_2, and the total H_2O in the wood and supplied steam is gathered.
- The mass and molar amounts of carbon, hydrogen, oxygen, sulfur, nitrogen, and ash (as a pseudo-element) are determined from the biomass's ultimate analysis.
- The amount of syngas and its composition is determined from the gasifier correlations.
- The amount of carbon in the syngas and tar is determined. Residual carbon is parsed in the char.
- The amount of oxygen in the syngas is determined. A minimum fraction of the biomass oxygen is required to be parsed to the char based on equation 11 above. If there is a deficit of oxygen, then the associated water is decomposed to make sure that this amount of oxygen is parsed to the char; if there is excess oxygen, then that is parsed to the char without decomposing hydrogen.
- A set amount of sulfur is parsed to the char (8.4%). All remaining sulfur is set as H_2S in the syngas.
- A set amount of nitrogen is parsed to the char (3.4%). All remaining nitrogen is set as NH_3 in the syngas.
- The amount of hydrogen in the syngas (including tar, H_2S, NH_3, and decomposed water) is determined. All remaining hydrogen is parsed to the char.
- All ash is parsed to the char.
- The heat of formation of the char is estimated from the resulting ultimate analysis from this elemental material balance and is used for the energy balance calculations.

APPENDIX F

Individual cost per equipment

Direct Gasification case

Block	Type	Area	Equipment Cost [USD]	Installed Cost [USD]	Year	Source	Installed Cost [USD] in 2015
B29	Compr	Methanol Synthesis	1,331,300.00	3,288,311.00	2013	Icarus	3,307,439.20
B60	Compr	Methanol Synthesis	2,535,300.00	6,262,191.00	2013	Icarus	6,298,618.34
B62-flash vessel	Flash2	Methanol Synthesis	113,800.00	281,086.00	2013	Icarus	282,721.09
B68-flash vessel	Flash2	Methanol Synthesis	30,400.00	75,088.00	2013	Icarus	75,524.79
B70	Compr	Methanol Synthesis	2,050,600.00	5,064,982.00	2013	Icarus	5,094,445.14
METH-REA	RGibbs	Methanol Synthesis	224,700.00	555,009.00	2013	Icarus	558,237.50
B20	Compr	Methanol Synthesis	2,014,300.00	4,975,321.00	2013	Icarus	5,004,262.58
B1	Compr	Methanol Synthesis	255,000.00	629,850.00	2013	Icarus	633,513.86
B77-cond	RadFrac	Methanol Synthesis	324,200.00	800,774.00	2013	Icarus	805,432.12
B77-cond acc	RadFrac	Methanol Synthesis	37,300.00	92,131.00	2013	Icarus	92,666.93
B77-reb	RadFrac	Methanol Synthesis	122,800.00	303,316.00	2013	Icarus	305,080.40
B77-reflux pump	RadFrac	Methanol Synthesis	14,300.00	35,321.00	2013	Icarus	35,526.46
B77-tower	RadFrac	Methanol Synthesis	1,107,300.00	2,735,031.00	2013	Icarus	2,750,940.75
MET-DME	RStoic	MTP	38,500.00	95,095.00	2013	Icarus	95,648.17
PUMP1	Pump	MTP	29,200.00	72,124.00	2013	Icarus	72,543.55
B84	RStoic	MTP	78,200.00	193,154.00	2013	Icarus	194,277.58
RXX2	RStoic	MTP	83,000.00	205,010.00	2013	Icarus	206,202.55
RXX3	RStoic	MTP	97,400.00	240,578.00	2013	Icarus	241,977.45
RXX4	RStoic	MTP	117,200.00	289,484.00	2013	Icarus	291,167.94
B104	Compr	MTP	1,799,200.00	4,444,024.00	2013	Icarus	4,469,875.01
B25	Pump	Separation	62,500.00	154,375.00	2013	Icarus	155,273.00
B49	Pump	Separation	53,100.00	131,157.00	2013	Icarus	131,919.94
B63	Pump	Separation	59,200.00	146,224.00	2013	Icarus	147,074.59
B64	DSTWU	Separation	1,045,000.00	2,581,150.00	2013	Icarus	2,596,164.62
B67	DSTWU	Separation	511,300.00	1,262,911.00	2013	Icarus	1,270,257.39
B85	Pump	Separation	7,500.00	18,525.00	2013	Icarus	18,632.76
B18	MCompr	Separation	2,660,100.00	6,570,447.00	2013	Icarus	6,608,667.47
B17	Sep	Separation	30,800.00	76,076.00	2013	Icarus	76,518.54
B54	Pump	Separation	64,200.00	158,574.00	2013	Icarus	159,496.43
B3	Compr	Work Production	10,578,700.00	26,129,389.00	2013	Icarus	26,281,384.39
B11	Pump	Work Production	266,600.00	658,502.00	2013	Icarus	662,332.52
B12	Compr	Work Production	1,272,800.00	3,143,816.00	2013	Icarus	3,162,103.67
B14	Compr	Work Production	2,334,000.00	5,764,980.00	2013	Icarus	5,798,515.05
B2	Compr	Work Production	4,273,000.00	10,554,310.00	2013	Icarus	10,615,704.72
B47	Compr	Work Production	2,917,700.00	7,206,719.00	2013	Icarus	7,248,640.69
B50	Pump	Work Production	164,600.00	406,562.00	2013	Icarus	408,926.98
B22	Compr	Work Production	3,232,500.00	7,984,275.00	2013	Icarus	8,030,719.75
Dryer		Handling	3,813,728.00	9,419,908.16	2002	alcohol	13,586,955.50
Direct Gasifier	-	Gasification	7,158,010.95	17,680,287.05	2002	alcohol	25,501,445.38
Tar reformer	-	Gas Cleanup	8,959,706.69	22,130,475.53	2002	alcohol	31,920,246.05
Tar Refomer Catalyst Regenerator	-	Gas Cleanup	3,642,016.28	8,995,780.22	2002	alcohol	12,975,207.77
Syngas Quench	-	Gas Cleanup	-	-	2002	alcohol	-
Syngas Venturi Scrubber	-	Gas Cleanup	-	-	2002	alcohol	-
Water knockout Vessel	-	Gas Cleanup	234,428.92	579,039.44	2002	alcohol	835,186.82
Amine System	-	Gas Cleanup	5,019,074.67	12,397,114.43	2002	alcohol	17,881,176.68
ZnO beds	-	Gas Cleanup	438,560.00	1,083,243.20	2002	task2	1,562,433.19
ASU including Air compressor	-	ASU	9,122,577.70	22,532,766.93	1999	alcohol	32,916,530.49
Post ASU O2 compressor	-	ASU	3,247,984.44	8,022,521.58	2004	alcohol	10,305,382.29
E-138	Heat Exch	PINCH	213,400.00	527,098.00	2013	Icarus	530,164.14
E-177	Heat Exch	PINCH	36,500.00	90,155.00	2013	Icarus	90,679.43
E-132	Heat Exch	PINCH	43,050.00	106,333.50	2013	Icarus	106,952.04
E-130	Heat Exch	PINCH	166,300.00	410,761.00	2013	Icarus	413,150.41
E-189	Heat Exch	PINCH	65,710.00	162,303.70	2013	Icarus	163,247.83
E-127	Heat Exch	PINCH	264,900.00	654,303.00	2013	Icarus	658,109.10
E-121	Heat Exch	PINCH	10,970.00	27,095.90	2013	Icarus	27,253.52
E-184	Heat Exch	PINCH	21,170.00	52,289.90	2013	Icarus	52,594.07
E-182	Heat Exch	PINCH	173,400.00	428,298.00	2013	Icarus	430,789.42
E-186	Heat Exch	PINCH	50,100.00	123,747.00	2013	Icarus	124,466.84
E-188	Heat Exch	PINCH	190,900.00	471,523.00	2013	Icarus	474,265.86
E-113	Heat Exch	PINCH	12,990.00	32,085.30	2013	Icarus	32,271.94
E-117	Heat Exch	PINCH	70,790.00	174,851.30	2013	Icarus	175,868.41
E-168	Heat Exch	PINCH	10,260.00	25,342.20	2013	Icarus	25,489.62
E-172	Heat Exch	PINCH	81,090.00	200,292.30	2013	Icarus	201,457.41
E-190	Heat Exch	PINCH	221,100.00	546,117.00	2013	Icarus	549,293.78
E-167	Heat Exch	PINCH	120,700.00	298,129.00	2013	Icarus	299,863.22
E-128	Heat Exch	PINCH	83,400.00	205,998.00	2013	Icarus	207,196.30
E-122	Heat Exch	PINCH	18,340.00	45,299.80	2013	Icarus	45,563.31
E-165	Heat Exch	PINCH	42,900.00	105,963.00	2013	Icarus	106,579.39
E-181	Heat Exch	PINCH	25,720.00	63,528.40	2013	Icarus	63,897.95
E-183	Heat Exch	PINCH	10,420.00	25,737.40	2013	Icarus	25,887.12
E-118	Heat Exch	PINCH	17,470.00	43,150.90	2013	Icarus	43,401.91
E-114	Heat Exch	PINCH	149,300.00	368,771.00	2013	Icarus	370,916.15
E-116	Heat Exch	PINCH	33,460.00	82,646.20	2013	Icarus	83,126.96
E-109	Heat Exch	PINCH	268,000.00	661,960.00	2013	Icarus	665,810.64
E-105	Heat Exch	PINCH	96,830.00	239,170.10	2013	Icarus	240,561.36
E-169	Heat Exch	PINCH	146,100.00	360,867.00	2013	Icarus	362,966.17
E-171	Heat Exch	PINCH	17,550.00	43,348.50	2013	Icarus	43,600.66
E-175	Heat Exch	PINCH	22,490.00	55,550.30	2013	Icarus	55,873.44
E-173	Heat Exch	PINCH	78,050.00	192,783.50	2013	Icarus	193,904.93
E-129	Heat Exch	PINCH	468,900.00	1,158,183.00	2013	Icarus	1,164,920.18
E-166	Heat Exch	PINCH	26,200.00	64,714.00	2013	Icarus	65,090.44
E-180	Heat Exch	PINCH	16,160.00	39,915.20	2013	Icarus	40,147.39
E-178	Heat Exch	PINCH	273,600.00	675,792.00	2013	Icarus	679,723.10
E-150	Heat Exch	PINCH	205,900.00	508,573.00	2013	Icarus	511,531.38
E-152	Heat Exch	PINCH	177,100.00	437,437.00	2013	Icarus	439,981.58
E-115	Heat Exch	PINCH	27,840.00	68,764.80	2013	Icarus	69,164.81
E-108	Heat Exch	PINCH	119,700.00	295,659.00	2013	Icarus	297,378.86
E-104	Heat Exch	PINCH	18,280.00	45,151.60	2013	Icarus	45,414.25
E-170	Heat Exch	PINCH	17,800.00	43,966.00	2013	Icarus	44,221.75
E-120	Heat Exch	PINCH	12,540.00	30,973.80	2013	Icarus	31,153.98
E-124	Heat Exch	PINCH	11,170.00	27,589.90	2013	Icarus	27,750.39
E-185	Heat Exch	PINCH	16,730.00	41,323.10	2013	Icarus	41,563.48
E-179	Heat Exch	PINCH	69,450.00	171,541.50	2013	Icarus	172,539.36
E-187	Heat Exch	PINCH	67,890.00	167,688.30	2013	Icarus	168,663.75
E-101	Heat Exch	PINCH	46,910.00	115,867.70	2013	Icarus	116,541.71
E-103	Heat Exch	PINCH	90,940.00	224,621.80	2013	Icarus	225,928.43

Indirect Gasification case

Block	Type	Area	Equipment Cost [USD]	Installed Cost [USD]	Year	Source	Installed Cost [USD] in 2015
B77-cond	RadFrac	Methanol Synthesis	311,700.00	769,899.00	2013	Icarus	774,377.52
B77-cond acc	RadFrac	Methanol Synthesis	40,000.00	98,800.00	2013	Icarus	99,374.72
B77-overhead split	RadFrac	Methanol Synthesis	0.00	0.00	2013	Icarus	0.00
B77-reb	RadFrac	Methanol Synthesis	230,400.00	569,088.00	2013	Icarus	572,398.40
B77-reflux pump	RadFrac	Methanol Synthesis	14,600.00	36,062.00	2013	Icarus	36,271.77
B77-tower	RadFrac	Methanol Synthesis	1,145,000.00	2,828,150.00	2013	Icarus	2,844,601.43
RLVALVE2	Valve	Methanol Synthesis	0.00	0.00	2013	Icarus	0.00
B29	Compr	Methanol Synthesis	1,377,600.00	3,402,672.00	2013	Icarus	3,422,465.44
B60	Compr	Methanol Synthesis	2,580,000.00	6,372,600.00	2013	Icarus	6,409,669.59
B62-flash vessel	Flash2	Methanol Synthesis	128,100.00	316,407.00	2013	Icarus	318,247.55
B68-flash vessel	Flash2	Methanol Synthesis	30,500.00	75,335.00	2013	Icarus	75,773.23
B70	Compr	Methanol Synthesis	2,036,100.00	5,029,167.00	2013	Icarus	5,058,421.81
B72	Valve	Methanol Synthesis	0.00	0.00	2013	Icarus	0.00
METH-REA	RGibbs	Methanol Synthesis	313,900.00	775,333.00	2013	Icarus	779,843.13
B20	Compr	Methanol Synthesis	2,022,700.00	4,996,069.00	2013	Icarus	5,025,131.27
B1	Compr	Methanol Synthesis	307,600.00	759,772.00	2013	Icarus	764,191.62
MET-DME	RStoic	MTP	41,600.00	102,752.00	2013	Icarus	103,349.71
PUMP1	Pump	MTP	29,800.00	73,606.00	2013	Icarus	74,034.17
RXX1	RStoic	MTP	78,200.00	193,154.00	2013	Icarus	194,277.58
RXX2	RStoic	MTP	83,000.00	205,010.00	2013	Icarus	206,202.55
RXX3	RStoic	MTP	97,400.00	240,578.00	2013	Icarus	241,977.45
RXX4	RStoic	MTP	123,000.00	303,810.00	2013	Icarus	305,577.27
B104	Compr	MTP	1,816,600.00	4,487,002.00	2013	Icarus	4,513,103.02
B17	Sep	Separation	30,800.00	76,076.00	2013	Icarus	76,518.54
B18	MCompr	Separation	2,660,100.00	6,570,447.00	2013	Icarus	6,608,667.47
B25	Pump	Separation	62,800.00	155,116.00	2013	Icarus	156,018.31
B49	Pump	Separation	53,400.00	131,898.00	2013	Icarus	132,665.25
B63	Pump	Separation	61,700.00	152,399.00	2013	Icarus	153,285.51
B64	DSTWU	Separation	1,133,000.00	2,798,510.00	2013	Icarus	2,814,789.01
B67	DSTWU	Separation	511,300.00	1,262,911.00	2013	Icarus	1,270,257.39
B85	Pump	Separation	7,600.00	18,772.00	2013	Icarus	18,881.20
B54	Pump	Separation	43,100.00	106,457.00	2013	Icarus	107,076.26
B3	Compr	Work Production	11,362,000.00	28,064,140.00	2013	Icarus	28,227,389.89
B11	Pump	Work Production	267,000.00	659,490.00	2013	Icarus	663,326.27
B12	Compr	Work Production	1,331,900.00	3,289,793.00	2013	Icarus	3,308,929.82
B14	Compr	Work Production	2,442,300.00	6,032,481.00	2013	Icarus	6,067,572.11
B2	Compr	Work Production	7,104,700.00	17,548,609.00	2013	Icarus	17,650,689.75
B47	Compr	Work Production	1,759,200.00	4,345,224.00	2013	Icarus	4,370,500.29
B50	Pump	Work Production	94,600.00	233,662.00	2013	Icarus	235,021.22
B22	Compr	Work Production	1,948,900.00	4,813,783.00	2013	Icarus	4,841,784.91
B90	Compr	Work Production	1,518,200.00	3,749,954.00	2013	Icarus	3,771,767.59
Dryer	-	Handling	3,813,728.00	9,419,908.16	2002	Indirect Alco	13,586,955.50
Indirect Gasifier	-	Gasification	3,002,636.47	7,416,512.09	2002	Indirect Alco	10,697,325.07
Tar reformer	-	Gas Cleanup	10,131,064.19	25,023,728.56	2002	Indirect Alco	36,093,375.93
Tar Refomer Catalyst Regenerator	-	Gas Cleanup	4,118,159.45	10,171,853.84	2002	Indirect Alco	14,671,536.40
Syngas Quench	-	Gas Cleanup	-	-	2002	Indirect Alco	-
Syngas Venturi Scrubber	-	Gas Cleanup	-	-	2002	Indirect Alco	-
Multistage Compressor	-	Gas Cleanup	5,480,635.24	13,537,169.05	2002	Indirect Alco	19,525,552.73
Water knockout pre Compressor	-	Gas Cleanup	187,573.36	463,306.20	2002	Indirect Alco	668,257.12
Amine System	-	Gas Cleanup	3,683,161.52	9,097,408.96	2002	Indirect Alco	13,121,793.61
ZnO beds	-	Gas Cleanup	438,560.00	1,083,243.20	2002	Indirect Alco	1,562,433.19
E-138	Heat Exch	PINCH	213,400.00	527,098.00	2013	Icarus	530,164.14
E-177	Heat Exch	PINCH	36,500.00	90,155.00	2013	Icarus	90,679.43
E-132	Heat Exch	PINCH	43,050.00	106,333.50	2013	Icarus	106,952.04
E-130	Heat Exch	PINCH	166,300.00	410,761.00	2013	Icarus	413,150.41
E-189	Heat Exch	PINCH	65,710.00	162,303.70	2013	Icarus	163,247.83
E-127	Heat Exch	PINCH	264,900.00	654,303.00	2013	Icarus	658,109.10
E-121	Heat Exch	PINCH	10,970.00	27,095.90	2013	Icarus	27,253.52
E-184	Heat Exch	PINCH	21,170.00	52,289.90	2013	Icarus	52,594.07
E-182	Heat Exch	PINCH	173,400.00	428,298.00	2013	Icarus	430,789.42
E-186	Heat Exch	PINCH	50,100.00	123,747.00	2013	Icarus	124,466.84
E-188	Heat Exch	PINCH	190,900.00	471,523.00	2013	Icarus	474,265.86
E-113	Heat Exch	PINCH	12,990.00	32,085.30	2013	Icarus	32,271.94
E-117	Heat Exch	PINCH	70,790.00	174,851.30	2013	Icarus	175,868.41
E-168	Heat Exch	PINCH	10,260.00	25,342.20	2013	Icarus	25,489.62
E-172	Heat Exch	PINCH	81,090.00	200,292.30	2013	Icarus	201,457.41
E-190	Heat Exch	PINCH	221,100.00	546,117.00	2013	Icarus	549,293.78
E-167	Heat Exch	PINCH	120,700.00	298,129.00	2013	Icarus	299,863.22
E-128	Heat Exch	PINCH	83,400.00	205,998.00	2013	Icarus	207,196.30
E-122	Heat Exch	PINCH	18,340.00	45,299.80	2013	Icarus	45,563.31
E-165	Heat Exch	PINCH	42,900.00	105,963.00	2013	Icarus	106,579.39
E-181	Heat Exch	PINCH	25,720.00	63,528.40	2013	Icarus	63,897.95
E-183	Heat Exch	PINCH	10,420.00	25,737.40	2013	Icarus	25,887.12
E-118	Heat Exch	PINCH	17,470.00	43,150.90	2013	Icarus	43,401.91
E-114	Heat Exch	PINCH	149,300.00	368,771.00	2013	Icarus	370,916.15
E-116	Heat Exch	PINCH	33,460.00	82,646.20	2013	Icarus	83,126.96
E-109	Heat Exch	PINCH	268,000.00	661,960.00	2013	Icarus	665,810.64
E-105	Heat Exch	PINCH	96,830.00	239,170.10	2013	Icarus	240,561.36
E-169	Heat Exch	PINCH	146,100.00	360,867.00	2013	Icarus	362,966.17
E-171	Heat Exch	PINCH	17,550.00	43,348.50	2013	Icarus	43,600.66
E-175	Heat Exch	PINCH	22,490.00	55,550.30	2013	Icarus	55,873.44
E-173	Heat Exch	PINCH	78,050.00	192,783.50	2013	Icarus	193,904.93
E-129	Heat Exch	PINCH	468,900.00	1,158,183.00	2013	Icarus	1,164,920.18
E-166	Heat Exch	PINCH	26,200.00	64,714.00	2013	Icarus	65,090.44
E-180	Heat Exch	PINCH	16,160.00	39,915.20	2013	Icarus	40,147.39
E-178	Heat Exch	PINCH	273,600.00	675,792.00	2013	Icarus	679,723.10
E-150	Heat Exch	PINCH	205,900.00	508,573.00	2013	Icarus	511,531.38
E-152	Heat Exch	PINCH	177,100.00	437,437.00	2013	Icarus	439,981.58
E-115	Heat Exch	PINCH	27,840.00	68,764.80	2013	Icarus	69,164.81
E-108	Heat Exch	PINCH	119,700.00	295,659.00	2013	Icarus	297,378.86
E-104	Heat Exch	PINCH	18,280.00	45,151.60	2013	Icarus	45,414.25
E-170	Heat Exch	PINCH	17,800.00	43,966.00	2013	Icarus	44,221.75
E-120	Heat Exch	PINCH	12,540.00	30,973.80	2013	Icarus	31,153.98
E-124	Heat Exch	PINCH	11,170.00	27,589.90	2013	Icarus	27,750.39
E-185	Heat Exch	PINCH	16,730.00	41,323.10	2013	Icarus	41,563.48
E-179	Heat Exch	PINCH	69,450.00	171,541.50	2013	Icarus	172,539.36
E-187	Heat Exch	PINCH	67,890.00	167,688.30	2013	Icarus	168,663.75
E-101	Heat Exch	PINCH	46,910.00	115,867.70	2013	Icarus	116,541.71
E-103	Heat Exch	PINCH	90,940.00	224,621.80	2013	Icarus	225,928.43

APPENDIX G

Discounted cash flow for minimum propylene price evaluation

Direct Gasification case

Year	0	1	2	3	4	5	6	7	8	9	10	11	12
Fixed Capital	365,125,083.56												
Working Capital	21,907,505.01												
Propylene Sales		-98,044,505.52	-98,044,505.52	-98,044,505.52	-98,044,505.52	-98,044,505.52	-98,044,505.52	-98,044,505.52	-98,044,505.52	-98,044,505.52	-98,044,505.52	-98,044,505.52	-98,044,505.52
Byproduct Credit		-44,292,230.04	-44,292,230.04	-44,292,230.04	-44,292,230.04	-44,292,230.04	-44,292,230.04	-44,292,230.04	-44,292,230.04	-44,292,230.04	-44,292,230.04	-44,292,230.04	-44,292,230.04
Annual Sales		-142,336,735.56	-142,336,735.56	-142,336,735.56	-142,336,735.56	-142,336,735.56	-142,336,735.56	-142,336,735.56	-142,336,735.56	-142,336,735.56	-142,336,735.56	-142,336,735.56	-142,336,735.56
Annual Manufacturing Cost													
Feedstock		49,418,806.75	49,418,806.75	49,418,806.75	49,418,806.75	49,418,806.75	49,418,806.75	49,418,806.75	49,418,806.75	49,418,806.75	49,418,806.75	49,418,806.75	49,418,806.75
Tar catalyst		50,838.31											
Methanol Catalyst		294,240.15					294,240.15					294,240.15	
Propylene Catalyst		803,621.49					803,621.49					803,621.49	
Eletricity		-6,657,866.75	-6,657,866.75	-6,657,866.75	-6,657,866.75	-6,657,866.75	-6,657,866.75	-6,657,866.75	-6,657,866.75	-6,657,866.75	-6,657,866.75	-6,657,866.75	-6,657,866.75
Utilities		8,784.27	8,784.27	8,784.27	8,784.27	8,784.27	8,784.27	8,784.27	8,784.27	8,784.27	8,784.27	8,784.27	8,784.27
Natural Gas		15,312,295.63	15,312,295.63	15,312,295.63	15,312,295.63	15,312,295.63	15,312,295.63	15,312,295.63	15,312,295.63	15,312,295.63	15,312,295.63	15,312,295.63	15,312,295.63
Sand/ash disposal		318,158.24	318,158.24	318,158.24	318,158.24	318,158.24	318,158.24	318,158.24	318,158.24	318,158.24	318,158.24	318,158.24	318,158.24
Fixed Operation Costs		20,376,480.84	20,376,480.84	20,376,480.84	20,376,480.84	20,376,480.84	20,376,480.84	20,376,480.84	20,376,480.84	20,376,480.84	20,376,480.84	20,376,480.84	20,376,480.84
Annual Depreciation		105,886,274.23	58,724,329.75	41,694,274.12	29,602,934.62	21,018,083.58	14,922,839.34	10,595,215.93					
Remaining Value		202,497,688.78	143,773,359.03	102,079,084.91	72,476,150.29	51,458,066.70	36,535,227.36	25,940,011.43					
Net Revenue		43,474,897.61	-4,835,746.82	-21,865,802.45	-33,957,141.94	-42,541,992.98	-47,539,375.59	-52,964,860.63	-63,560,076.57	-63,560,076.57	-63,560,076.57	-62,462,214.93	-63,560,076.57
Losses Forward		-	43,474,897.61	38,639,150.79	16,773,348.35	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Taxable Income		43,474,897.61	38,639,150.79	16,773,348.35	-17,183,793.59	-42,541,992.98	-47,539,375.59	-52,964,860.63	-63,560,076.57	-63,560,076.57	-63,560,076.57	-62,462,214.93	-63,560,076.57
Income Tax		0.00	0.00	0.00	6,701,679.50	16,591,377.26	18,540,356.48	20,656,295.65	24,788,429.86	24,788,429.86	24,788,429.86	24,360,263.82	24,788,429.86
Annual Cash Income		62,411,377	63,560,077	63,560,077	56,858,397	46,968,699	43,921,858	42,903,781	38,771,647	38,771,647	38,771,647	38,101,951	38,771,647
Discount Factor	1.00	0.90	0.81	0.73	0.66	0.59	0.53	0.48	0.43	0.39	0.35	0.31	0.28
Annual Present Value	387,032,588.57	56,170,238.96	51,483,662.02	46,335,295.82	37,304,794.31	27,734,547.25	23,341,876.38	20,520,745.41	16,689,922.58	15,020,930.33	13,518,837.29	11,956,795.99	10,950,258.21

Direct Gasification case (cont.)

Year	13	14	15	16	17	18	19	20
Fixed Capital								
Working Capital								
Propylene Sales	-98,044,505.52	-98,044,505.52	-98,044,505.52	-98,044,505.52	-98,044,505.52	-98,044,505.52	-98,044,505.52	-98,044,505.52
Byproduct Credit	-44,292,230.04	-44,292,230.04	-44,292,230.04	-44,292,230.04	-44,292,230.04	-44,292,230.04	-44,292,230.04	-44,292,230.04
Annual Sales	-142,336,735.56	-142,336,735.56	-142,336,735.56	-142,336,735.56	-142,336,735.56	-142,336,735.56	-142,336,735.56	-142,336,735.56
Annual Manufacturing Cost								
Feedstock	49,418,806.75	49,418,806.75	49,418,806.75	49,418,806.75	49,418,806.75	49,418,806.75	49,418,806.75	49,418,806.75
Tar catalyst								
Methanol Catalyst				294,240.15				
Propylene Catalyst				803,621.49				
Eletricity	-6,657,866.75	-6,657,866.75	-6,657,866.75	-6,657,866.75	-6,657,866.75	-6,657,866.75	-6,657,866.75	-6,657,866.75
Utilities	8,784.27	8,784.27	8,784.27	8,784.27	8,784.27	8,784.27	8,784.27	8,784.27
Natural Gas	15,312,295.63	15,312,295.63	15,312,295.63	15,312,295.63	15,312,295.63	15,312,295.63	15,312,295.63	15,312,295.63
Sand/ash disposal	318,158.24	318,158.24	318,158.24	318,158.24	318,158.24	318,158.24	318,158.24	318,158.24
Fixed Operation Costs	20,376,480.84	20,376,480.84	20,376,480.84	20,376,480.84	20,376,480.84	20,376,480.84	20,376,480.84	20,376,480.84
Annual Depreciation								
Remaining Value								
Net Revenue	-63,560,076.57	-63,560,076.57	-63,560,076.57	-62,462,214.93	-63,560,076.57	-63,560,076.57	-63,560,076.57	-63,560,076.57
Losses Forward	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Taxable Income	-63,560,076.57	-63,560,076.57	-63,560,076.57	-62,462,214.93	-63,560,076.57	-63,560,076.57	-63,560,076.57	-63,560,076.57
Income Tax	24,788,429.86	24,788,429.86	24,788,429.86	24,360,263.82	24,788,429.86	24,788,429.86	24,788,429.86	24,788,429.86
Annual Cash Income	38,771,647	38,771,647	38,771,647	38,101,951	38,771,647	38,771,647	38,771,647	38,771,647
Discount Factor	0.25	0.23	0.21	0.19	0.17	0.15	0.14	0.12
Annual Present Value	9,855,232.39	8,869,709.15	7,982,738.23	7,060,368.46	6,466,017.97	5,819,416.17	5,237,474.55	4,713,727.10

Indirect Gasification case

year	0	1	2	3	4	5	6	7	8	9	10	11	12
Fixed Capital	313,180,804.88												
Working Capital	18,790,848.29												
Propylene Sales		-82,269,418.14	-82,269,418.14	-82,269,418.14	-82,269,418.14	-82,269,418.14	-82,269,418.14	-82,269,418.14	-82,269,418.14	-82,269,418.14	-82,269,418.14	-82,269,418.14	-82,269,418.14
Byproduct Credit		-47,330,593.03	-47,330,593.03	-47,330,593.03	-47,330,593.03	-47,330,593.03	-47,330,593.03	-47,330,593.03	-47,330,593.03	-47,330,593.03	-47,330,593.03	-47,330,593.03	-47,330,593.03
Annual Sales		-129,600,011.17	-129,600,011.17	-129,600,011.17	-129,600,011.17	-129,600,011.17	-129,600,011.17	-129,600,011.17	-129,600,011.17	-129,600,011.17	-129,600,011.17	-129,600,011.17	-129,600,011.17
Annual Manufacturing Cost													
Feedstock		49,418,806.75	49,418,806.75	49,418,806.75	49,418,806.75	49,418,806.75	49,418,806.75	49,418,806.75	49,418,806.75	49,418,806.75	49,418,806.75	49,418,806.75	49,418,806.75
Tar catalyst		50,838.31											
Methanol Catalyst		384,313.66					384,313.66					384,313.66	
Propylene Catalyst		850,690.82					850,690.82					850,690.82	
Eletricity		-421,140.60	-421,140.60	-421,140.60	-421,140.60	-421,140.60	-421,140.60	-421,140.60	-421,140.60	-421,140.60	-421,140.60	-421,140.60	-421,140.60
Utilities		33,138.53	33,138.53	33,138.53	33,138.53	33,138.53	33,138.53	33,138.53	33,138.53	33,138.53	33,138.53	33,138.53	33,138.53
Natural Gas		9,058,400.42	9,058,400.42	9,058,400.42	9,058,400.42	9,058,400.42	9,058,400.42	9,058,400.42	9,058,400.42	9,058,400.42	9,058,400.42	9,058,400.42	9,058,400.42
Sand/ash disposal		318,158.24	318,158.24	318,158.24	318,158.24	318,158.24	318,158.24	318,158.24	318,158.24	318,158.24	318,158.24	318,158.24	318,158.24
Fixed Operation Costs		18,363,405.73	18,363,405.73	18,363,405.73	18,363,405.73	18,363,405.73	18,363,405.73	18,363,405.73	18,363,405.73	18,363,405.73	18,363,405.73	18,363,405.73	18,363,405.73
Annual Depreciation		90,822,433.42	63,092,843.58	44,795,918.94	31,805,102.45	22,581,622.74	16,032,952.14	11,383,396.02					
Remaining Value		217,561,529.59	154,468,686.01	109,672,767.07	77,867,664.62	55,286,041.88	39,253,089.73	27,869,693.71					
Net Revenue		39,279,034.12	10,263,601.49	-8,033,323.15	-21,024,139.65	-30,247,619.36	-35,561,285.46	-41,445,846.07	-52,829,242.10	-52,829,242.10	-52,829,242.10	-51,594,237.61	-52,829,242.10
Losses Forward		-	39,279,034.12	49,542,635.60	41,509,312.45	20,485,172.80	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Taxable Income		39,279,034.12	49,542,635.60	41,509,312.45	20,485,172.80	-9,762,446.55	-35,561,285.46	-41,445,846.07	-52,829,242.10	-52,829,242.10	-52,829,242.10	-51,594,237.61	-52,829,242.10
Income Tax		0.00	0.00	0.00	0.00	3,807,354.16	13,868,901.33	16,163,879.97	20,603,404.42	20,603,404.42	20,603,404.42	20,121,752.67	20,603,404.42
Annual Cash Income		51,543,399	52,829,242	52,829,242	52,829,242	49,021,888	37,725,336	36,665,362	32,225,838	32,225,838	32,225,838	31,472,485	32,225,838
Discount Factor	1.00	0.90	0.81	0.73	0.66	0.59	0.53	0.48	0.43	0.39	0.35	0.31	0.28
Annual Present Value	331,971,653.18	46,389,059.37	42,791,686.10	38,512,517.49	34,661,265.74	28,946,934.61	20,048,790.44	17,536,929.04	13,872,166.44	12,484,949.79	11,236,454.81	9,876,399.26	9,101,528.40

Indirect Gasification case (cont.)

year	13	14	15	16	17	18	19	20
Fixed Capital								
Working Capital								
Propylene Sales	-82,269,418.14	-82,269,418.14	-82,269,418.14	-82,269,418.14	-82,269,418.14	-82,269,418.14	-82,269,418.14	-82,269,418.14
Byproduct Credit	-47,330,593.03	-47,330,593.03	-47,330,593.03	-47,330,593.03	-47,330,593.03	-47,330,593.03	-47,330,593.03	-47,330,593.03
Annual Sales	-129,600,011.17	-129,600,011.17	-129,600,011.17	-129,600,011.17	-129,600,011.17	-129,600,011.17	-129,600,011.17	-129,600,011.17
Annual Manufacturing Cost								
Feedstock	49,418,806.75	49,418,806.75	49,418,806.75	49,418,806.75	49,418,806.75	49,418,806.75	49,418,806.75	49,418,806.75
Tar catalyst								
Methanol Catalyst				384,313.66				
Propylene Catalyst				850,690.82				
Eletricity	-421,140.60	-421,140.60	-421,140.60	-421,140.60	-421,140.60	-421,140.60	-421,140.60	-421,140.60
Utilities	33,138.53	33,138.53	33,138.53	33,138.53	33,138.53	33,138.53	33,138.53	33,138.53
Natural Gas	9,058,400.42	9,058,400.42	9,058,400.42	9,058,400.42	9,058,400.42	9,058,400.42	9,058,400.42	9,058,400.42
Sand/ash disposal	318,158.24	318,158.24	318,158.24	318,158.24	318,158.24	318,158.24	318,158.24	318,158.24
Fixed Operation Costs	18,363,405.73	18,363,405.73	18,363,405.73	18,363,405.73	18,363,405.73	18,363,405.73	18,363,405.73	18,363,405.73
Annual Depreciation								
Remaining Value								
Net Revenue	-52,829,242.10	-52,829,242.10	-52,829,242.10	-51,594,237.61	-52,829,242.10	-52,829,242.10	-52,829,242.10	-52,829,242.10
Losses Forward	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Taxable Income	-52,829,242.10	-52,829,242.10	-52,829,242.10	-51,594,237.61	-52,829,242.10	-52,829,242.10	-52,829,242.10	-52,829,242.10
Income Tax	20,603,404.42	20,603,404.42	20,603,404.42	20,121,752.67	20,603,404.42	20,603,404.42	20,603,404.42	20,603,404.42
Annual Cash Income	32,225,838	32,225,838	32,225,838	31,472,485	32,225,838	32,225,838	32,225,838	32,225,838
Discount Factor	0.25	0.23	0.21	0.19	0.17	0.15	0.14	0.12
Annual Present Value	8,191,375.56	7,372,238.00	6,635,014.20	5,831,915.00	5,374,361.50	4,836,925.35	4,353,232.82	3,917,909.54

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