ABSTARACT

The purpose of this project is to design the process for producinga DME. This was done using two different approaches, the direct method and the indirect method. The required capacity was 3000 ton/yr and the desired purity of the product was 99 wt%. Throughout this project the main emphasis was on how to structure and simulate a process plant, and on the construction of an economic analysis for the plant. The other considerations in this project were maximizing the energy recovery and minimizing the raw material consumption.

Contents

2 DME Production: Direct method

3 DME Production: Indirect method

1 Introduction

Natural gas can be used to produce a large amount of petrochemicals, including methanol and ammonia. These substances however, use a relatively small percentage of the gas reserve and have limited markets. Liquids and other petroleum products are cheaper to transport, market, and distribute. These can be moved in existing pipelines or product tankers for NG and even blended with existing crude oil or product streams. Further, no special contractual arrangements are required for their sale with many suitable domestic and foreign markets.

New technology is being developed and applied to convert natural gas to liquids in gas to liquids technology (GTL[1]). As a generalization however, GTL is not competitive against conventional oil production unless the gas has a low opportunity value and is not readily transported. The GTL process not only adds value, but is capable of producing products that could be sold or blended into refinery stock to reduce superior products with fewer pollutants for which there is growing demand.

Catalytic conversion of NG[2] to more useful chemicals and fuels is a challenge for the 21st century. Dimethyl ether (DME) made from natural gas is one such possible process. As DME is so easily liquefied at ambient temperature (GTL process), and the fact that liquids are easier to transport over great distances than compressed gases makes DME an interesting substance. LPG[3] existing infrastructures such as tanks and tankers could be used with minor modifications.

DME is potentially a highly competitive renewable alternative to today's fossil fuels. DME has several properties that make it attractive as a fuel for diesel engines, including no sulfur emission, very low particulate emission and high cetane number. Combustion and emission tests have proven that after minor modifications of a diesel engine, DME can be added to diesel fuels, thus lowering smoke and NO_x emissions, but with the same thermal efficiency. Traditionally DME has been used to produce intermediate chemicals such as dimethyl sulfate or oxygenated compounds. Today DME is used mainly as a propellant for spray cans, but the beneficial properties of using DME as a substitute for LPG (industrial and residential) and

---

[1] Gas to liquid
[2] Natural gas
[3] Liquefied petroleum gas

LNG[4] in power plants, and as diesel oil substitute in vehicles makes DME one of the superior candidates for high-quality fuel for the next generation.

What is DME?

Dimethyl ether (DME) is the simplest ether having the chemical formula: CH_3OCH_3. Table 1.1 contains physical properties and combustion characteristics of DME and relating fuels of current interest.

Table 1.1: Physical properties of DME and other relevant fuels [1]

Properties	DME	Propane	Methane	Diesel fuel
Chemical formula	CH_3OCH_3	C_3H_8	CH_4	
Boiling Point [°C]	-25,1	-42,0	-161,5	180 - 370
Liquid density [g/cm^3]at 20°C	0,67	0,49	0,42	0,84
Liquid viscosity [kg/ms] at 25 °C	0,12 - 0,15	0,2	-	2 - 4
Relative density of gas [ratio air]	1,59	1,52	0,55	-
Vapor pressure [Mpa] at 25 °C	0,61	0,93	-	-
Explosion limit [%]	3,4 - 17	2,1 – 9,4	5 - 15	0,6 – 6,5
Cetane number	55-60	5	0	40 - 55
Net calorific value [kcal/Nm^3]	14,200	21,800	8,600	-
Net calorific value [kcal/kg]	6,900	11,100	12,000	10,000

DME is a chemically stable and colourless gas. It has a boiling point of - 25.1°C and a vapour pressure of about 0.6 MPa at ambient temperature, which makes DME easily liquefied. The physical properties of DME are very similar to those of LPG, thus DME can be distributed and stored (etc.) using LPG handling technology.

DME decomposes in the troposphere and does not affect the greenhouse effect and ozone layer. The substance does not corrode any metals. However some elastomers would swell in a liquid DME. In addition DME is non carcinogenic and harmless in any way as demonstrated by decades of use in human care products.

DME plants

The worldwide production and use of DME has been relatively small. Approximately 10 000 ton/yr are produced in Japan, and no more than 150 000 ton/yr worldwide. Existing DME plants are small and selling DME in high price chemical market. Table 1.2 describes the world production of DME per company and country.

---

[4] Liquefied natural gas

Table 1.2: Existing DME plants in the world per June 2006[2].

Company	Country	Capacity [ton/yr]
Shell/RWE	Germany	60 000
Hamburg DME Co	Germany	10 000
AKZO	The Netherlands	10 000
DuPont	West Virginia, USA	15 000
MGC	Sumitomo, Japan	10 000
	Australia	10 000
	Taiwan	15 000
Liutianhua group	Luthianhua, China	110 000 - for fuel
Jiutai group	Jiutai etc. China	120 000 - for fuel from coal
Ningxia Coal Group	China	210 000 ton/yr - for fuel from coal

To be competitive in the fuel marked the DME-plant has to have a capacity of at least 1-2 millions ton/yr (about 3000 ton/d). The two plants considered in this report both have a capacity of about almost 2880 ton/day. DME commercial plant projects around the world are listed below [2].

China: Liutianhua group completed a 10 000 ton/yr DME plant in September 2003. This group also successfully started up a 110 000 ton/yr DME plant that was finished in 2006 in Sichuan Province. Ningxia Coal Group also started up a 210 000 ton/yr DME plant from coal in 2007. In Addition Jiutai group plans to build a 1 million ton/yr DME plant from coal in Mongolia.

Iran: Zagros Petrochemical has reported to construct 800 000 ton/yr DME plant in Bandar Assaluyeh. (European Chemical News - June/July, 2004). The current situation is not clear.

Japan: Three big groups (JFE, Mitsubishi, Mitsui) are separately planning production of about 2 000 000 ton/yr DME in the Middle East, Australia or South East Asia. These companies want to import DME to Japan.

Fuel DME Production Co., Ltd. (“FDME”), a joint venture from Japan made its first delivery of DME to its customers in January 2009. In June 2008, FDME successfully completed a trial operation of the Fuel DME Promotion Plant (Niigata City, Japan) with a capacity of 80 000 ton/yr. The Indian Oil Corporation (IOC) is courting three major Japanese companies, including Marubeni Corp, for a possible tie-up for setting up a $600 million plant for producing DME for use as alternate fuel in power plants. The 1.8 million tonne capacity DME plant would be located in one of the natural gas producing Middle-East Asian countries and would be built at an estimated cost of $500 million.

Preparation of DME

Nowadays, DME is commercially prepared by dehydration of methanol using acidic porous catalysts such as zeolites, silica–alumina, alumina, etc. Using synthesis gas as a starting material, DME can be prepared in a one-step process (Wen-Zhi Lu, 2004).This method is more thermodynamically and economically favourable than the two-step process. In this process both the methanol formation reaction and the methanol dehydration reaction, to form DME, takes place in the same reactor over a dual catalyst. In the two-step process synthesis gas is first converted to methanol and then further to DME. This project has investigated both processes. Figure 1.1 present both synthesis pathways.

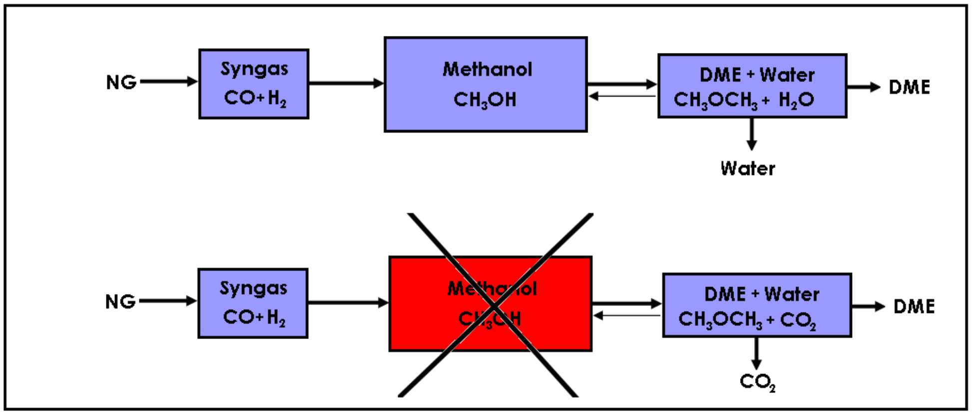


Figure 1.1: The indirect method above, and the direct method below [2].

DME Market

As the world population is growing, the increase in fuel demand is taking off. The fuels used in the world today consist mainly of fossil fuels, which is harmful to the environment. Today the climate changes have come to an extreme point (there are seen large environmental changes). For example the CO_2 concentration in the atmosphere has increased with approximately 36 % during the last 250 years[3]. See figure 1.2 for the supposed increase in CO_2 emission in the future. This is considered the most important contribution to the increasing atmospheric greenhouse effect.

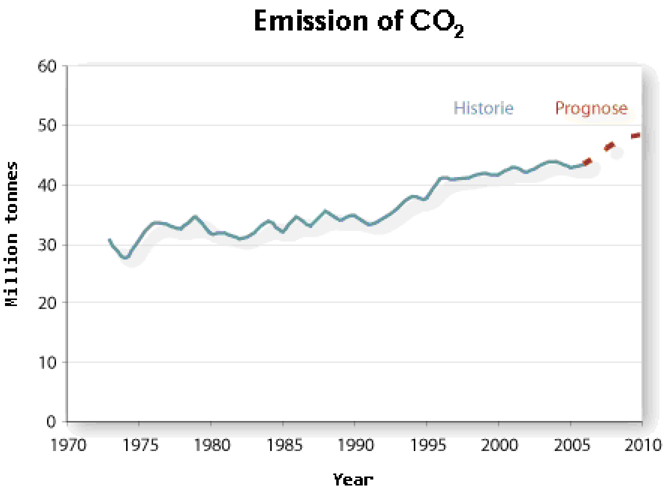


Figure 1.2: CO_2 emission in millions ton from 1973 till today, and the supposed emission in year 2010[4]

Almost 5 % of the natural carbon cycle is man-made emission, which is around 32 billion ton of CO_2 pr year. Burning of fossil fuels, like coal, oil and gas, is one of the largest contributions. The world leaders have taken action and restricted the amount of emission of pollution. As the population is growing and the people of the world is getting more enlightened and engaged about the environment, major companies have seen the possibilities and advantages of more environmentally benign fuels such as DME.

As mentioned, DME decomposes in the troposphere and does not affect the greenhouse effect and ozone layer. The substance does not contain sulphur or ash. When burned it has lower CO_2-emission and does not generate any SO_x or particulate matter. It is a clean fuel of high cetane, has excellent combustion characteristics and extremely low toxicity. Therefore it has more environmentally attractive properties than existing fuels. Thus DME is potentially a highly competitive renewable alternative to today's fossil fuels and other disadvantageous chemicals. In the LPG market DME/LPG blend (up to 30%) appear promising. The technology for storage and transportation already exist. Only minor modifications are needed. For the power generation market DME is often competing with other fuels such as LNG, coal, and nuclear.

The diesel market is the most promising area. The diesel engines need only minor changes to run on liquid DME. However the concept might need more time to grow. Considering the fuel cell market much depends on the fuel cell development. As petrochemical feedstock DME has potential. One example is the production of olefin from DME. There is a growing olefin market in Asia.

2 DME Production: Direct method

2.1 Project basis

A preliminary block diagram for a DME process is shown in the in Figure 2.1. The raw materials are natural gas, water and oxygen. Natural gas is fed to the plant at 50°C and 70 bar. Water, at 25°C and 1 bar, is coming from the sea which has been processed and purified by the desalination membrane. It is assumed that oxygen, as the third feed, is entered the plant at 50°C and 30 bar. DME as a final product should be almost pure. The target of our project is producing 3000 metric tons per day of 99 wt% purity DME.

The other considerations in this project are maximizing the energy recovery by producing HPS[5], MPS[6] and LPS[7] or heat integration in the plant, as well as minimizing the raw material consumption. The location for the two plants considered in this project is chosen to be the available land at Tjeldbergodden (industrial site near the sea).

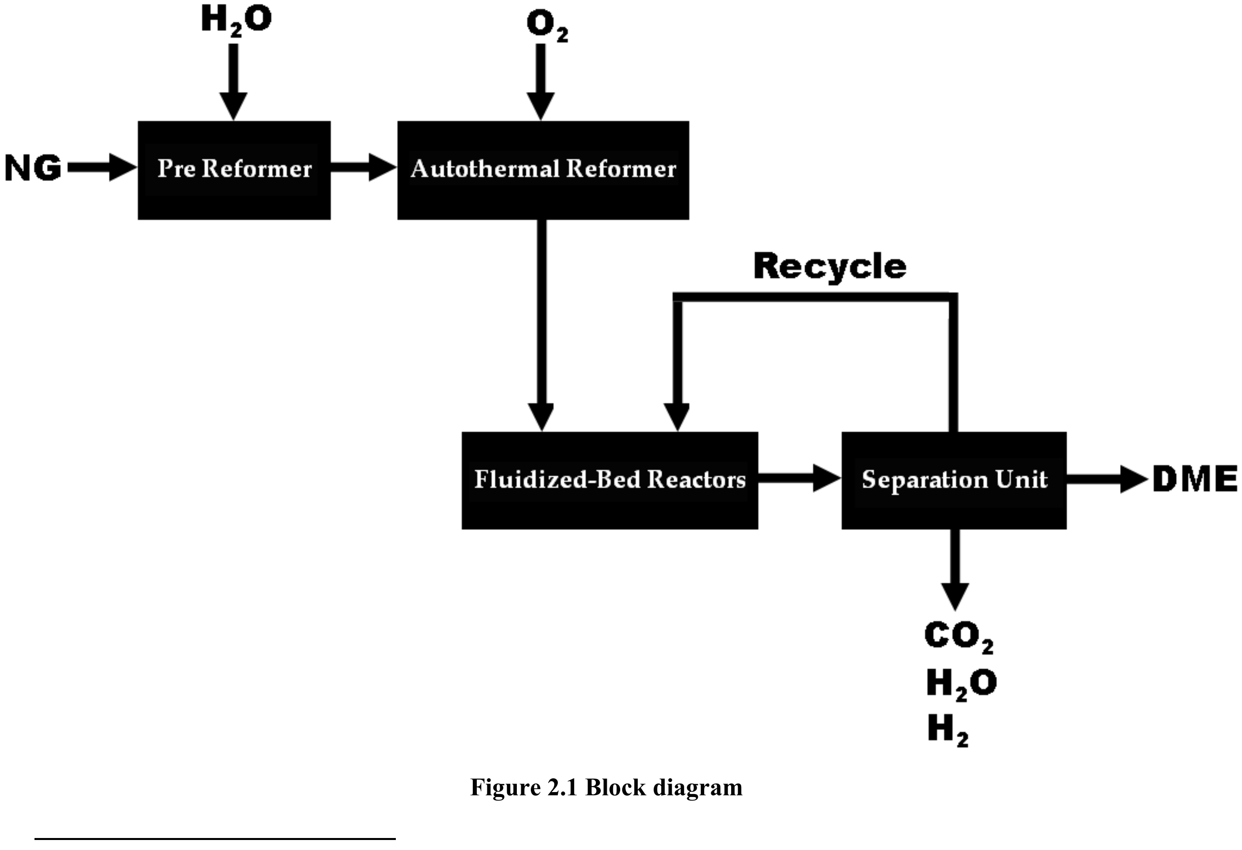


Figure 2.1 Block diagram

---

[5] High pressure steam
[6] Medium pressure steam
[7] Low pressure steam

2.2 Process description

2.2.1 Flowsheet

The detailed flowsheet for the production of DME from natural gas (direct method) is shown in figure 2.2. The feed for the process is natural gas with given composition (see appendix A) and condition (50^{o}C, 70 bar), and water, fed to the process at 25 ^{o}C and 1 bar. To reach the pre-reformer reactor conditions (455 ^{o}C and 30 bar) the natural gas had to be expanded by using K-100 and heated. The water stream had to be compressed by P-100 and heated. It is assumed that there is no pressure drop in any of the heat exchangers including E-100 and E-101.In the pre-reforming part, the alkane steam reforming and water gas shift reaction take place.

In the autothermal reformer part, oxygen and the pre-reformer product had to be heated to 550°c before entering the autothermal reformer. In the autothermal reformer, partial oxidation of methane is conducted in order to produce the heat required for the endothermic reforming reactions. The product of ATR has high temperature (1000°C).

In order to cool the high temperature gaseous product and separating water, this stream is entered to the series of heat exchangers (E-104, E-105 and E-106) for producing high, medium and low pressure steam. After cooling the gases, waste water is separated in V-100.

Because of the FBR[8] conditions, the gaseous outlet of V-100 is heated to 260°c, in E-107, and is combined with recycled reactant, stream 49, and then the mixture is fed to the three parallel fluidized-bed reactors (FBR series). A series of reactions takes place in the reactors and the end products are DME, methanol, CO_2, H_2, CO and H_2O.

The product is sent to a 3-phase separator V-101 for primary separation. The gaseous outlet, stream 34, is sent to the V-102 in order to separate DME from the gases, stream 53. Stream 35, mostly DME and CO_2, is mixed with stream 53 and then they are conducted to the first distillation column, T-100. In T-100, the bottom outlet, stream 41 consists of DME and methanol and has to be sent to T-103 for separation of DME from methanol. The overhead of T-100 is sent to T-101 and then top stream of T-101 is conducted to T-102 for separating DME from CO_2. T-104 is for separating methanol from water.

---

[8] Fluidized-Bed reactor

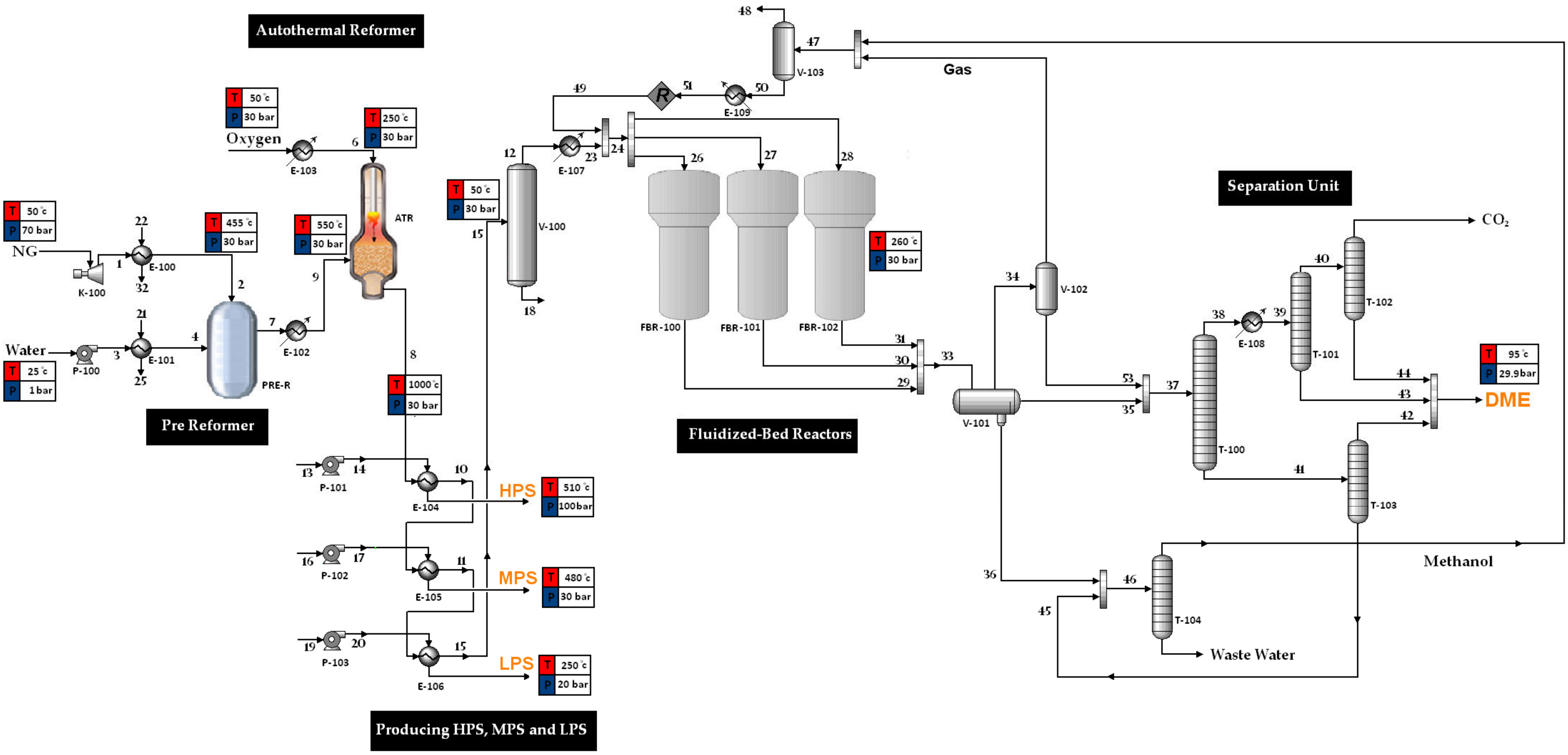


Figure 2.2 PFD

2.2.2 Process Concepts

2.2.2.1 Reforming Process

A typical way for production of synthesis gas based on ATR is shown in Figure 2.3. The key steps in the process scheme are desulphurization (for raw materials such as coal or oil), adiabatic pre-reforming, autothermal reforming, and heat recovery.

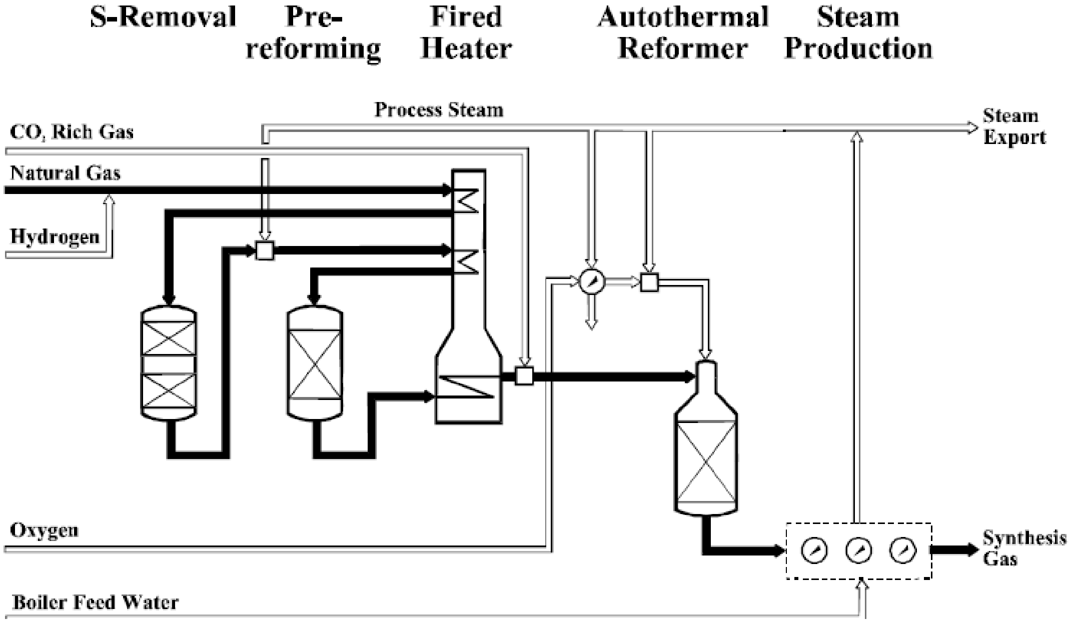


Figure 2.3 Process Concepts for Synthesis Gas Production by Adiabatic Pre-reforming and Autothermal Reforming

Production methods from natural gas to syngas are largely divided into three types: steam reforming, oxyreforming, and CO_2 reforming.

The steam reforming process is mainly used for hydrogen and syngas production. Syngas produced from steam reforming has the high synthetic ratio (H2/CO) of 3 and is thus usually consumed by hydrogen production or ammonia synthesis processes. For methanol production, with a primary synthetic ratio of 2, it is adjusted the synthetic ratio by lowering the hydrogen concentration through a water-gas shift reaction, or by a secondary reforming reaction, such as autothermal reforming (Wilhelm, D.J, 2001).For DME production, a synthetic ratio of 1 is preferred.

The oxyreforming process (e.g., autothermal reforming) uses oxygen as a reactant to produce syngas and is generally used to adjust the synthetic ratio. Oxygen, or air with a high concentration of oxygen, is fed into the autothermal reforming reaction (or "ATR") by oxidant, and to the case, steam is added with the feedstock. This reaction is the most preferable when taking into account the thermodynamics ($\Delta H < 0$) among several reforming processes and can produce syngas with a lower synthetic ratio. This H_2/CO ratio can be obtained through recirculation of CO_2 or a CO rich of gas, as well as by reducing the amount of steam in the feed (Ruiz, J. et al, 2008). In this project, the autothermal reforming process was used to produce syngas with a synthetic ratio of 2, which is being used in a DME pilot plant (50 kg/d) by the Korean gas company (Chul-Jin Lee, et al, 2009).

2.2.2.2 Adiabatic pre-reforming

Adiabatic pre-reforming is used for the reforming of natural gas. The process is carried out in a fixed-bed upstream the tubular reformer. Higher hydrocarbons are completely converted into CO, H_2 and CH_4. The reactions taking place in the pre-reformer are (Dybkjær, I., 1995):

$$C_nH_m + nH_2O \rightarrow nCO + (n+m/2)H_2 \qquad (2.1)$$

In case of natural gas as feedstock, the overall process is endothermic, and therefore will result in a temperature drop since the reactor is adiabatic. For higher hydrocarbon feed stocks, the pre-reforming is exothermic or thermo neutral. With installing a pre-reformer, all higher hydrocarbons are completely converted into CO, H_2 and CH_4 (Dybkjær, I., 1995).

2.2.2.3 Autothermal reforming

In autothermal reforming (ATR), partial oxidation of methane is conducted in order to produce the heat required for the endothermic reforming reactions. Characteristic of the autothermal process is that the oxygen added to generate heat is chemically bound in the product gas, which makes the H_2/CO ratio in the product gas lower than in other processes. Typical operating conditions are 850–1000 °C and 20–100 bar (Moulijin, J., et al, 2001).The maximum temperature is not limited by the tube material but by the stability of the catalyst and the refractory lining of the reactor.

There are two types of autothermal reformers: pure catalytic, and with a pre-combustion unit. In the pure catalytic reformer, the reactants (methane, oxygen and steam) enter the catalyst bed directly after mixing. This performance, without any residence time in the empty space above the catalyst bed, results in no carbon formation, even at low preheat temperatures of the feedstock (methane). Steam reforming reactions take place more quickly than the Boudouard reaction equilibrium is tuned in. Boudouard reaction is:

$$2CO \rightarrow CO_2 + C \qquad (2.2)$$

This makes it possible to use less steam, and hence less oxygen, which results in a higher CO/CO_2 ratio in the product gas. The drawbacks with this purely catalytic process are high thermal and mechanical loads on the catalyst in the immediate vicinity of the burner. Temperature variations during start-up and shut-down and high gas velocities lead to attrition and catalyst disintegration, which in turn makes it necessary to replace the catalyst every two years (K. Sommer, 1989).

Reforming with pre-combustion in the empty space above the catalyst bed is preferred for gases that have very low risk of carbon deposition, i.e. gases with high H_2 content and low hydrocarbon content. This type of reforming requires slightly more oxygen than the pure catalytic type, and the gas velocities must be lower (K. Sommer, 1989). For natural gas autothermal reforming, the concept with the pre-combustion zone is preferred, and will be described further.

ATR[1], as a concept, is a stand-alone process in which the entire natural gas conversion is carried out by means of internal combustion with oxygen. Secondary reforming is a process in which partially converted process gas from a tubular steam reformer is further converted by means of internal combustion. The secondary reformer in an ammonia plant will be air-blown, while that of a methanol plant will be oxygen blown (Dybkjær, I., 1995).

The autothermal reforming is usually not used on its own, due to high investment costs for separation of the oxygen from air. It is rather used downstream a steam reformer, i.e. as a secondary reformer, in order to reform the unreacted methane from the steam reformer. This makes it possible to increase the pressure without increasing the temperature in the steam reformer, which is not favourable for the equilibrium but economically favourable if the syngas will be used for a high-pressure chemical synthesis.

The ATR and the secondary reformer are, however, very similar in reactor design. They consist of a refractory-lined pressure vessel (and therefore stands higher pressures and temperatures than the steam reformer) with a burner, combustion chamber and catalytic bed.

---

[1] Auto thermal reforming

The reactor space can be divided into three zones (see Figure 2.4) in which different reactions take place according to Table 2.1(Dybkjær, I., 1995).

Table 2.1 Reaction zones in an ATR

Reactor equipment	Reaction zones
Burner	provide mixing
Combustion chamber	Combustion zone - Thermal zone
Catalyst bed	Catalytic zone

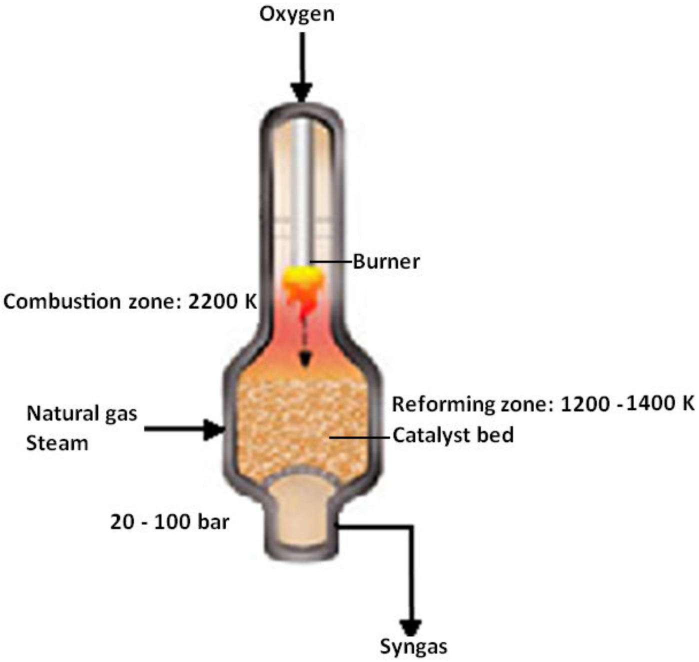


Figure 2.4 Schematic picture of an ATR (Moulijin, J., et al, 2001).

Burner

The burner provides the mixing of the feed streams in a turbulent diffusion flame. The core of the flame has a high temperature, often above 2000 ºC. This is why it is important to minimize the transfer of heat back to the burner from the flame.

Combustion zone

This is the turbulent zone in which the hydrocarbon and oxygen are mixed and combusted. The exothermic combustion reactions are very fast. The overall oxygen to hydrocarbon ratios in the combustion zone varies between 0.55 and 0.6, which means that the conditions are substoichiometric with respect to complete combustion. The combustion reactions are numerous complex radical reactions, but for modeling purposes, it is often enough to describe the reactions by an overall one molecular reaction. In case of natural gas (Dybkjær, I., 1995):

$$CH_4 + 3/2\ O_2 \leftrightarrow CO + 2H_2O \qquad (2.3)$$

All oxygen is consumed in the combustion zone, and the unconverted CH_4 will continue down to the thermal zone. In case of a secondary reformer, also H_2 will be burnt to water in the combustion zone according to reaction.

Thermal zone

In the thermal zone, the conversion of the hydrocarbon proceeds via homogeneous gas phase reactions. The main reactions are thermal methane reforming (2.4) and WGS (2.7).

$$CH_4 + H_2O \leftrightarrow CO + 3H_2 \qquad (2.4)$$

Catalytic zone

The catalytic zone is a fixed-bed, in which the methane is finally converted through heterogeneous catalytic reactions. At the exit of the catalytic zone, the gas mixture will be in equilibrium with respect to reactions (2.4) and (2.7) at the exit temperature and pressure. The syngas is completely free of oxygen.

2.2.2.4 DME production in the Fluidized-Bed Reactor

Three reactions take place in the syngas-to-DME process, namely:

Methanol synthesis:

$$CO2 + 3H2 \leftrightarrow CH3OH + H2O \qquad \Delta H = -56.33\ kJ/mol \qquad (2.5)$$

Methanol dehydration:

$$2CH3OH \leftrightarrow CH3OCH3 + H2O \qquad \Delta H = -21.255\ kJ/mol \qquad (2.6)$$

Water gas shift:

$$CO + H2O \leftrightarrow H2 + CO2 \qquad \Delta H = -40.9 kJ/mol \qquad (2.7)$$

Overall reaction

$$3CO + 3H2 \leftrightarrow CH3OCH3 + CO2 \qquad \Delta H = -256.615\ kJ/mol \qquad (2.8)$$

Reactions (2.5) and (2.7) are catalyzed by a methanol synthesis catalyst (Cu/ZnO/Al2O3) and reaction (2.6) by an acidic catalyst (e.g. HZSM-5). These three reactions form a synergistic system yielding higher syngas conversion or greater productivity when compared to the syngas-to-methanol process. The synergy works in the following manner: methanol, which would otherwise be near its equilibrium value, is consumed by reaction (2.6), and water formed by reactions (2.5) and (2.6) is consumed by reaction (2.7), while reaction (2.7) generates hydrogen which improves reaction (2.5) but consumes CO which is not favorable. All the three reactions are reversible and exothermic.

Moreover, the catalyst for reactions (2.5) and (2.7) is subject to severe deactivation when overheated to above 270 ºC. To avoid thermodynamic limitations and excessive catalyst deactivation, conventional gas-phase reactors must be operated at a low per-pass conversion to maintain reactor temperature below 270 ºC, implementing a high-syngas recycle rate, and resulting in large capital investments and operating costs. In addition, in order to avoid serious pressure drop, the diameter of catalyst particles in fixed-bed reactor is usually over 4mm, which brings a certain inner mass-transfer resistance.

The fluidized-bed reactor is proposed as an ideal reactor for the DME synthesis (Xiao, W.D., et al, 2002).Compared with the slurry reactor and fixed-bed reactor, the gas–solid mass transfer resistance in a fluidized-bed reactor is so small that it can be neglected, and excellent temperature control is also achievable due to the vigorous mixing of catalyst particles in the bed.

Effect of reaction temperature (Wen-Zhi Lu, et al, et al, 2004)

The effect of temperature is shown in Figure 2.5, which reveals that with the increase of temperature, there exists an optimum temperature for CO conversion and DME productivity between 280 and 290 ºC. The existence of optimum is partly due to the declining equilibrium value of CO conversion with temperature increase, and more due to the synergy of the different methanol synthesis and methanol dehydration catalyst component with different active temperature regions. But it should be noted that the catalyst has to be exposed to lower temperatures, less than 270 ºC, to avoid excessive deactivation. Moreover, DME selectivity increases a little, because higher temperature is more favorable for the activity of methanol dehydration catalyst rather than methanol synthesis catalyst.

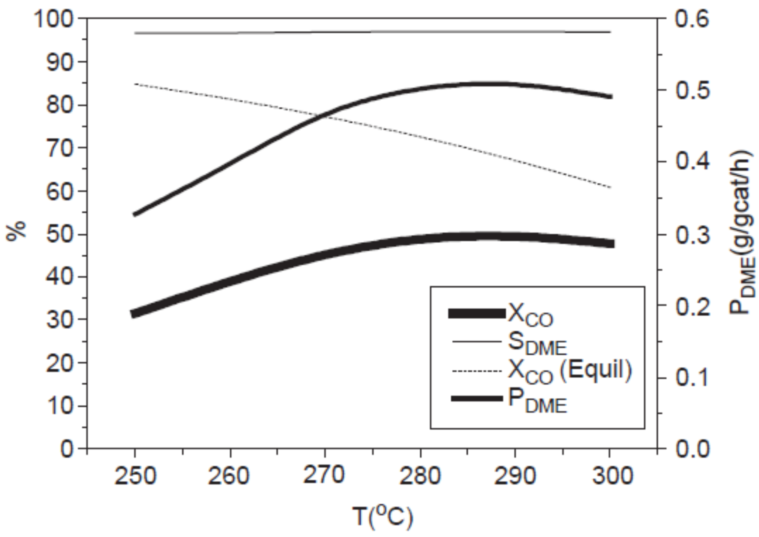


Figure 2.5 Effect of temperature on reactor performance H2/CO = 1, SV = 3000 ml/gcat/h, P = 3MPa.

Effect of reactor pressure (Wen-Zhi Lu, et al, et al, 2004)

As is shown in Figure 2.6, increasing the pressure results an increase in CO conversion and DME productivity, because the increase of pressure accelerates the methanol synthesis and the whole reaction as well. In addition, because methanol dehydration reaction approaches to equilibrium catalyzed by HZSM-5 catalyst, DME selectivity keeps a high level with the increase in pressure.

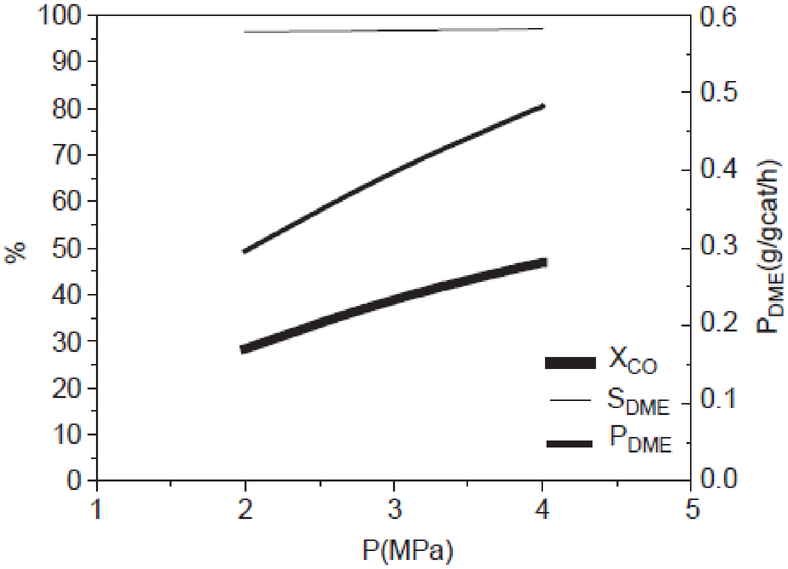


Figure 2.6 Effect of pressure on reaction results: SV = 3000 ml/gcat/h, H2/CO = 1, T = 260 ◦C.

2.3 Simulation in UniSim

Production of DME from natural gas has been simulated using UniSim with **PRSV**[1] fluid package. There are several useful thermodynamic packages in UniSim such as **SRK** and **PR**. (UniSim doesn't recommend PR and SRK for DME).

These fluid packages allow us to predict properties of mixtures ranging from well defined light hydrocarbon systems to complex oil mixtures and highly non-ideal (non-electrolytic) chemical systems. UniSim provides enhanced equations of state for rigorous treatment of hydrocarbon systems; semi empirical and vapour pressure models for the heavier hydrocarbon systems; steam correlations for accurate steam property predictions; and activity coefficient models for chemical systems. All of these equations have their own inherent limitations and one has to become familiar with the application of each of them. For the Chemical industry due to the common occurrence of highly non-ideal systems, the **PRSV** EOS is a good alternative. It is a two-fold modification of the PR equation of state that extends the application of the original PR method for highly non-ideal systems.

We divided the simulation into several parts, namely pre-reforming, auto thermal reforming, producing high-, medium- and low pressure steams, production of DME in fluidized-bed reactors, separation and heat integration as new simulation.

2.3.1 Pre-reforming

The feed for the process is natural gas with given composition and condition (50°C, 70 bar), and water, fed to the process at 25°C and 1 bar. To reach the pre-reformer reactor conditions (455 °C and 30 bar) the natural gas feed had to be expanded and heated. The water stream had to be compressed and heated. It is assumed that there is no pressure drop in E-100 and E-101.

There are three conversion reactions and one equilibrium reaction taking place in the pre-reformer. To simulate the pre-reformer in UniSim we therefore added both a conversion reactor and an equilibrium reactor. Two reaction sets had to be defined, one set for the three conversion reactions and one for the equilibrium reaction. Also we defined the reactors adiabatically and with no pressure drop.

The operating pressure of the pre-reformer is 30 bar. Three main components has to be present in the reformer make the reactions occur. These are natural gas ,stream 2 ,which

---

[1] Peng Robinson-Stryjek-Vera

contains methane, ethane, propane and n-butane, steam (stream 4) and catalyst (NiO). The catalyst are not directly modelled in the reactor because these components are not consumed during the reforming reactions.

Shell and tube heat exchangers were used to simulate the E-100 and E-101. HPS and MPS, produced from the hot gas leaving the ATR, were used for heating. The hot steams run through the shell side and the fluids being heated run on the tubes.

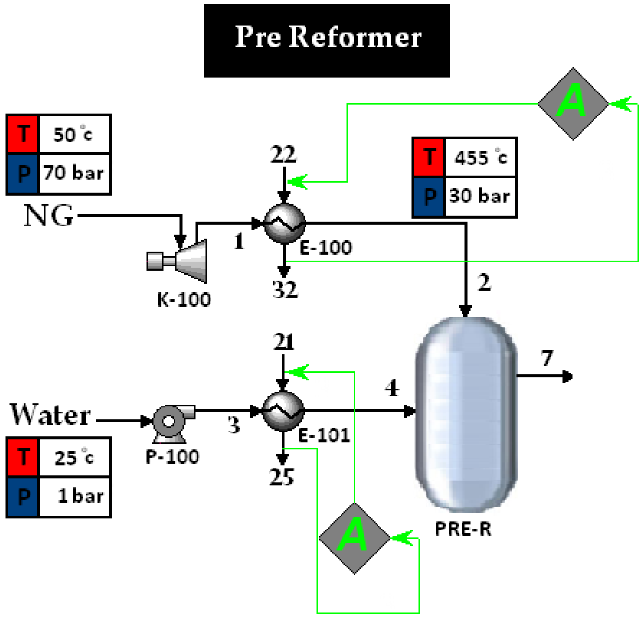


Figure 2.8 Pre-reforming unit

The temperature of the outflow steam was set by using an Adjust loop. This Adjust loop calculated the amount of MPS needed to reach the specified temperature in the outflow steam. Outflow steam temperature was found by recognising that ΔT between cold stream in and hot stream out should be approximately 25 ºC. Finally, the product is leaving the pre-reformer at 455 ºC and 30 bar through stream 7.

2.3.2 Autothermal reforming

To further lower the synthetic ratio a secondary reforming process was added, namely autothermal reforming. This oxyreforming process uses oxygen as a reactant to produce syngas at 1000 ºC. So oxygen had to be added as a feed stream. To meet the reactor conditions the oxygen stream had to be heated (E-103).The stream leaving the pre-reformer also had to be heated(E-102).To reach a high enough temperature in this stream a non-reactive fired heater had to be added. In UniSim this is simulated by a general heater. The reactions happening in the reactor were added and one set was defined for them. There are three equilibrium reactions thus the ATR is simulated by an equilibrium reactor. As the oxidation of methane is highly exothermic, the stream leaving the reactor has a high temperature.The ATR product is leaving the reactor at 1000°C and 30 bar. This stream was utilized to produce HPS, MPS and LPS.

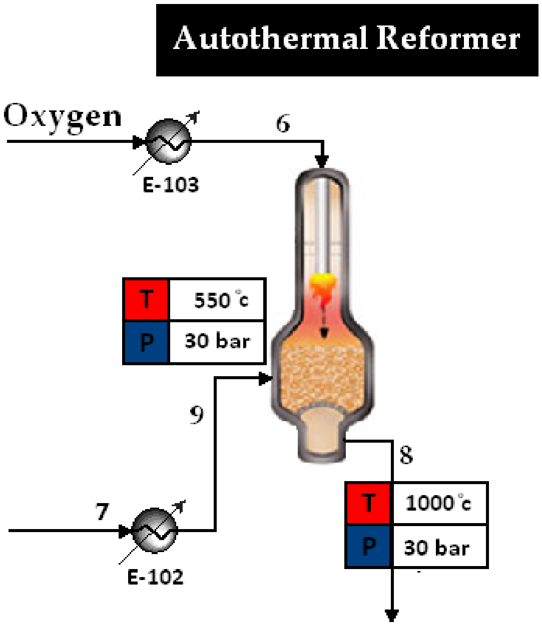


Figure 2.9 Autothermal unit

2.3.3 Producing high, medium and low pressure steam

As illustrated in figure 2.10, outlet of ATR has high temperature (1000 ºC) and this stream can be utilized to produce HPS, MPS, and LPS. Water at ambient temperature and pressure, was compressed and heat exchanged with the hot stream from the ATR. Shell and tube heat exchangers were chosen to simulate this process.

The specifications for the different steams were given to us by our supervisor [14].The pressures in the outflow steams were set and the temperatures were set by using an Adjust loop. This Adjust loop calculated the amount of water needed to reach the specified temperature in the HPS, MPS and LPS. The water being heated runs through the shell side, and the hot gas runs through the tubes.

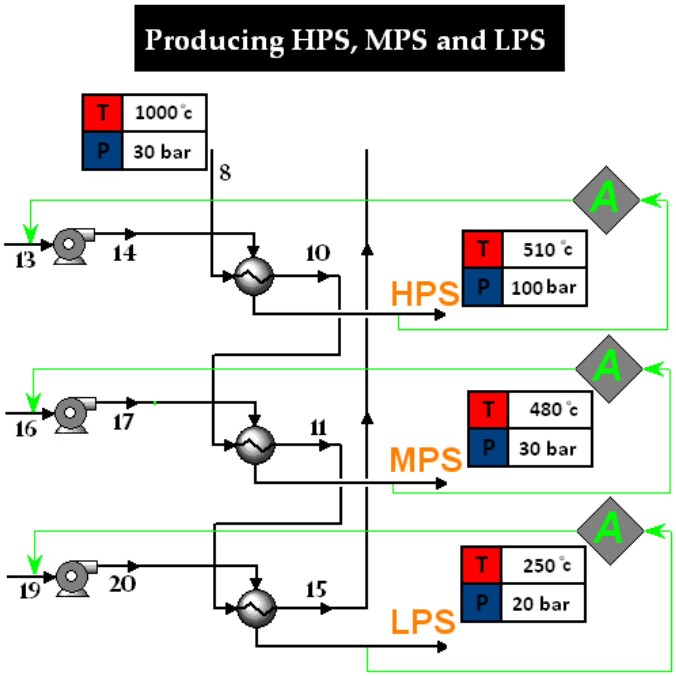


Figure 2.10 Producing HPS, MPS and LPS

After the autothermal reforming process there was a lot of water in the stream. This had to be removed because of the reactions in FBR reactors. A gas-liquid phase separator was chosen for separating the water. The temperature in outlet of the separator was set as a specification.

2.3.4 Production of DME in fluidized-bed reactors

The problem with fluidized bed reactors is that they do not correspond to any of the easily-modelled ideal reactors. While most of the gas flows upward through the liquid-like suspended particles, some passes through in bubbles with scant contact with any catalyst particles. In addition, there is generally some circulation and turbulent back-mixing. Since Unisim is not set up to model this, we had to use an approximate method. Thus three parallel CSTR-reactors were chosen to simulate the FBR reactors.

The stream had to be split into three equal streams before entering the reactors. There are three reactions taking place in the reactor and a set of these reactions were added. In addition, the reaction kinetics was loaded into UniSim (see appendix B). The specifications for the reactors were temperature of outlet streams, volumes and assuming there is no pressure drop. After the reactor the three streams had to be mixed.

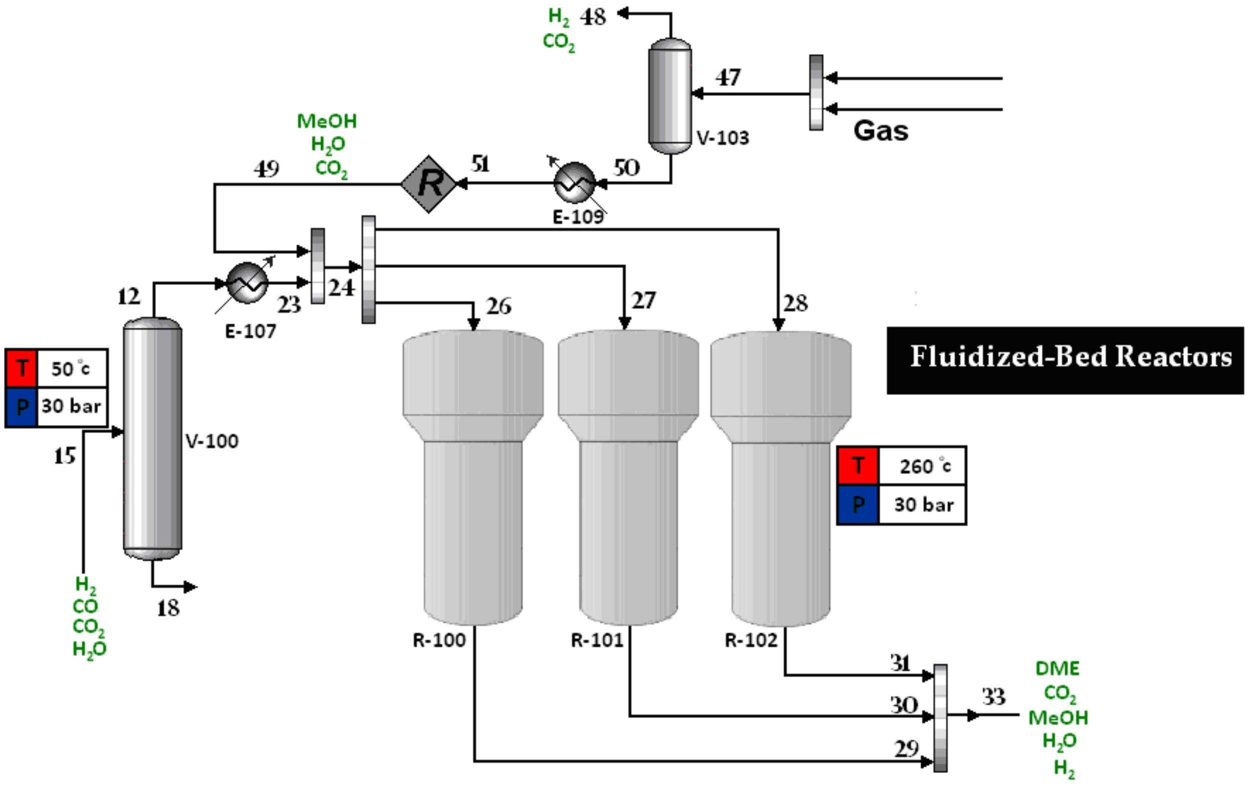


Figure 2.11 Production of DME in fluidized-bed reactors

2.3.5 Separation

In order to purify DME from other components one three-phase separator, two general separators, one cooler, one heater, three mixers and five distillation columns are used. The outlet of reactors is consisting of DME, CO_2, methanol, water and hydrogen. The three-phase separator is used as primary separator. We used the V-102 to separate the gases, especially H_2, from the DME.

T-100 is used to purify stream 37 from methanol and water. In the overhead stream of T-100 there are only DME and CO_2. First, we wanted to separate CO_2 by using CO_2 capture unit. But the UniSim didn't recommend Amin package for DME, Thus two distillation columns are used to separate CO_2 from DME. The specs for distillation columns are illustrated in table 2.2.

Table 2.2 The specs of distillation columns

Column	Specs
T-100	Reflux ratio – Temperature of condenser
T-101	Reflux ratio – Mole fraction of DME in bottom outlet
T-102	Reflux ratio – Mole fraction of DME in bottom outlet
T-103	Reflux ratio – Mole fraction of DME in bottom outlet
T-104	Reflux ratio – Mole fraction of H_2O in bottom outlet

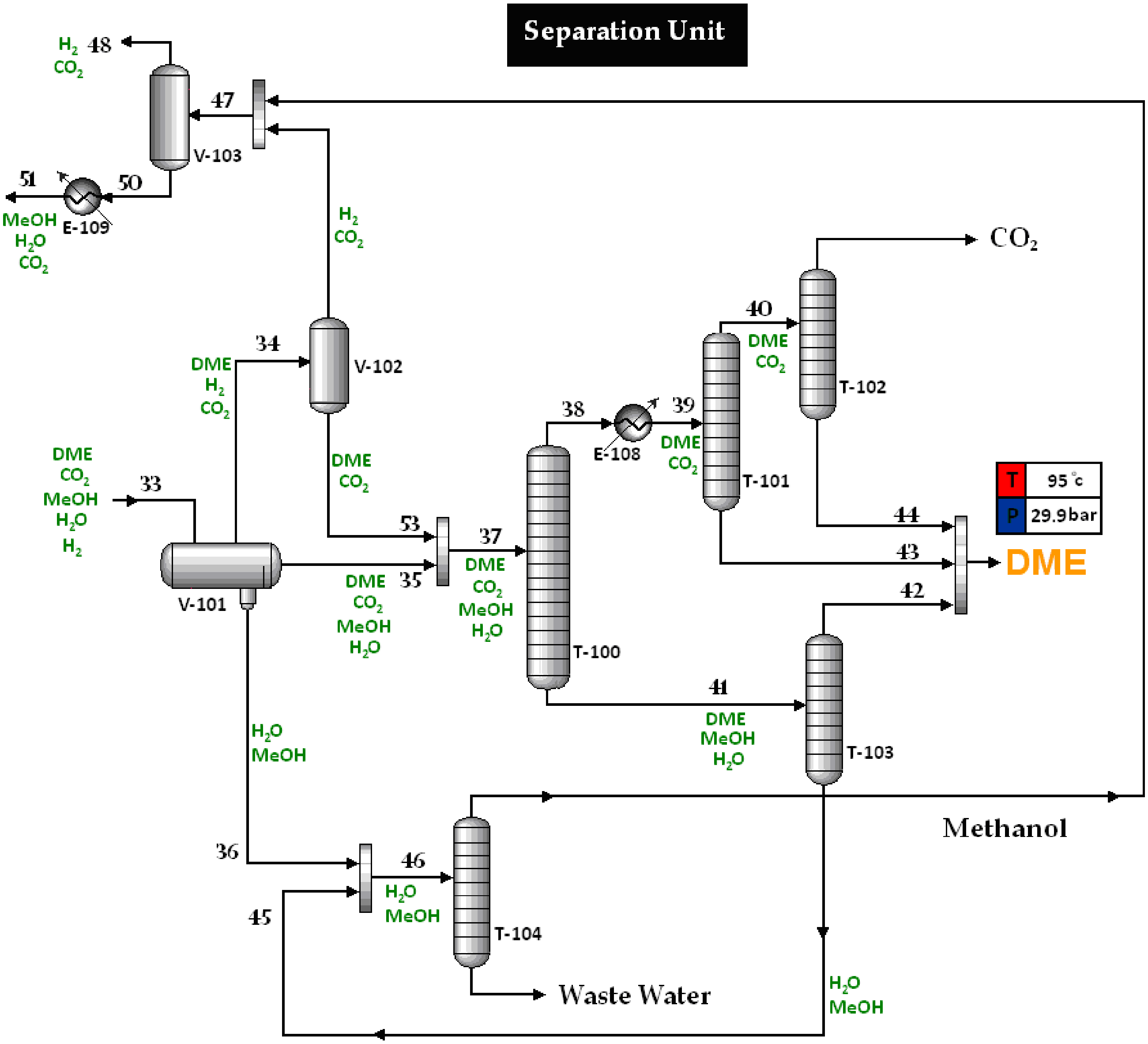


Figure 2.12 Separation unit

T-103 is used to separate DME from methanol and water. Methanol for recycle, is separated from water in T-104. (For all the distillation columns except from T-100, the pressure drop is assumed to be 5 kpa. For T-100, it is assumed to be 10 kpa). For more information see appendix C.

2.3.6 Heat Integration

(We did the heat integration separately as new simulation and all cost estimations are based on producing HPS, MPS and LPS, see appendix D).

The natural gas and water had to be heated to 455 °C, oxygen and pre-reformer products are needed to reach to 550 °C. Some other streams had to be heated. In the other side autothermal effluent has high temperature, 1000°C, and needs to cool to 50 °C. Thus there are some opportunities for heat integration.

As illustrated in the figure 2.13, the autothermal effluent is used to heat oxygen from 50°C to 550°C and then for heating the pre-reformer products from 297°C to 550 °C and water from 25 °C to 455 °C.

This stream after heating water is used for preheating natural gas from 50°C to 340°C and V-100 outlet from 50 °C to 165 °C. Finally recycle stream is preheated from 10 °C to 165 °C by this hot stream.

Note: The ΔT for the heat exchangers should be all around 25°C because of economical considerations. But Here we didn’t have time to take this into consideration. Finally, we will send the simulation with heat integration in 1 week.

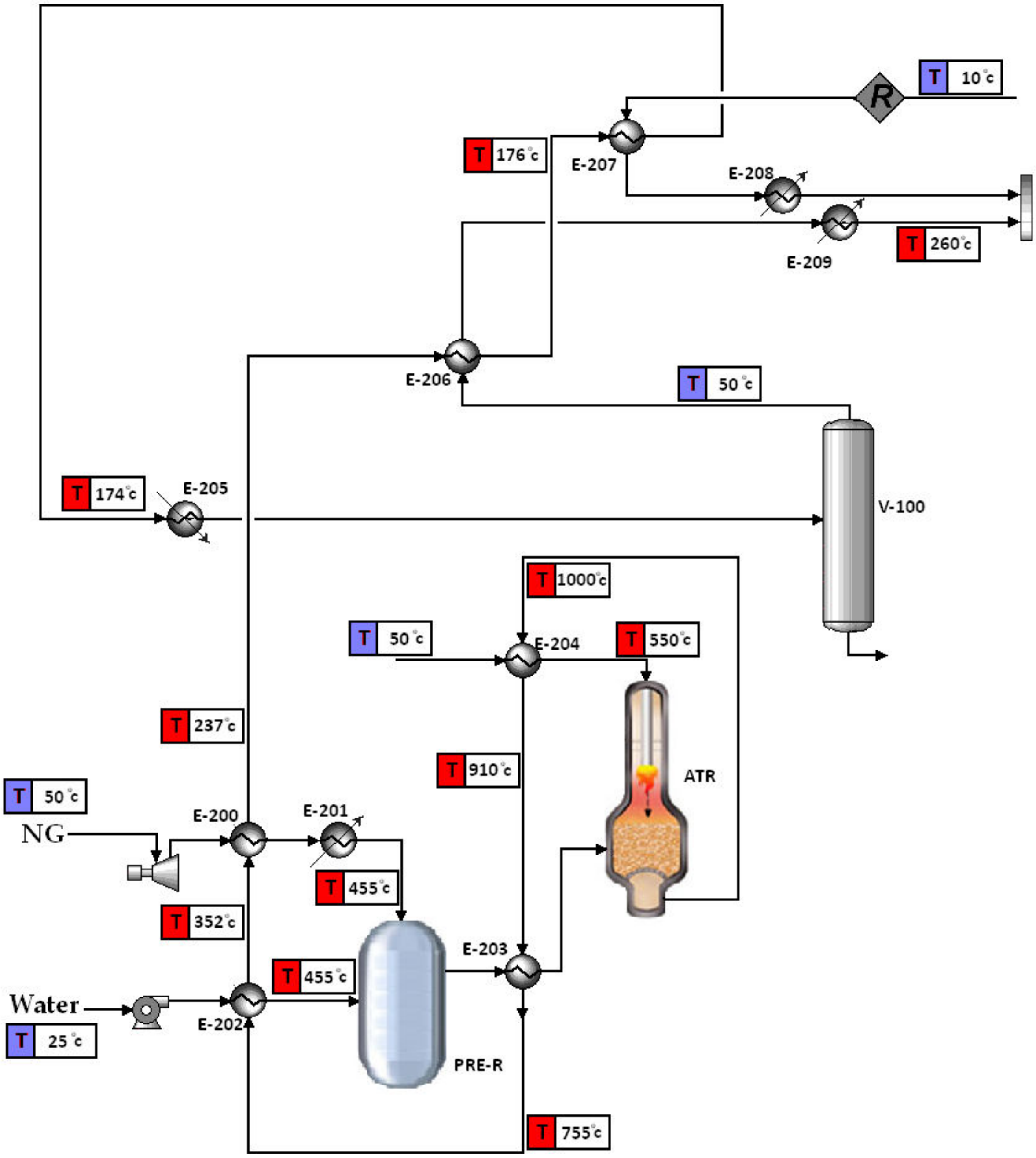


Figure 2.13 Heat integration

2.3.7 Case studies

Effect of reactor volume on DME production

As illustrated in figure 2.14, for reactor volumes less than 7000 m^3, the production of DME increases with increasing the reactor volume with the high slope. After this volume the slope will decrease rapidly. The optimal amount of 7200 m^3 is selected. (Three parallel reactors with 2400 m^3 volume)

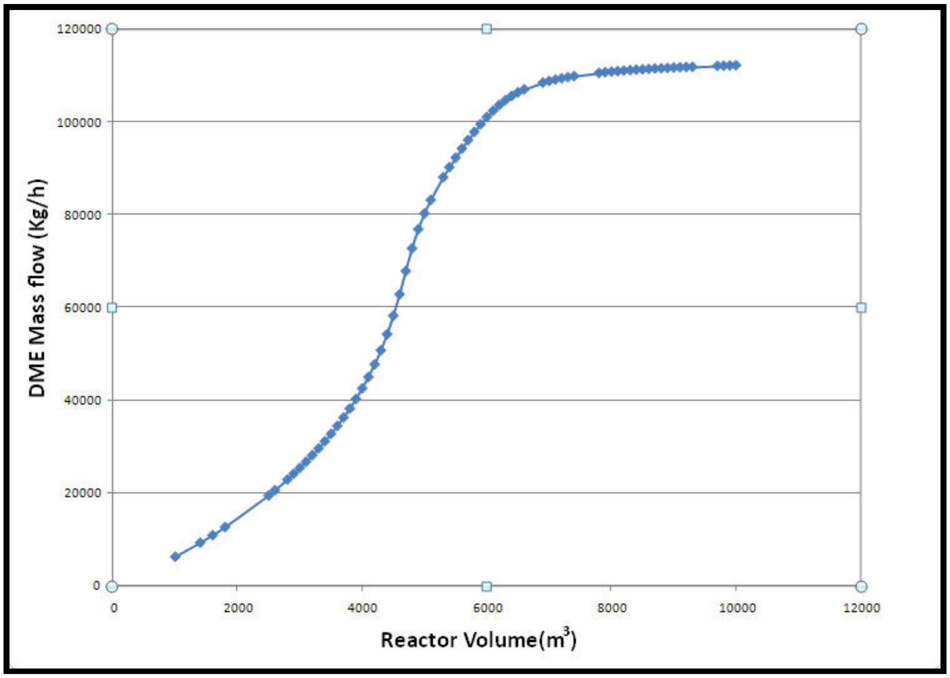


Figure 2.14 Effect of reactor volume on DME production

Effect of natural gas as a feed on DME production

According to figure 2.15, the production of DME increases and then decreases with increasing the molar flow of natural gas. For this plant 7500 is selected.

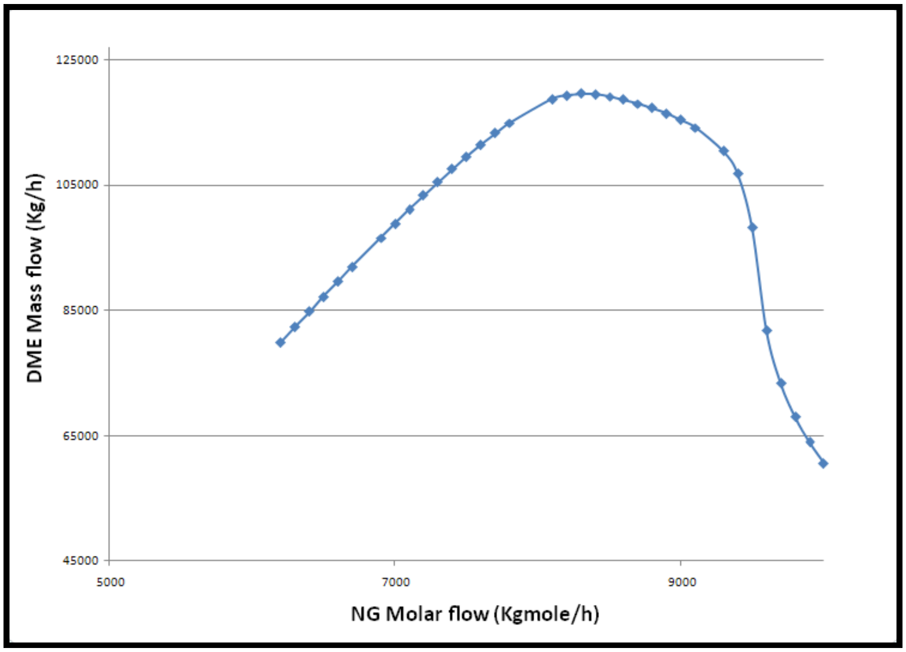


Figure 2.15 Effect of natural gas(molar flow) on DME production

Effect of oxygen as a feed on DME production

As we will see in figure 2.16, oxygen has the same effect of natural gas. During the increasing the molar flow of oxygen there are optimal points. We will suggest 5800-6000 kgmol/h, in current condition.

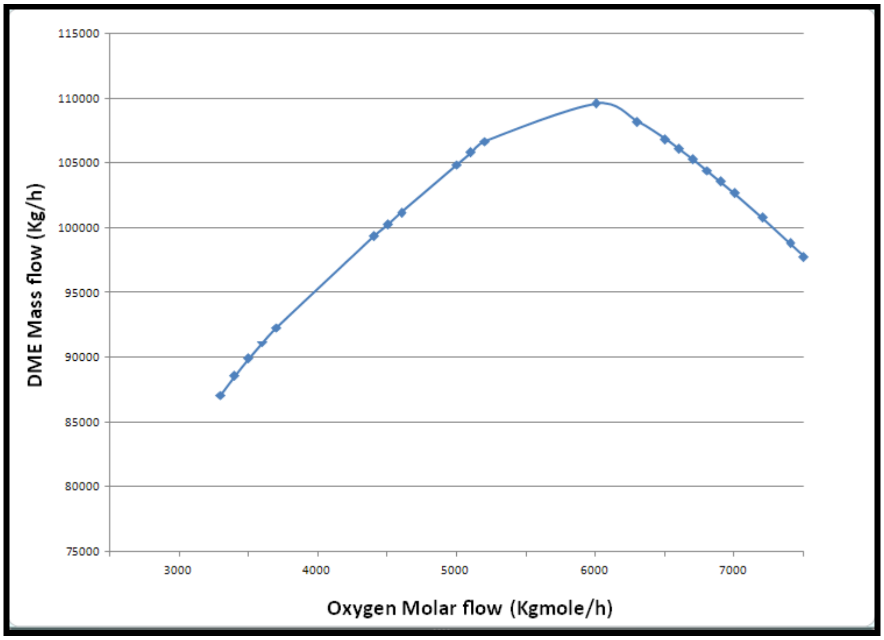


Figure 2.16 Effect of natural gas (molar flow) on DME production

2.4 Equipment description

All of the equipments used in the plant are chosen to be constructed of stainless steel. This is due to corrosive water in the streams and high pressure.

2.4.1 Reactors

ATR

The ATR (autothermal reformer) consists of a fixed bed reactor (assumed to be a process vessel in our cost calculations) in which the reforming process takes place. The catalyst used in this process is assumed to be ruthenium [6].

FBR (FBR-1, FBR-2, FBR-3)

The FBR reactors consists of vessel (assumed to be a process vessel in our cost calculations), a compressor (to reach the high velocities needed for fluidization), and a heat exchanger (discussed in another section). In the FBR (fluidized bed reactor), the gas is passed through a granular solid material (here the dual Cu-ZnO-Al_2O_3/HZSM-5 catalyst) at high enough velocities to suspend the solid and cause it to behave as though it were a fluid. This process is known as fluidization.

To be able to estimate the cost of the reactors according to appendix E, the volume [m^3] of the vessel had to be estimated. This was done by assuming the vessel volume to be 50% of the volume that a tank can be filled by liquid in 30 min. The standard ideal liquid volumetric flow rate of the outflow was used. To find the pressure factor the diameter of the vessel was assumed to be 0.3% of the volume (volume [m^3]·0.3%= diameter [m]).

2.4.2 Separators

Three phase separator (V-101)

V-101 is a three phase separator, separating the gases from the organic compounds (DME and methanol) and water (methanol as well). For the cost estimation this separator was assumed to be a vertical process vessel, see the next section.

General separators (V-100, V-102, V-103)

Gas-liquid phase separators are usually vertical. A vapor-liquid separator drum is a vessel into which a liquid and vapour mixture (or a flashing liquid) is fed and wherein the liquid is separated by gravity, falls to the bottom of the vessel, and is withdrawn. The vapour travels upward and exits the top of the vessel. Figure 2.17 shows a schematic representation of the gas-liquid separator.

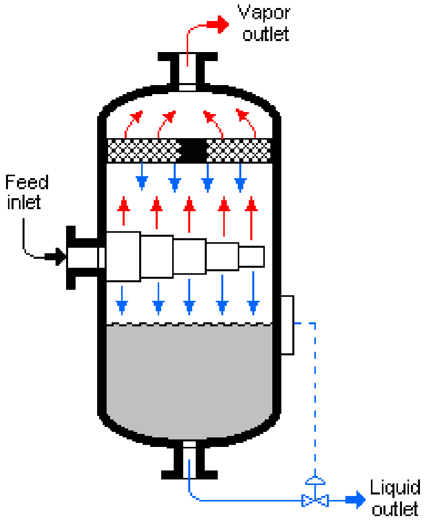


Figure 2-17: A schematic representation of the gas-liquid separator.

The vessels are assumed to be process vessels. To be able to estimate the cost of the separators according to appendix E, the volume [m^3] of the vessel had to be estimated. This was done by assuming the vessel volume to be 50 % of the volume that a tank can be filled by liquid in 30 min. The standard ideal liquid volumetric flow rate of the liquid outflow was used. To find the pressure factor, the diameter of the vessel was assumed to be 3 % of the volume (volume [m^3]· 3 % = diameter [m]).

2.4.3 Distillation towers (T-100, T-101, T-102, T-103, T-104)

All of the towers are distillation columns with sieve trays. The ideal numbers of trays were found by scaling up the number of trays found in UniSim. This was done by assuming 50 % tray efficiency ($N_{actual} = N_{UniSim}/0.5$). To estimate the cost of the columns as described in appendix E, the diameter and the volume of the towers needed to be found. UniSim has a default size for the diameter of the towers, and the volume was found by multiplying the volume between trays (from UniSim) with the actual number of trays.

2.4.4 Storage tanks

We have to use storage tanks for NG, O_2, CO_2, DME, H_2 and Gas recycle. All of the storage tanks are assumed to be API, fixed roof tanks. Cost calculations for the storage tanks are based on tank volume [m^3]. To find the volume of the storage tanks, the density of the different fluids being stored had to be estimated. This is because the volume flow is not available in Unisim, so the volume flow must be calculated from the mass flow (Volume = mass/density). The fluids entering the tanks are assumed to be at STP. After finding the volume flow for STP the gases are assumed to be compressed to 1/100 of the volume at STP.

2.4.5 Heat exchangers

Stream exchangers (E-101, E-103, E-104, E-104, E-105, E-106, E-107, E-108, E-109)

For the cost estimation all of the heat exchangers in our plant are assumed to be shell and tube, floating head and stainless steel. The configuration gives a large heat transfer area in a small volume, has a good shape for pressure operations, is easily cleaned and can be constructed from a wide range of materials. The floating head type is chosen because the thermal expansion of the fluids running through the heat exchanger might be significant. We have chosen to use exhangers with one shell per tube pass. The reason for this choice is the temperature differences (ΔT_H and ΔTc), described in figure 2-18. The most economical difference was set to be 25 °C [5]. An even number of tube passes is usually the preferred arrangement, as this positions the inlet and outlet nozzles at the same end of the exchanger, which simplifies the pipe work, however the temperature differences in our case favours the arrangement of one shell per tube pass.

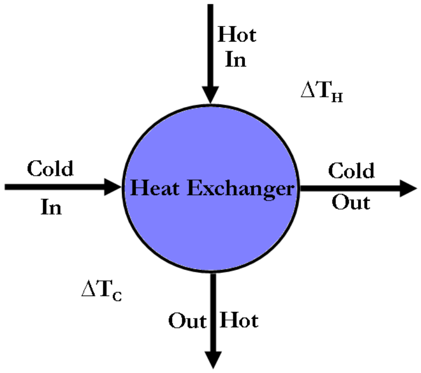


Figure 2-18: Illustration of the temperature differences that determines the ratio between number of shells and number of tubes.

Steam is flowing through the tube side. This is because of the advantages involved with having the most corrosive fluid in the tubes to reduce the cost of expensive alloys, and because the tubes are easier to clean. In addition steam has the highest temperature so placing steam in the tubes will reduce the shell surface temperature and hence the need for lagging to reduce heat loss.

To be able to estimate the cost of the exchangers according to appendix E, the heat transfer areas had to be estimated. This was done using a simulation program called ASPEN B-jac. The parameters added to the program were temperature, heat flow, mass flow, and components in both the cold and hot stream.

2.4.6 Reactor exchangers (ATR, FBR-1, FBR-2, FBR-3)

In addition to the stream exchangers there are one heat exchanger in each of the reactors. The reactions taking place in the ATR and the three FBR`s are exothermic, so the reactors have to be cooled. The heat transfer area in these reactors was estimated based on the duties for these reactor coolers (which can be found in UniSim) and the duties of the exchangers that we did find the area for. A more detailed description and the cost estimation of these exchangers is provided in the section above.

2.4.7 Fired heaters

Direct fired heaters are generally used in processes where the process temperature required is greater than 400 °C. This is the case for the stream entering the ATR, and therefore E-102 is chosen to be a non-reactive fired heater. The pre-reformer reaction process is endothermic and the operating temperature of the reactor is 455 °C. This means that the reactor is requiring a high level of heat input.

Pre-reformer (PRE-C, PRE-E)

The pre-reformer consists of a vessel (with catalyst filled tubes), a reformer furnace and a NG fired burner[7]. The furnace may "stand alone", or operate in conjunction with the pre-reformer. In the furnace, the reforming of steam-hydrocarbon mixtures is accomplished in catalyst-filled tubes. A variety of catalyst (nickel-based) is available for a given feed and product requirement. We chose the NiO catalyst[7].

To be able to estimate the cost of the pre-reformer according to appendix E, the volume [m^3] of the vessel had to be estimated. This was done by assuming the vessel volume to be 50% of the volume that a tank can be filled by liquid in 30 min. The standard ideal liquid volumetric flow rate out of the reactor was used. Cost estimations had to be done for the fired heater as well. A reformer furnace was assumed and the capacity needed for the cost calculations was the duty [kW] (collected from UniSim).

Furnace (E-102)

E-102 is assumed to be a non-reactive fired heater. Cost estimations for this type of equipment are done according to appendix E. The capacity needed for the cost calculation is the duty [kW] (collected from UniSim).

2.4.8 Pumps (P-1, P-100, P-101, P-102)

All of the pumps used in our plant is assumed to be centrifugal, electric drive and made of stainless steel. Pump selection is based on flow rate and head required. In addition special care should be made when considering corrosion (in our process water is present, and the pressure is high). To be able to estimate the cost of the exchangers according to appendix E, the shaft power [kW] had to be found. This is found directly from UniSim.

2.4.9 Turbine (K-1)

Where high pressure gas process streams are being throttled to lower pressures, energy can be recovered by carrying out the expansion in a suitable turbine. The energy recovered by expansion is often used to drive a compressor directly (Richard Turton, 2009). It is assumed that this is being done in our plant. It is assumed that the energy required to compress a gas is the energy found in the Workbook in UniSim. In reality there is an efficiency factor involved. This factor has not been counted in when estimating the electric power needed for the plant. The K-1 expander in the flow sheet is assumed to be an axial-flow gas turbine. For the cost estimations (appendix E) the capacity needed is the shaft power [kW]. This is found in UniSim.

2.5 Mass and energy balances

It is important to check that the mass and energy balances from the flowsheet in Unisim are correct. The mass balances are correct when the follow the equation given below:

$$mass_{in} - mass_{out} = 0$$

$$Energy_{in} - Energy_{out} = 0$$

- Mass balance

The total mass balance is shown in table 2.3. For the mass balances for all important units see appendix F.

Table 2-3: Total mass balance

TOTAL MASS BALANCE		
STREAM		**ton/day**
IN	NG	3019.76
	Water	3242.72
	Oxygen	4992
OUT	DME	2888.2
	48	1135.9
	CO_2	1623.42
	Water.out	1238.
	18	4368.7
STREAM ERROR		0.002%

The error is because of recycle unit in simulation.

- Energy balance

The total energy balance is shown in table 2.4. For the energy balances for all important units see appendix F.

Table 2-4: Total energy balance

TOTAL ENERGY BALANCE			
IN			
STREAM		KJ/h	MW
IN	**Q-102**	518633.1969	0.144065
IN	**Q-103**	0	0
IN	**Q-104**	0	0
IN	**Q-105**	178212995,8	49,50361
IN	**Q-106**	40569260.34	11.26924
IN	**Q-107**	-1122281319,44	-311,7448
IN	**Q-108**	1607271.638	0.446464
IN	**Q-109**	315827.2245	0.08773
IN	**Q-110**	696036.8196	0.193344
IN	**Q-111**	-8.38E-07	-2.3E-13
IN	**Q-112**	133420845.6	37.06135
IN	**Q-113**	-194142936	-53.9286
IN	**Q-114**	-194142936	-53.9286
IN	**Q-115**	-194142936	-53.9286
IN	**Q-116**	-350765795	-97.4349
IN	**Q-117**	-18664380.9	-5.18455
IN	**Q-120**	58211887.8	16.16997
IN	**Q-122**	26060870.22	7.239131
IN	**Q-124**	2894420.543	0.804006
IN	**Q-126**	31539077.88	8.760855
IN	**Q-128**	2159905444	599.9737
IN	**Q-129**	-39313815.4	-10.9205
IN	**Q-130**	47072878.81	13.0758
IN	**13**	-1944511269	-540.142
IN	**16**	-1304391451	-362.331
IN	**19**	-4387680450	-1218.8
IN	**21**	-1720478069	-477.911
IN	**22**	-649848844.2	-180.514
IN	**NG**	-568412498.5	-157.892
IN	**Water**	-2141996179	-594.999
IN	**Oxygen**	3203961.418	0.889989

TOTAL ENERGY BALANCE			
OUT			
STREAM		KJ/h	MW
OUT	**Q-101**	10295538.36	2.859872
OUT	**Q-118**	30229652.11	8.397126
OUT	**Q-119**	1569170.143	0.435881
OUT	**Q-121**	3388405.375	0.941224
OUT	**Q-123**	3517547.635	0.977097
OUT	**Q-125**	6853537.768	1.90376
OUT	**Q-127**	2064154384	573.3762
OUT	**18**	-2866242405	-796.178
OUT	**25**	-2157410065	-599.281
OUT	**32**	-819356302.8	-227.599
OUT	**48**	-375258090.4	-104.238
OUT	**DME**	-2141996179	-594.999
OUT	**HPS**	-1543279817	-428.689
OUT	**MPS**	-1033415971	-287.06
OUT	**LPS**	-3609663120	-1002.68
OUT	**Gas**	-398484813.2	-110.69
OUT	**CO_2**	-606142681.9	-168.373
OUT	**Water.out**	-767461818.3	-213.184

2.6 Economic estimation

2.6.1 Fixed capital cost

The fixed capital cost is estimated to get an approximate price for the total plant installed and up and running. These calculations are based on given percentages (West, Ronald E., et al, 2003). Major equipment costs are calculated as described in appendix G. The major costs for the direct method plant are shown in table 2.7.

Table 2.7: Major equipment in the plant for direct method

Equipment	Cost [$]
Vessels	4 517 498
Pumps	561 891
Turbins	664 705
Heat exchangers	9 435 518
Fired Heater	118 423 412
Reactor vessels	309 977 437
Towers+trays	5 248 523
Storage tanks	1 831 894
Major equipment cost	450 660 879

The fixed capital costs for the direct method are listed in table 2.8.

Table 2.8: Fixed Capital cost for the DME direct plant

Fixed Capital cost	Factor[%]	cost [M$]
Major equipment cost	0,219	450,46
Purchased equipment installation	0,083	169
Instrumentation and controls (installed)	0,092	189
Piping (installed)	0,073	150
Elecrical systems (installed)	0,046	95
Buildings (including services)	0,046	95
Yard improvements	0,018	37
Service facilities (installed)	0,138	284
Land	0,01	21
Engineering and supervision	0,073	150
Construction expenses	0,092	189
Legal expenses	0,018	37
Contractor`s fee	0,018	37
Contingency	0,073	150
Fixed Capital cost	**0,999**	**2057**

2.6.2 Working capital cost

The working capital is the amount of capital required to start up the plant and to finance the first couple of months of operation before the plant starts earning. This capital is used to cover salaries, raw material inventories, and contingencies. It will be recovered at the end of the project and represents a float of money to get the project started. These costs are necessary at start-ups and it implies raw materials and intermediates in the process. The working capital was assumed to be 3 % of the fixed capital cost (West, Ronald E., et al, 2003).The total investment for the plant is listed in table 2.9.

Table 2.9: The total investment for the direct method

Investment	Cost [M$]
Fixed Capital cost	2057
Working capital cost	61,71
Total investment	2119

2.6.3 Operating cost

The operating cost for the direct method is listed in appendix H. The main costs are listed in table 2.10.

Table 2.10: Operating cost for the DME-direct plant

Item	Cost [M$/yr]
Sales revenue total	1094
Manufactoring cost	485
Fixed cost	285
Operating cost	771

For the calculation of the operating cost we needed to find the price for the utilities needed in the two plants (direct and indirect), and also the catalyst price for the plants. These calculations are described below for both plants.

Stream factor

To be able to calculate the yearly cost of raw materials and utilities, on needs to know the fraction of time that the plant is operating in a year. This is the stream factor and can be calculated as described below:

Stream factor = # days a plant operates per year
365

Our calculations are based on an SF of 1. This is not realistically. Even the most reliable and well managed plants must expect to be shut down for two weeks a year for maintenance, giving an SF of 0, 96 (Richard Turton, 2009).

Utilities

Steam

In the direct plant HPS (510 ºC, 100 bar), MPS (480 ºC, 30 bar), and LPS (250 ºC, 20 bar), are produced. These utilities can either be used in the plant or sold. For the two first heat exchangers in the flow sheet MPS and HPS is used as a heating medium. The rest of the steam is being sold at the price of 30 $/ton (Richard Turton, 2009). The price is based on the fact that all of the steams, produced in our plant, have higher temperature and pressure than the ones described in the source. To find the amount of MPS we need to buy, an energy balance over each heat exchanger was set up, eqn. 2.1. ΔH_{vap} for steam is 1699,3 kJ/kg (Richard Turton, 2009).

$$\dot{m}_{steam} = \frac{Q}{\Delta H_{vap}} \tag{2.1}$$

Table 2.11 show the different Q`s and the corresponding mass flows for the different heat exchangers.

Table 2.11: Heat flows and mass flows for the different heat exchangers.

Heat exchanger	E-103	E-109	E-108	E-107
Q [kJ/yr]	3,55 E+11	4,12 E+11	2,65 E+11	1,17 E+12
Mass flow [ton/yr]	208910	242453	155947	688520

Table 2.12 shows how much steam is being produced, how much is used for the plant and how much we can sell

Table 2.12: The amount of steam produced, used and the amount of steam we can sell/buy.

Steam	HPS	MPS	LPS
Amount produced [ton/yr]	1074852	720773	2424768
Amount used [ton/yr]	452454	2495950	0
Amount to sell [ton/yr]	622398	-1775177	2424768

Table 2.12 show that we can sell HPS and LPS, and that we need to buy some MPS. Table 2.13 show the sales revenue and the cost for the different steams.

Table 2.13: Sales revenue and cost for the three different steams.

Steam	HPS	MPS	LPS
Price [$]	30	30	30
Sales revenue [$/yr]	18671940		72743040
Cost [$/yr]		53255310	

NG for fired heaters

To calculate the yearly cost for natural gas required for the fired heaters in the direct plant we assume that the heaters are indirect, fired heaters, and that the thermal efficiency is 90 %. The cost of natural gas is 11,10 $/GJ (Richard Turton, 2009), and the heating value is 0,0377GJ/m^3 (Richard Turton, 2009). To find the yearly cost of natural gas we use eqn. 2.2.

$$Cost = \frac{Q \cdot Cost_{NG}}{efficiency} \tag{2.2}$$

Table 2.14 show the yearly cost of natural gas for the different heaters.

Table 2.14: Duty and cost (of natural gas as a heating medium) for the different heaters.

Heater	E-102	Pre-reformer furnace
Q [GJ/yr]	76562	1436640
Yearly cost [$/yr]	944265	17718560

Cooling water

To estimate the yearly cost for cooling water we assume water at 30 ºC, and a ΔT_{cw} = 10 ºC (Richard Turton, 2009), and a price of 0,354$/GJ for the cooling water (Richard Turton, 2009). To calculate the cost eqn. 2.3 is used.

$$Cost = Q \cdot Cost_{cw} \tag{2.3}$$

Table 2.15show the cost for cooling water for the different coolers.

Table 2.15: Duty for the different coolers and the yearly cost for cooling water.

Cooler	FBR-100	FBR-101	FBR-102	ATR
Q [GJ/yr]	170069	170069	170069	2337274
Yearly cost [$/yr]	60204	60204	60204	827395

Electricity

To estimate the cost for the electricity to run the two plants for a year all of the remaining duties were summed together (the duty for the compressors, pumps and reboilers are added and the duty for turbines and condensers are subtracted). The cost for the electricity was found by assuming 90 % efficiency and an electrical power price of 0,06 $/kWh (Richard Turton, 2009) for both the direct and the indirect method. Eqn. 2.4 was used to estimate the cost for a year.

$$Cost = \frac{W_{el} \cdot Cost_{el}}{efficiency} \tag{2.4}$$

Table 2.16 show the yearly cost for electrical power for both the direct plant and the indirect plant.

Table 2.16: Amount of electrical power needed and the yearly cost for the direct and indirect plant.

Direct	
Amount of electrical power needed [kW]	53325
Yearly cost [$/yr]	31141935
Indirect	
Amount of electrical power needed [kW]	-29148
Yearly cost [$/yr]	-17022491

Now it should be mentioned that all of the duties for the indirect method is assumed to be electricity. This is done for simplicity. If we on the other hand had concidered the use of steam and cooling water for heating and cooling processes then the project would have become more profitable (the electricity assumption is just a gross estimate).

Catalyst price

To find the price for the catalysts for the two plants we first had to find the volume [m^3] of catalyst in the reactor and then the amount [kg]. To find the volume of the catalyst in the reactor we had to assume a void fraction. The assumed void fractions and the densities for the different catalysts in direct method are listed in table 2.17. For the indirect method the void fraction and the density of the catalyst is given in table 2.18.

Table 2.17: Density and void fraction for the three different catalysts, and the volume of the three different types of reactors used in the plant for the direct method.

Reactor	Pre-reformer (NiO)[9]	ATR (ruthenium)[6]	FBR (Cu-ZnOAl$_2$O$_3$/HZSM-5)
Void fraction [-]	0.55	0.55	0.50
Density [kg/m^3]	6670	12370	1982.5
Volume of reactor [m^3]	460.9	434.2	7200

Table 2.18: Density and void fraction for the catalyst, and the volume of the reactor used in the plant for the indirect method.

Reactor	PFR (HZSM-5)
Void fraction [-]	0.5
Density [kg/m^3]	1982.5
Volume of reactor [m^3]	2483

Eqn. 2.5 is used to find the volume of the catalyst.

$$Volume_{cat} = (1 - voidfraction) \cdot volume_{reactor} \tag{2.5}$$

To find the amount of catalyst needed eqn. 2.6 was used.

$$Amount_{cat} = volume_{cat} \cdot \rho_{cat} \tag{2.6}$$

To estimate the price of catalyst one has to take into account that the catalysts get deactivated. Therefore the catalyst price should be included in the fixed operating costs. One can assume that the catalyst lasts for four years before it has to be replaced. So the price per year can be estimated as described in eqn. 2.7.

$$Cost_{cat} = amount_{cat} \cdot \frac{price}{kg} \cdot \frac{1}{4} \tag{2.7}$$

Table 2.19 shows the amount of catalyst needed and the estimated price per year for the direct method. Table 2.20 shows the amount of catalyst needed and the estimated price per year for the indirect method. (1 NOK = 0,18 USD[10])

Table 2.19: Amount of catalyst needed and the price for catalyst per kg and per year for the direct method.

Catalyst	NiO	Ruthenium	Cu-ZnO-Al_2O_3/HZSM-5
Amount [kg]	1383391	2416974	6423300
Price [$/kg][7]	18	18	18
Price [$/yr]	6225260	10876383	28904850

Table 2.20: Amount of catalyst needed and the price for catalyst per kg and per year for the direct method.

Catalyst	HZSM-5
Amount [kg]	3103750
Price [$/kg]	18
Price [$/yr]	11075732

2.7 Investment analysis

2.7.1 Evaluation parameters

The cumulative cash flow and the discounted cash flow are both shown in figure 2-19. The payback time for the two cash flows is 8 years for the non-discounted and 14 years for the discounted. The profit made after 15 years at a discount rate of 10 % is 68.69 M$. The discount rate is chosen on the basis of the interest rate that a central bank charges depository institutions that borrow reserves from it. We have chosen to double that rate for our discount rate.

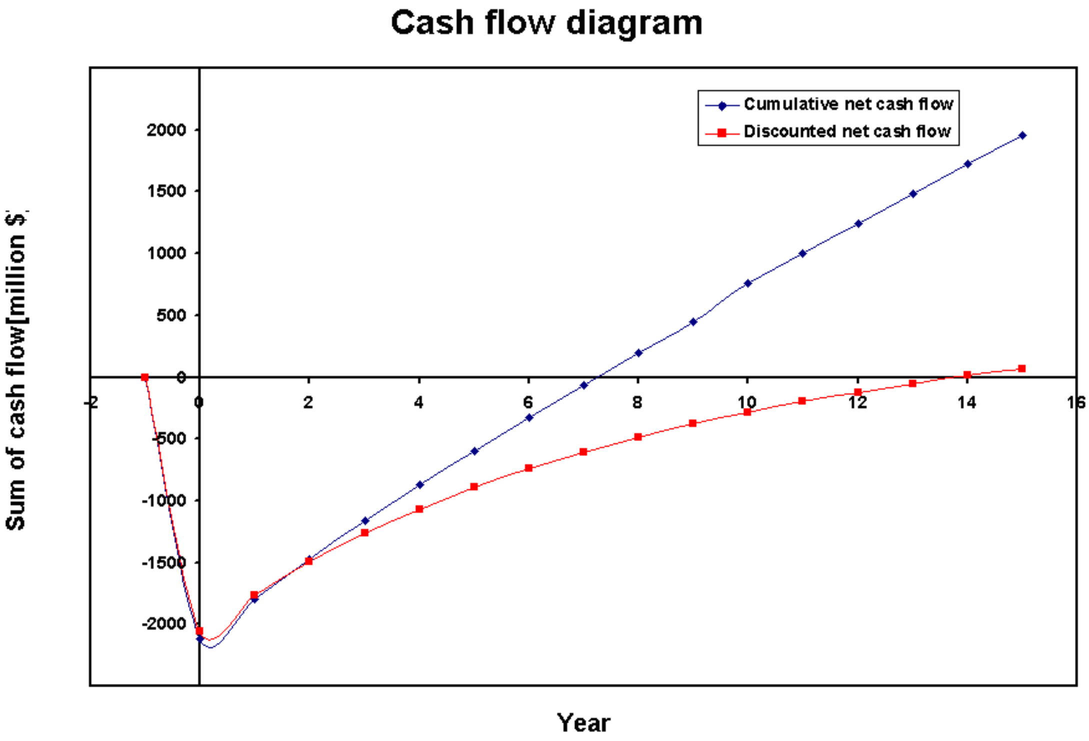


Figure 2-19: Cash flow diagram

The economic evaluation parameters, net present worth, net future worth and the discounted cash-flow rate of return, were found by using excel and the results are listed below in table 2.21. Detailed calculations for finding these parameters are described in appendix I.

Table 2.21: Economic evaluation parameters

Evaluation method	Result
Net present worth (NPW) [M$]	68.69
Net future worth (NFW) [M$]	238
Discounted cash flow rate of return (DCFRR) [%]	10.62

2.7.2 Sensitivity analysis for variations and ROI (return on investment)

Payback time is a useful criterion for judging projects with short lifetimes. It defines the time required after the start of the project to pay off the initial investment from income. The calculations for finding the payback time and the ROI are shown in appendix J. The payback time result is shown in table 2.22. The payback time when we varied the prices for raw materials, product (DME, H_2), electrical power, major equipment and in addition varied the utility price of the plant is listed in table 2.23. The variations were 20% increase and decrease. The graphical result is shown in figure 2-16. The time for paying back the invested cost without variation was 8.9 years.

Table 2.22: Payback time result

Calculation for Payback time	
Investment [M$]	2119
Operating costs [M$]	771
Sales revenue [M$]	1094
Depreciation [M$]	18.6
Payback time [yr]	8.9

Table 2.23: Payback time for variation in different variables

Payback time for variation in different variables			
Variation[%}	-20	0	20
Raw material price [yr]	7.4	8.9	10.06
Product price [yr]	19.04	8.9	5.5
electrical power price [yr]	8.38	8.9	8.69
Utility price [yr]	8.62	8.9	8.44
Equipment cost [yr]	6.518	8.9	10.74

The return on investment result is shown in table 2.24.

Table 2.24: Return on investment result

ROI	
Total sales revenue [M$]	1094
Operating cost [M$]	771
Investment [M$]	2119
ROI [%]	0.15

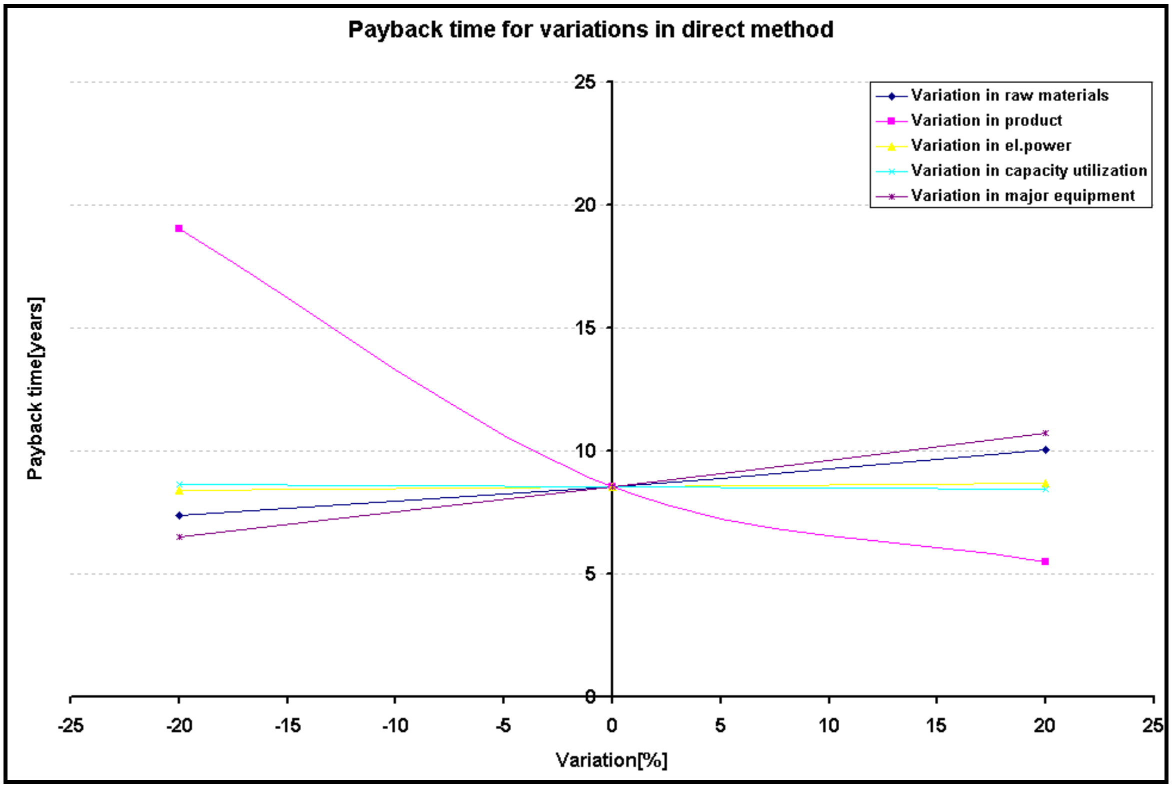


Figure 2-16: Payback time for variation in different variables method

2.7.3 Break even analysis

The break even method is used to determine the point at which sales revenue will cover operating cost. Figure 2-17 shows the breakeven point for the direct plant case. The operating cost, which is a sum of the fixed cost and the variable cost, is plotted in the same graph as sales revenue. The intersection is where the revenue, generated from the sales, just covers the total operating cost. The variable cost is the sum of the costs that vary with production of DME, and the fixed cost is the sum of the costs that does not.

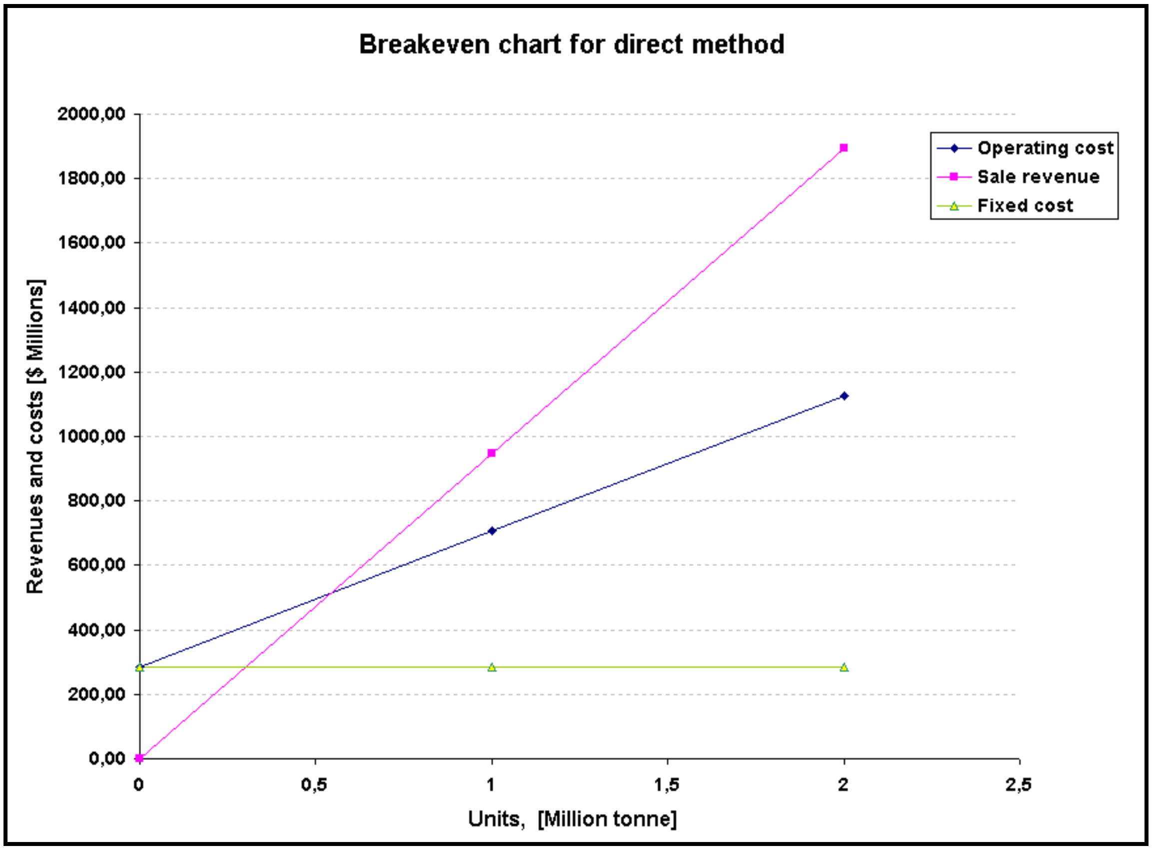


Figure 2-17: Break even chart for the direct plant

3 DME Production: Indirect method

3.1 Project basis

The block diagram for DME production from methanol is shown in the in Figure 3.1. The raw material is methanol. Methanol arrives at the plant at 25°C and 1bar. Methanol dehydration takes place in the fixed-bed reactor and then DME as final product is purified in separation unit. As we saw in last chapter producing 3000 metric tons per day of 99 wt% purity DME is the target of our project. The other consideration in this project is maximizing the energy recovery by using partial heat integration in the plant.

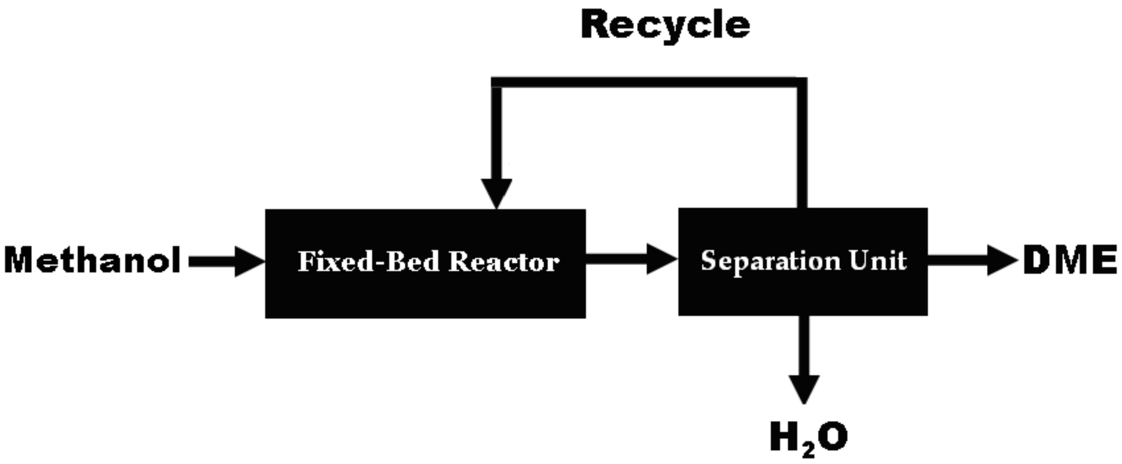


Figure 3.1 Block diagram

3.2 Process description

3.2.1 Flowsheet

A PFD of the process is shown in Figure 3.2 and the belonging stream conditions are given in appendix A. The essential operations in the process are the preheating of the raw material (nearly pure methanol), dehydration of methanol to form DME, product separation and methanol separation and recycle.

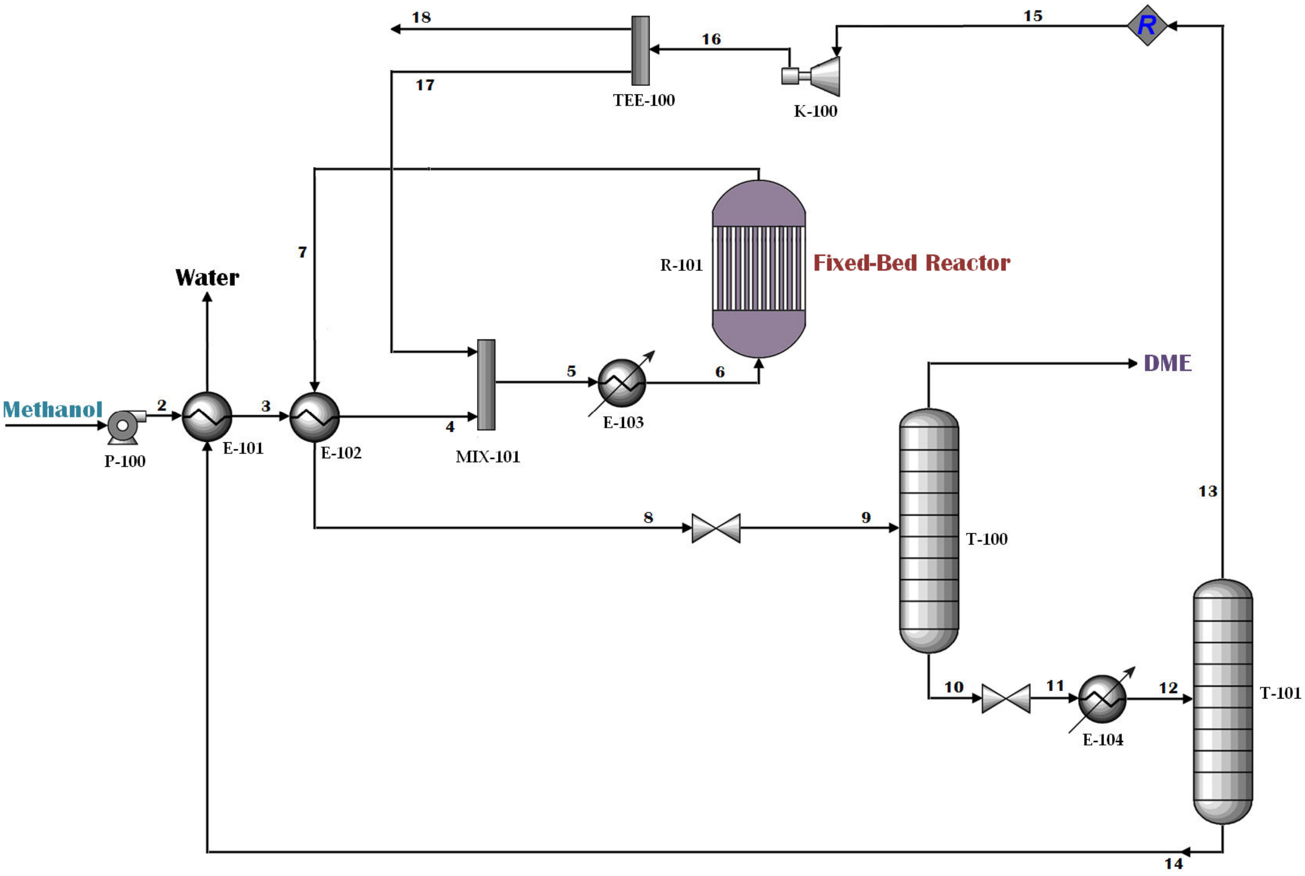


Figure 3.2 Production of DME from Methanol

Methanol as a liquid pumped up to 15.5 bar. The stream 2 preheated with streams 14 and 7. After preheating the stream 4 combined with Stream 17, methanol recycle stream. Stream 5 is then sent into heat exchanger E-103 where it is heated to a temperature of 250°C before sending to the fixed-bed reactor, R-101, to form DME. The reaction is slightly exothermic and the reaction products are heated to approximately 365°C before leaving the reactor.

The reactor effluent is cooled in E-102 and then throttled to 10.4 bar before entering T-100. Here, the dimethyl ether is separated from the other components as distillate, Stream DME. The bottom product, Stream 10, is throttled to 7.4 bar and sent to T-101 where the methanol are separated from the waste components. The waste components exit as the bottoms stream, Stream 14. Methanol exits the column as a distillate, Stream 13. This stream is then compressed to 15.5 bar and recycled back to mix with methanol, Stream 17 in mixer MIX-101.

3.2.2 Process Concepts

The production of DME is via the catalytic dehydration of methanol over an amorphous alumina catalyst treated with 10.2% silica. A methanol conversion of about 80% is achieved in the reactor. DME is produced by the following reaction:

$$2CH_3OH \rightleftarrows CH_3OCH_3 + H_2O$$

The reaction is equilibrium limited. Based on the catalyst and reaction kinetics, the reactor must operate at 15 bar. The reactor operates adiabatically, and, since the reaction is exothermic, the reactor effluent temperature will be above 250°C.

Reaction Kinetics and Reactor Configuration

The reaction taking place is mildly exothermic with a standard heat of reaction:

$$H_{reac}(25°C) = -11,770 \text{ kJ/kmol}$$

The equilibrium constant for this reaction at three different temperatures is given in table 3.1.

Table 3.1

T	K_p
200°C	34.1
300°C	12.4
400°C	6.21

The corresponding equilibrium conversions for pure methanol feed over the above temperature range are greater than 83%. This reaction is kinetically controlled at the conditions used in this process.

In the temperature range of normal operation, there are no significant side reactions, and the equilibrium conversion for pure methanol feed exceeds 92%. Therefore, the reactor is kinetically controlled in the temperature range of normal operation. Above 250°C, the rate equation is given below (Bondiera and Naccache, 1991):

$$-r_{methanol} = k_0 . e^{-\frac{E}{RT}} . P_{methanol}$$

Where k_0 = 1.21×10$_6$ kmol/(m^{3}reactor.h.kPa), E_a = 80.48 kJ/mol, and $P_{methanol}$ = partial pressure of methanol (kPa). Significant catalyst deactivation occurs at temperatures above 400°C, and the reactor should be designed so that this temperature is not exceeded anywhere in the reactor. Since the DME reaction is not highly exothermic, the proper temperatures can be maintained by preheating the feed to no more than 250°C and running the reactor adiabatically.

3.3 Simulation in UniSim

Production of DME from methanol has been simulated using UniSim with **PRSV**[1] fluid package and three pure components consisting of methanol, water and DME are added. In order to explain, the simulation is divided into several parts, namely feed conditioning, production of DME in fixed-bed reactor, separation.

3.3.1 Feed Conditioning

The feed for the process is methanol at 50°C and 70 bar. To reach the fixed-bed reactor conditions (260 °C and 15 bar) the feed had to be compressed and heated.

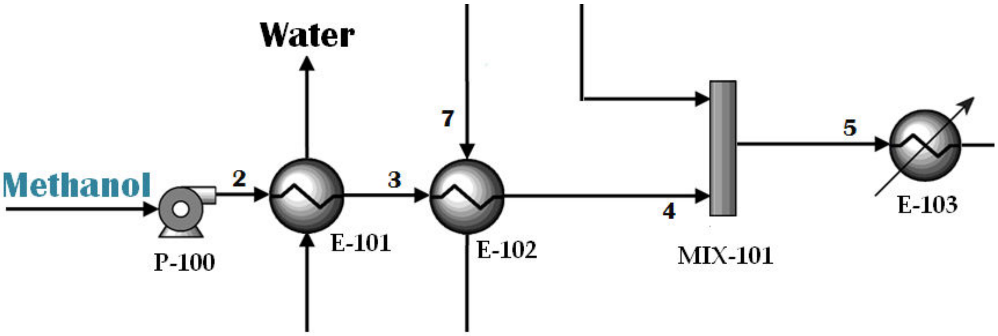


Figure 3.3 Feed conditioning

Equipments in feed conditioning:

Pump (P-100):

This pump increases the pressure of the feed to a minimum of 15 bar.

Heat Exchanger (E-101 and E-102):

These units are used for preheating the feed.(It is assumed that the pressure drop in heat exchangers is between 20-30 kpa.)

Heat Exchanger (E-103):

This unit heats, vaporizes, and superheats the feed to 250°C at 14.7 bar.

---

[1] Peng Robinson-Stryjek-Vera

3.3.2 Production of DME in fixed bed reactor

Since Unisim is not set up to model for the fixed-bed reactors, we had to use an approximate method such as plug flow reactor is selected. One reaction takes place in the fixed-bed reactor. We defined the reaction as a kinetic reaction and also one set for the reaction. The specifications for the reactor were temperature of outlet stream, rating parameters such as: tube dimensions and tube packing. Also we defined the reactor adiabatically and with no pressure drop.

After running the simulation, we found the conversion of 100% for methanol. As we know conversion of methanol is about 80% in the reactor. We checked all articles and probably there is some mistake in the kinetic. Finally the conversion reactor is used instead of the fixed-bed reactor. Of course, we defined a conversion reaction with 80% conversion of methanol.

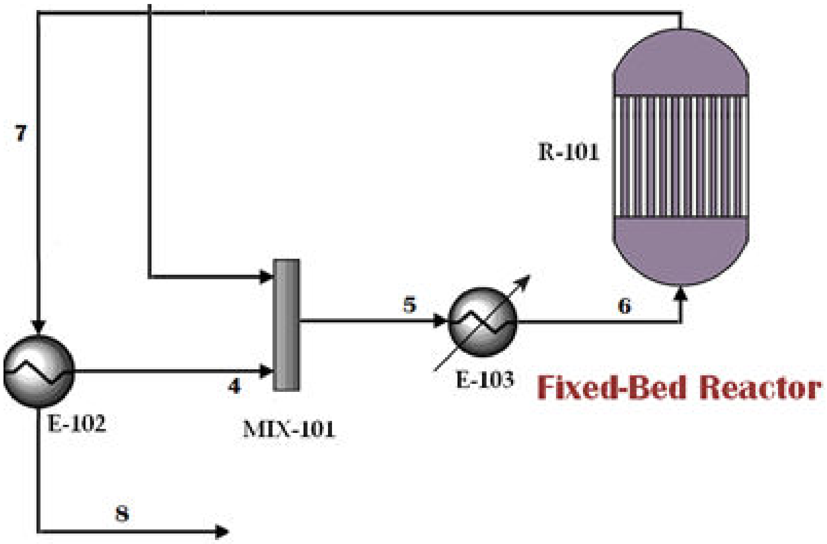


Figure 3.4 Fixed-Bed Reactor

E-102 cools and partially condenses the reactor effluent. The valve after this heat exchanger reduces the pressure. This exit pressure may be at any pressure below the reactor pressure, but must be identical to the pressure at which next distillation column, T-100, operates.

3.3.3 Separation

The first distillation column, T-100, separates DME from methanol and water. The temperature of the distillate is the temperature at which DME condenses at the chosen column pressure.

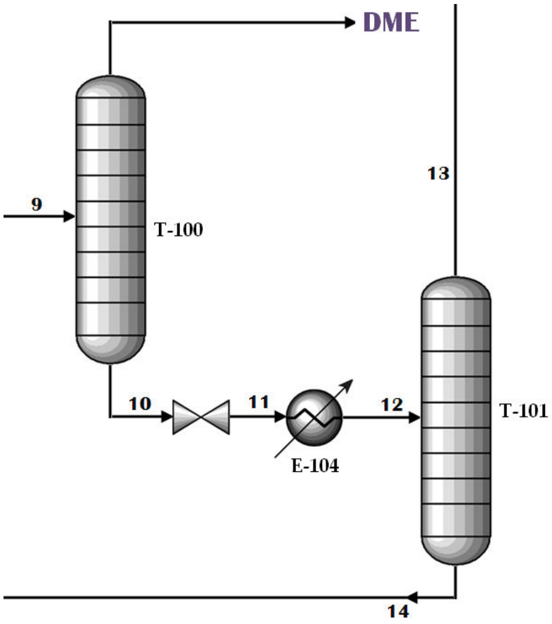


Figure 3.5 Separation Units

E-204 is used for decreasing the temperature of stream 11 before entering to the second distillation column, T-101. This distillation column separates methanol for recycle from water. Water stream is actually a waste water stream, and there is a cost for its treatment but this stream is used for preheating the feed. The temperature of the distillate is the temperature at which methanol condenses at the chosen column pressure. The valve before T-101 is optional. It is needed if the pressure of T-101 is chosen to be lower than that of T-100. If the pressures are the same, the valve can be eliminated.

3.4 Equipment description

All of the equipments used in the plant are chosen to be constructed of stainless steel. This is due to corrosive water in the streams and high pressure.

3.4.1 Reactor

For cost estimations the PFR is assumed to be a process vessel. The capacity needed for the cost estimations is the volume of the reactor. This was found the same way as for the pre-reformer and ATR in the direct method. The same cost estimation method as in the direct method is used here.

3.4.2 Storage tanks

For the cost estimations all of the storage tanks are assumed to be API, fixed roof tanks made of stainless steel. The cost calculations for the tanks needed to store methanol and water are done in the same way as for the storage tanks in the direct method.

3.4.3 Compressor (K-100)

The compressor used in the plant is assumed to be a centrifugal compressor made of stainless steel. It is assumed that the energy required to compress a gas is the energy found in the Workbook in UniSim. In reality there is an efficiency factor involved. This factor has not been counted in when estimating the electric power needed for the plant. For the cost estimations (see appendix E) the capacity needed is the shaft power [kW]. This is found directly from UniSim.

3.4.4 Heat exchangers (E-101, E-102, E-103, E-104)

All of the heat exchangers in the plant are assumed to be shell and tube, floating head and stainless steel. The reason for this choice is the same as for the direct plant.The estimation of the cost for the heat exchangers is done the same way as for the exchangers in the direct plant.

3.4.5 Pump (P-100)

The pump used in the plant is assumed to be centrifugal, electric drive and made of stainless steel. Pump selection is based on flow rate and head required. In addition special care should be made when considering corrosion (in this process some water is present, and the pressure is high). To be able to estimate the cost of the exchangers according to appendix E, the shaft power [kW] had to be found. This is found directly from UniSim.

3.4.6 Towers (T-100, T-101)

The towers in the plant are distillation columns with sieve trays. The ideal numbers of trays were found by scaling up the number of trays found in UniSim. This was done by assuming 50 % tray efficiency ($N_{actual} = N_{UniSim}/0.5$). To estimate the cost for the columns as described in appendix E, the same procedure was utilized as described in section 2.4.3 for the direct plant.

3.5 Mass and energy balances

- Mass balance

It is important to check that the mass and energy balances from the flowsheet in Unisim are correct. The mass balances are correct when the follow the equation given below:

$$mass_{in} - mass_{out} = 0$$

$$Energy_{in} - Energy_{out} = 0$$

- Mass balance

The total mass balance is shown in table 2.3. For the mass balances for all important units see appendix F.

Below gives an overwiev over the mass streams coming in and out for the total process

TOTAL MASS BALANCE		
STREAM		**ton/day**
IN	Methanol	4155.20808
OUT	DME	2880.0672
	Water	1232.84232
	18	44.76
STREAM ERROR		0.004%

The error is because of recycle unit in simulation.

- Energy balance

The total energy balance is shown in table 2.4. For the energy balances for all important units see appendix F.

Below gives an overwiev over the energy streams coming in and out for the total process

TOTAL ENERGY BALANCE			
STREAM		KJ/h	MW
IN	**Q-101**	531668.5246	0.147686
IN	**Q-102**	201571100.6	55.99197
OUT	**Q-104**	7527602195	2091.001
IN	**Q-105**	7309172577	2030.326
OUT	**Q-106**	17849461.63	4.958184
OUT	**Q-107**	2055394.708	0.570943
IN	**Q-108**	105903045.3	29.41751
IN	**Q-109**	9132653.055	2.536848
OUT	**18**	-16513274.04	-4.58702
OUT	**DME**	-479859335.3	-133.294
OUT	**Water**	-770589022.2	-214.053
IN	**Methanol**	-1344839261	-373.566

3.6 Economical estimation

3.6.1 Fixed capital cost

The fixed capital cost is estimated to get an approximate price for the total plant installed and up and running. These calculations are based on given percentages (West, Ronald E., et al, 2003).Major equipment costs are calculated as described in appendix G. The major costs for the indirect method plant are shown in table 3.2.

Table 3.2: Major equipment for the indirect plant

Equipment	Cost[$]
Pumps	62689
Heat exchangers	2955726
Reactor	1886663
Towers and Trays	738060
Compressors	779594
Storage tanks	838627
Major equipment	7261360

The fixed capital costs for the direct method are listed in table 3.3.

Table 3.3: Fixed capital cost for the indirect plant

Item	Factor[%]	cost [M$]
Major equipment cost	0.219	7.26
Purchased equipment installation	0.083	3
Instrumentation and controls (installed)	0.092	3
Piping (installed)	0.073	2
Elecrical systems (installed)	0.046	2
Buildings (including services)	0.046	2
Yard improvements	0.018	1
Service facilities (installed)	0.138	5
Land	0.01	0
Engineering and supervision	0.073	2
Construction expenses	0.092	3
Legal expenses	0.018	1
Contractor`s fee	0.018	1
Contingency	0.073	2
Fixed Capital cost	***0.999***	*33*

3.6.2 Working capital cost

The working capital is the amount of capital required to start up the plant and to finance the first couple of months of operation before the plant starts earning. This capital is used to cover salaries, raw material inventories, and contingencies. It will be recovered at the end of the project and represents a float of money to get the project started. These costs are necessary at start-ups and it implies raw materials and intermediates in the process. The working capital was assumed to be 3 % of the fixed capital cost (West, Ronald E., et al, 2003).The total investment for the plant is listed in table 3.4.

Table 3.4: The total investment for the indirect method

Item	Cost [M$/yr]
Fixed Capital cost	33
Working capital cost	0.99
Total investment	34

3.6.3 Operating cost

The operating cost for the direct method is listed in appendix H. The main costs are listed in table 3.5.

Table 3.5: Operating cost for the indirect plant

Item	Cost [M$/yr]
Sales revenue total	986
Manufactoring cost	527
Fixed cost	44
Operating cost	571

For the calculation of the operating cost we needed to find the price for the utilities needed in the plant and also the catalyst price for the plant.

3.7 Investment analysis

3.7.1 Evaluation parameters

The cumulative cash flow and the discounted cash flow are both shown in figure 3.6. The payback time for the two cash flows is under one year for both the non-discounted and for the discounted. The profit made after 15 years with discount rate of 10 % is 2245.8 M$. The discount rate is chosen on the basis of the interest rate that a central bank charges depository institutions that borrow reserves from it. We have chosen to double that rate for our discount rate.

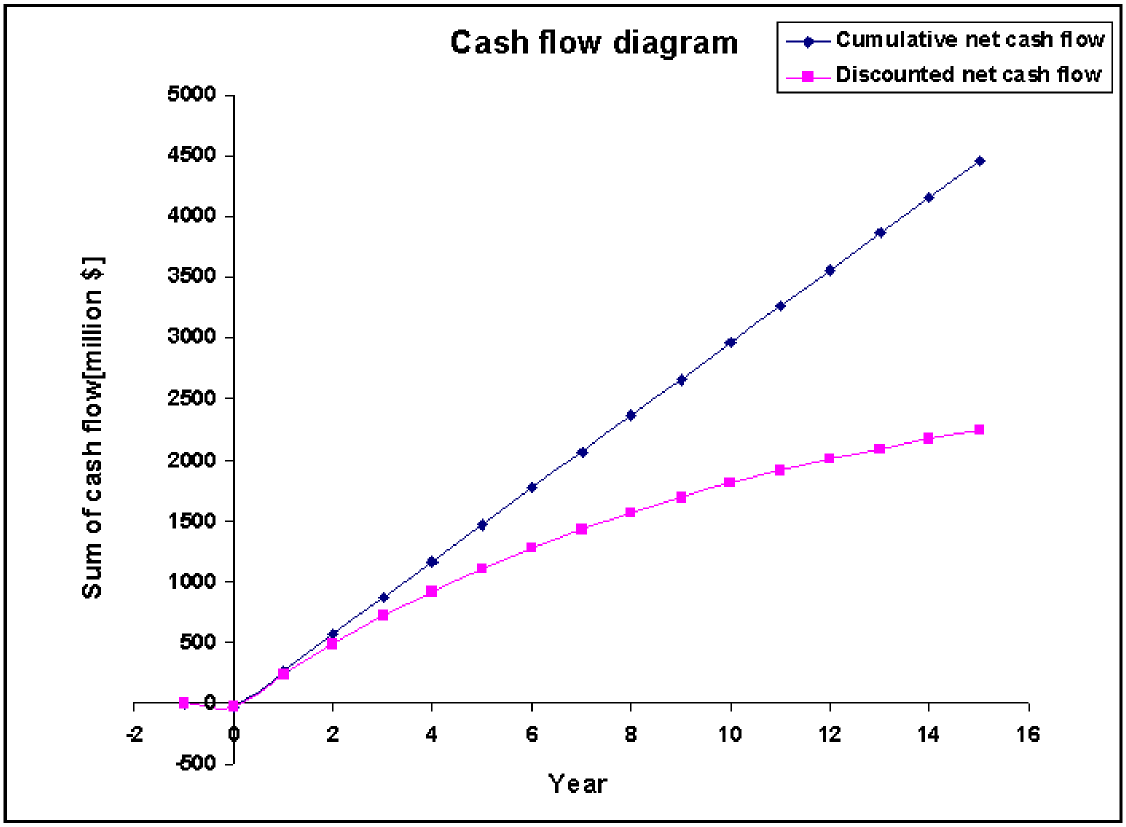


Figure 3.6: Cash flow diagram

The economic evaluation parameters, like the net present worth, the net future worth and the discounted cash-flow rate of return, were found by using excel and the results are listed in table 3.6. Detailed calculations for finding these parameters are described in appendix I.

Table 3.6: Economic evaluation parameters

Evaluation method	Result
Net present worth (NPW) [M$]	2246
Net future worth (NFW) [M$]	299
Discounted cash flow rate of return (DCFRR) [%]	911

3.7.2 Sensitivity analysis for variations and ROI (return on investment)

Payback time is a useful criterion for judging projects with short lifetimes. It defines the time required after the start of the project to pay off the initial investment from income. The calculations for finding the payback time and the ROI are shown in appendix B. The payback time result is shown in table 3.7. The payback time when we varied the prices for raw materials, product (DME), electrical power and major equipment of the plant is listed in table 3.8. The variations were 20 % increase and decrease. The graphical result is shown in figure 3.7. The pay back time for the invested cost without variation was 0.1 year.

Table 3.7: Payback time result

Calculation for Payback time	
Investment [M$]	34
Operating costs [M$]	571
Sales revenue [M$]	986
Depreciation [M$]	0.30
Payback time [yr]	**0.11**

Table 3.8: Payback time for variation in different variables

Payback time for variation in different variables			
Variation [%}	-20	0	20
Raw material [yr]	0.09	0.11	0.15
Product [yr]	0.21	0.11	0.08
Electrical power [yr]	0.12	0.11	0.11
Equipment cost [yr]	0.09	0.11	0.14
Variation [%}	-20	0	20

The return on investment result is shown in table 3.9.

Table 3.9: Return on investment result

Item	Result
Total sales revenue [M$]	986
Operating costs [M$]	571
Investment [M$]	34
ROI [%]	**12.1**

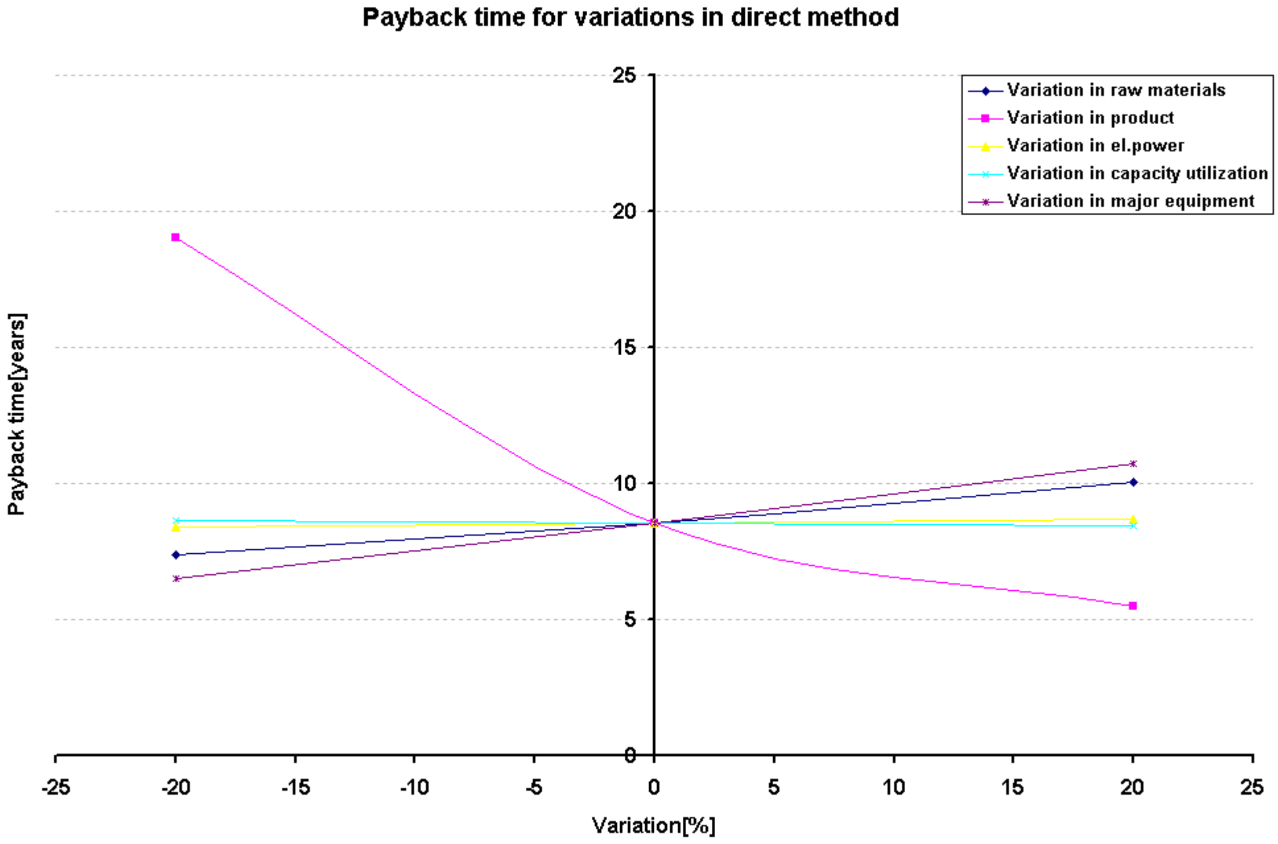


Figure 3.7: Payback time for variations in different variables

3.7.3 Break even analysis

The break even method is used to determine the point at which sales revenue will cover operating cost. Figure 3.8 shows the break even point for the direct plant case. The operating cost, which is a sum of the fixed cost and the variable cost, is plotted in the same graph as sales revenue. The intersection is where the revenue generated from the sales just covers the total operating cost. The variable cost is the costs that vary with production of DME, and the fixed cost is the costs that does not.

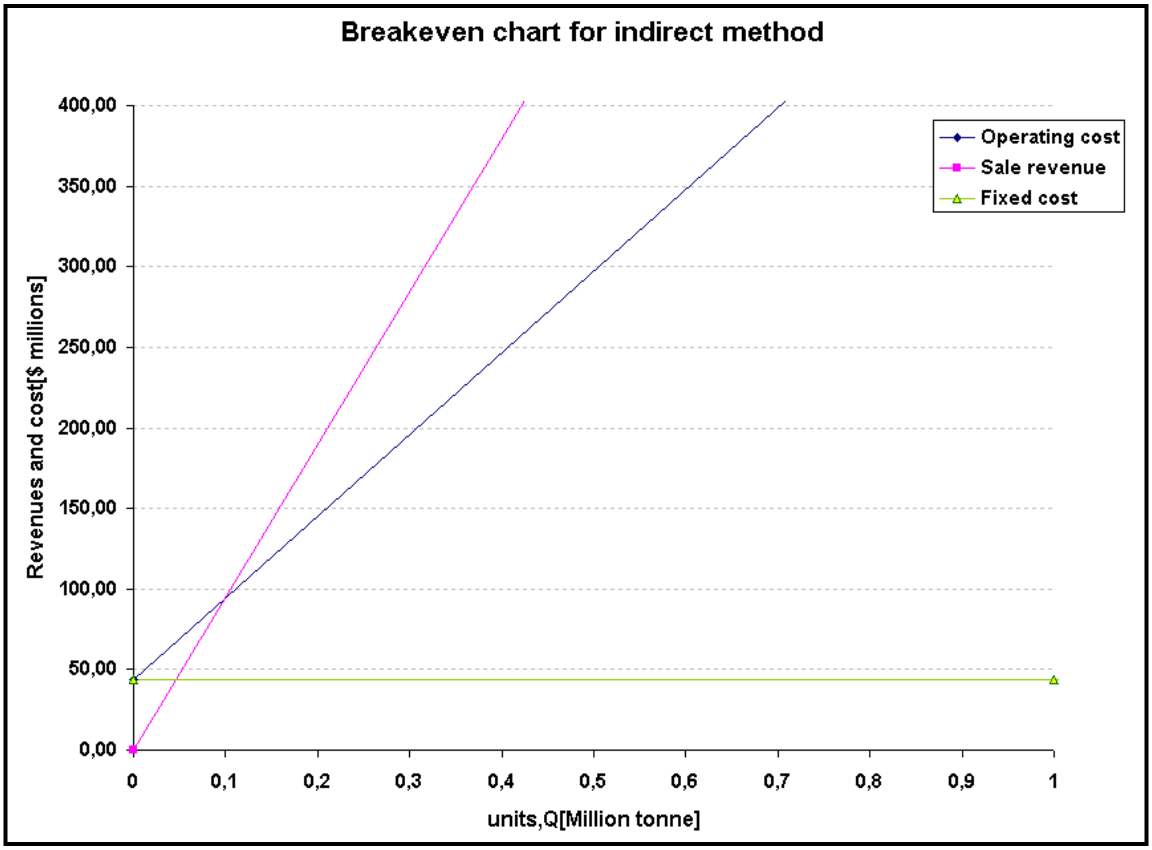


Figure 3.8: Break even chart for indirect plant

4 Discussion

4.1 Direct method

The overall reaction for the plant is given in reaction 4.1.

$$2CH_4 + C_2H_4 + C_3H_8 + C_4H_{10} + 13H_2O + 3/2O_2 = 7CO_2 + 22H_2 + 2DME \qquad (4.1)$$

This reaction illustrates that a lot of CO_2 is produced in this plant. Absorption of CO_2 should be a part of the process. This was not done. We wanted to separate CO_2 by using a CO_2 capture unit. However UniSim didn't recommend the Amin package, needed for the capture, for DME, thus two distillation columns are used to separate CO_2 from DME. For the purification of DME the separation method chosen is somewhat radical. This is due to no ideal gas mixtures in the product out of the FBR. In the simulation there are five distillation columns. It is possible with only three distillation columns (where the distillation towers, T-101 and T-102 become one and T-100 and T-103 become another one), but then the purity of the DME as a final product will decrease. In UniSim however this was not feasible. A lot of different approaches were tried. The method chosen is the simplest and the one we ended up with in UniSim. In addition CO_2 could have been recycled, but when applying a recycle stream the DME production was reduced. This is because the overall reaction taking place in the reactor is shifted towards syngas when the partial pressure of CO_2 is increased. **It is interesting that the separation unit in our plant is smaller than many of the existing plants.**

To find the optimal conditions for the plant, several "Case Studies" were made in UniSim. The result can be read in section 2.3.8.

One of the results from the case studies was that producing 3000 ton/d required a large reactor. This is not favorable, and is probably due to the nature of the kinetics used. Three parallel FBR reactors, each 2400 m^3, are needed to produce the required amount of DME. This is because tanks larger than 2500 m^3 are not easily transported. If one big reactor was to be needed, then this reactor would probably have to be constructed on site. In almost all cases it is more convenient to use one big reactor than three in parallel, but there could be some advantages with the tree in parallel configuration. For example, consider that something goes wrong. Then maybe only one of the reactors would have to be shut down, whilst the other two could still be running. On the other hand the type of reactor is fluidized-bed and constructing a FBR of the dimensions needed could become very difficult and is not realitic. Since UniSim is not set up to model the circulation and turbulent back-mixing that occurs when gas and catalyst particles collide, we had to use an approximate simulation method. Thus three parallel CSTR-reactors were chosen to simulate the FBR reactors.

4.2 Indirect method

Instead of producing synthesis gas first, DME can be produced directly from methanol. The overall plant reaction is shown in equation 4.2.

$$2CH_3OH = DME + H_2O \tag{4.2}$$

Simulation structure for this plant is more clear and the only problem was the kinetic for the reaction (discussed in section 3.3.2).

4.3 Economical evaluation

Major equipment cost contributes with 21% to the total investment. This means that when the goal is to reduce the total cost for the plant one should look into reducing the size of some of the equipment (when calculating the cost for the FBR reactors, the equations used has an upper limit for the reactor diameter of 4 m. Of course a reactor of our magnitude could not have a diameter of this size, but this was the only way to be able to calculate the cost).

The sensitivity analysis with 20 % increase and decrease of the most important cost variables shows that the effect of varying the product price has the largest effect on the two results for the two plants. The utility price affects the results to the smallest degree.

The plant for the **indirect method** shows uncertainty in the economic assessment. In reality it will **not be possible** to have a processing facility with a payback time in just **one month**. It is clear that the difference between sales revenue and the total investment cost is high. It is important to note that the product price is almost three times larger than the raw material. Another important assumption made for this plant is to use electricity for all the duties instead of steam and cooling water for the heat exchangers. However, this assumption should weaken the profitability, due to the fact that electricity is more expensive than heat integration and steam and cooling water consumption.

5 Conclusions and recommendation

The total investment needed for putting up the direct plant is 2119 M$ and the profit made at the end of the plant life will be 238 M$. The payback time for this plant is 8.9 years and the return on investment 15 %. It is clear that there are huge risks related to the direct method plant investment. The sensitivity analysis results shows that the product price for DME is the most sensitive parameter in this project (DME price = 948 $/ton). The project depends on a good and stable price for DME. The variation in utility price had minimum effect on payback time.

The heat integration part was done first after we calculated the plant cost. If we had done the cost calculations based on a better heat integration (like the one described in section 2.3.7) the operating costs would decrease.

The indirect plant has a total investment of 34 $ and a payback time less than one year. The sensitivity analysis results shows that the product price for DME is the most sensitive parameter in this project. The profit made at the end of the plant life will be 299 M$.

Our results strongly indicate that the indirect plant is more profitable than the direct plant. However, there are large uncertainties in our calculations.

List of symbols

Symbol	Unit	Description
A	m^2	Area
A	-	Capacity for cost estimation
A	-	Pre exponential factor
a	-	Declining balance rate
B_1, B_2	-	Constants for finding the bare module cost
C_0	$	investment
C^0_p	$	Bare cost of equipment
C_1,C_2,C_3	-	Constants for pressure factor estimation
C_{BM}	$	Bare module cost of equipment
D	m	Diameter
D	$	Depreciation
E	J/mol	Energy
F_{bm}	-	Bare module factor
F_m	-	Material factor
F_p	-	Pressure factor
$F_{p,vessel}$	-	Pressure factor for process vessels
Fq	-	Quantity factor
F_T	-	Superheat correction factor for steam boilers
ΔH	kJ/mol	Standard enthalpy change of reaction
ΔH_{vap}	kJ/mol	Enthalpy of vaporization
i	-	annual interest rate
K_i	-	Adsorption constant for component i
K_n	-	chemical reaction constant
$K_{P,n}$	-	Equilibrium constant for reaction n
K_1, K_2, K_3	-	Constants for bare cost estimation
k	$kgmol/m^3 \cdot h$	Rate constant
k_0	$kgmol/m^3 \cdot h.kpa$	Rate constant
m_{steam}	ton/yr	Mass flow
N	-	Number of trays
N	m^3/h	Flow rate
N_{id}	-	Ideal number of trays
N_{Unisim}	-	Actual number of trays
n	-	Index
n	-	year
P	barg	Pressure

Symbol	Unit	Description
P_i	kPa	Partial pressure of component i
ρ	kg/m^3	Density
Q	kJ/h	Duty/ power
R	J/K·mol	Gas constant
r	-	Discount rate
r_n	$kgmol/m^3 \cdot h$	Reaction rate for reaction n
s	-	Tax rate
T	°C	Temperature
ΔT_H	°C	Temperature diff. between hot stream in and cold stream out
ΔT_c	°C	Temperature diff. between cold stream in and hot stream out
ΔT	°C	Amount of superheat
T	year	Payback time
ΔT_{cw}	°C	Temperature diff. Between cooling water in and cooling water out
t_{vessel}	m	Vessel thickness
V	m^3	Volume
ν	m^3/h	Flow rate
W	kW	Shaft work
W_{el}	kW	Electric power

References

[1]. Aasberg-Petersen, K., Christensen, T., Nielsen, C., Dybkjaer, I. (2003), *Recent developments in autothermal reforming and pre-reforming for synthesis gas production in GTL applications*, Fuel. Proc. Tech., **83**, 253-261.

[2]. Biesheuvel, P., Kramer, G. (2003), *Two-section reactor model for autothermal reforming of methane to synthesis gas*, AIChe Journal, **49**, 1827-1837

[3]. Bondiera, J., and C. Naccache. (1991), *Kinetics of Methanol Dehydration in Dealuminated H-Mordenite: Model with Acid and Base Active Centres*, Applied Catalysis, **69**, 139-148.

[4]. Chul-Jin Lee, Youngsub Lim, Ho Soo Kim, and Chonghun Han (2009). *Optimal Gas-To-Liquid Product Selection from Natural Gas under Uncertain Price Scenarios*. Ind. Eng. Chem. Res., **48**, 794–800.

[5]. Dybkjaer, I. (1995), *Tubular reforming and autothermal reforming of natural gas – an overview of available processes*, Fuel. Proc. Tech., **42**, 85-107.

[6]. Lu, W.Z., Teng, L.H., Xiao, W.D. (2003). *Theoretical analysis of fluidized-bed reactor for dimethyl ether synthesis from syngas.* International Journal of Chemical Reactor Engineering, **1**, 1-10.

[7]. Moulijn, J., Makkee, M., van Diepen, A. (2001), *Chemical Process Technology*, John Wiley & Sons Ltd, England

[8]. Richard Turton, Richard C. Bailie, Wallace B. Whiting, Joseph A. Shaeiwitz (2009). Analysis, Synthesis, and Design of Chemical Processes, Third Ed., Prentice Hall PTR, New Jersey.

[9]. R. K. Sinnott (2008). Chemical Engineering Design, Fourth Ed., Elsevier, China.

[10]. Ruiz, J., Passos, F., Bueno, J., Souza-Aguiar, E., Mattos, L., Noronga, F. (2008). *Synthesis gas production by autothermal reforming of methane on supported platinum catalyst*. Appl. Catal., **334**, 259–267.

[11]. Sigurd Skogestad. (2009). *Chemical and energy process engineering*, Taylor & Francis, Boca Raton.

[12]. K. Sommer. (1989). *Ullman's Encyclopedia of Industrial Chemistry*, **A 12**, Fifth Ed., VCH, Germany.

[13]. Wen-Zhi Lu, Li-Hua Teng,Wen-De Xiao. (2004). *Simulation and experiment study of dimethyl ether synthesis from syngas in a fluidized-bed reactor*. Chemical Engineering Science, **59**, 5455.

[14]. Wihelm, D. J., Simbeck, D. R., Karp, A. D., Dickenson, R. L. (2001) *Syngas production for gas-to-liquids applications: technologies, issues and outlook*. Fuel Process. Technol., **71**, 139–148.

[15]. Xiao, W.D., Lu, W.Z. (2002). *A novel technology of DME synthesis from syngas.* Chemical Engineering Science, **47**, 3769-3776.

[16]. West, Ronald E., Peters, Max S., Timmerhaus, Klaus D. (2003). *Plant Design and Economics for Chemical Engineers*, Fifth Ed., MCGraw Hill Book Co., New York.

Other references

1.http://www.isope.org/publications/proceedings/ISOPE/ISOPE%202005/papers/008_NGGT_09.pdf

2.http://www.igu.org/html/wgc2006pres/data/wgcppt/pdf/WOC%20Working%20Committees/WOC%201/Challenges%20of%20new%20frontier%20gas/1.3EF.07.pdf

3. http://www.miljostatus.no/Tema/Klima/Klimagasser/

4.http://www.guardian.co.uk/environment/2007/feb/21/climatechange.climatechangeenvironment

5. Mehdi Panahi, conversation.

6. http://no.wikipedia.org/wiki/Ruthenium

7.http://www.fosterwheeler.it/pub/fh/HYDROGEN%20PLANT%20STEAM-HYDROCARBON%20REFORMERGLOBALE.pdf

8.http://www.topsoe.com/Business_areas/Methanol/Processes/~/media/PDF%20files/Ammonia/Topsoe_sec_ref_cat_RKS%202.ashx

9. http://en.wikipedia.org/wiki/Nickel(II)_oxide

10. http://www.kortogkontant.no/valutakurs-valuta/norske-kroner-nok/

APPENDIX A

Stream Condition – Direct Method

CONDITIONS	NG	Water	Oxygen	1	2	3	4
Vapour/Phase Fraction	1	0	1	1	1	0	1
Temperature [C]	50	25	50	-0.2147	455	25.27	455
Pressure [bar]	70	1	30	30	30	30	1
Molar Flow [kgmole/h]	7500	7500	6500	7500	7500	7500	7500
Mass Flow [kg/h]	125823.25	135113.25	208000	125823.25	125823.25	135113.25	135113.25
Std Ideal Liquid Volume Flow [m3/h]	411.5416	135.3859	182.82	411.5416	411.5416	135.3859	135.3859
COMPOSITION (Mole Fraction)							
Methanol	0	0	0	0	0	0	0
H_2O	0	1	0	0	0	1	1
DME	0	0	0	0	0	0	0
Methane	0.960774	0	0	0.960774	0.960774	0	0
Hydrogen	0	0	0	0	0	0	0
CO	0	0	0	0	0	0	0
Ethane	0.030181	0	0	0.030181	0.030181	0	0
Propane	0.00502	0	0	0.00502	0.00502	0	0
n-Butane	0.004024	0	0	0.004024	0.004024	0	0
CO_2	0	0	0	0	0	0	0
Oxygen	0	0	1	0	0	0	0

CONDITIONS	5	6	7	8	9	10	11
Vapour/Phase Fraction	1	1	1	1	1	1	1
Temperature [C]	279.2	250	455	1000	550	650	400
Pressure [bar]	30	30	30	30	30	30	30
Molar Flow [kgmole/h]	16372.79	6500	29999.98	30531.69	29999.98	30531.69	30531.69
Mass Flow [kg/h]	260936.69	208000	260942.82	468930.60	260942.82	468930.60	468930.60
Std Ideal Liquid Volume Flow [m3/h]	581.27	182.82	601	868.41	601	868.41	868.41
COMPOSITION (Mole Fraction)							
Methanol	0	0	0	0	0	0	0
H_2O	0.416154	0	0.374707	0.333982	0.374707	0.333982	0.333982
DME	0	0	0	0	0	0	0
Methane	0.440109	0	0.440109	0.004138	0.440109	0.004138	0.004138
Hydrogen	0.101815	0	0.143262	0.407527	0.143262	0.407527	0.407527
CO	0.041922	0	0.000476	0.171255	0.000476	0.171255	0.171255
Ethane	0	0	0	0	0	0	0
Propane	0	0	0	0	0	0	0
n-Butane	0	0	0	0	0	0	0
CO_2	0	0	0.041447	0.83098	0.041447	0.83098	0.83098
Oxygen	0	1	0	0	0	0	0

CONDITIONS	**12**	**13**	**14**	**15**	**16**	**17**	**18**
Vapour/Phase Fraction	1	0	0	1	0	0	0
Temperature [C]	50	25	25.92	50	25	25.27	50
Pressure [bar]	30	1	100	30	1	30	30
Molar Flow [kgmole/h]	20430	6809	6809	30531.69	4567	4567	10100
Mass Flow [kg/h]	286900	122700	122700	468930.60	82280	82280	182000
Std Ideal Liquid Volume Flow [m3/h]	686	122.9	122.9	868.41	82.44	82.44	182.4
COMPOSITION (Mole Fraction)							
Methanol	0	0	0	0	0	0	0
H_2O	0.004791	1	1	0.333982	1	1	0.999787
DME	0	0	0	0	0	0	0
Methane	0.006185	0	0	0.004138	0	0	0
Hydrogen	0.609016	0	0	0.407527	0	0	0.000003
CO	0.255924	0	0	0.171255	0	0	0.000008
Ethane	0	0	0	0	0	0	0
Propane	0	0	0	0	0	0	0
n-Butane	0	0	0	0	0	0	0
CO_2	0.124084	0	0	0.83098	0	0	0.000202
Oxygen	0	0	0	0	0	0	0

CONDITIONS	**19**	**20**	**21**	**22**	**HPS**	**MPS**	**LPS**
Vapour/Phase Fraction	0	0	1	1	1	1	1
Temperature [C]	25	25.18	480	510	510	480	250
Pressure [bar]	1	20	30	100	100	30	20
Molar Flow [kgmole/h]	15360	15360	7604	2867	6809	4567	15360
Mass Flow [kg/h]	276800	276800	137000	51650	122700	82280	276800
Std Ideal Liquid Volume Flow [m3/h]	277.3	277.3	137.3	51.75	122.9	82.44	277.3
COMPOSITION (Mole Fraction)							
Methanol	0	0	0	0	0	0	0
H_2O	1	1	1	1	1	1	1
DME	0	0	0	0	0	0	0
Methane	0	0	0	0	0	0	0
Hydrogen	0	0	0	0	0	0	0
CO	0	0	0	0	0	0	0
Ethane	0	0	0	0	0	0	0
Propane	0	0	0	0	0	0	0
n-Butane	0	0	0	0	0	0	0
CO_2	0	0	0	0	0	0	0
Oxygen	0	0	0	0	0	0	0

CONDITIONS	23	24	25	26	27	28	29
Vapour/Phase Fraction	1	1	1	1	1	1	1
Temperature [C]	260	258	50	258	258	258	260
Pressure [bar]	30	30	30	30	30	30	30
Molar Flow [kgmole/h]	20430	21280	7604	7093	7093	7093	3545
Mass Flow [kg/h]	286900	313300	137000	104433.33	104433.33	104433.34	104400
Std Ideal Liquid Volume Flow [m3/h]	686	718.8	137.3	239.6	239.6	239.6	150.9
COMPOSITION (Mole Fraction)							
Methanol	0	0.031278	0	0.031278	0.031278	0.031278	0.06531
H_2O	0.004791	0.009915	1	0.009915	0.009915	0.009915	0.279201
DME	0	0.000773	0	0.000773	0.000773	0.000773	0.250366
Methane	0.006185	0.005960	0	0.005960	0.005960	0.005960	0.011923
Hydrogen	0.609016	0.584756	0	0.584756	0.584756	0.584756	0.158725
CO	0.255924	0.245725	0	0.245725	0.245725	0.245725	0.001844
Ethane	0	0	0	0	0	0	0
Propane	0	0	0	0	0	0	0
n-Butane	0	0	0	0	0	0	0
CO_2	0.124084	0.121593	0	0.121593	0.121593	0.121593	0.232711
Oxygen	0	0	0	0	0	0	0

CONDITIONS	30	31	32	33	34	35	36
Vapour/Phase Fraction	1	1	1	1	1	0	0
Temperature [C]	260	260	20	260	10	10	10
Pressure [bar]	30	30	100	30	30	30	30
Molar Flow [kgmole/h]	3545	3545	2867	10640	3673	3412	3552
Mass Flow [kg/h]	104400	104400	51650	313300	88710	151700	72930
Std Ideal Liquid Volume Flow [m3/h]	150.9	150.9	51.75	452.8	160.9	213.6	78.25
COMPOSITION (Mole Fraction)							
Methanol	0.06531	0.06531	0	0.06531	0.0002	0.0204	0.1756
H_2O	0.279201	0.279201	1	0.279201	0.0004	0.0139	0.8223
DME	0.250366	0.250366	0	0.250366	0.113	0.6587	0.0003
Methane	0.011923	0.011923	0	0.011923	0.0308	0.004	0
Hydrogen	0.158725	0.158725	0	0.158725	0.4556	0.0044	0
CO	0.001844	0.001844	0	0.001844	0.0052	0.0002	0
Ethane	0	0	0	0	0	0	0
Propane	0	0	0	0	0	0	0
n-Butane	0	0	0	0	0	0	0
CO_2	0.232711	0.232711	0	0.232711	0.3948	0.2985	0.0019
Oxygen	0	0	0	0	0	0	0

CONDITIONS	37	38	39	40	41	42	43
Vapour/Phase Fraction	0.0002	1	0.0599	1	0	0	0
Temperature [C]	3.207	40	0	0.048	97.44	95.95	93.83
Pressure [bar]	30	29.9	29.9	29.85	30	29.95	29.9
Molar Flow [kgmole/h]	4285	2146	2146	1599	2139	2047	32.79
Mass Flow [kg/h]	19050	94280	94280	69150	96250	93700	1510
Std Ideal Liquid Volume Flow [m3/h]	265.5	122.9	122.9	85.44	142.7	139.6	2.252
COMPOSITION (Mole Fraction)							
Methanol	0.0164	0.0002	0.0002	0	0.0326	0.0046	0
H_2O	0.0114	0.001	0.001	0	0.0219	0.0079	0
DME	0.608	0.2717	0.2717	0.0259	0.9455	0.9874	0.9975
Methane	0.0043	0.0087	0.0087	0.0116	0	0	0
Hydrogen	0.0043	0.0086	0.0086	0.0115	0	0	0
CO	0.0002	0.0004	0.0004	0.0006	0	0	0
Ethane	0	0	0	0	0	0	0
Propane	0	0	0	0	0	0	0
n-Butane	0	0	0	0	0	0	0
CO_2	0.3553	0.7094	0.7094	0.9504	0	0	0.0025
Oxygen	0	0	0	0	0	0	0

CONDITIONS	44	45	46	47	48	49	50
Vapour/Phase Fraction	0	0	0	0.9130	1	1	0
Temperature [C]	93.74	195.1	17.83	110.3	10	260	10
Pressure [bar]	29.95	30.05	30	29.95	29.95	30	29.95
Molar Flow [kgmole/h]	547.1	92.27	36.44	3591	2743	848.3	848.3
Mass Flow [kg/h]	25130	2547	75480	73760	47330	26430	26430
Std Ideal Liquid Volume Flow [m3/h]	37.43	3.076	81.33	138.5	105.7	32.8	32.8
COMPOSITION (Mole Fraction)							
Methanol	0.0009	0.6536	0.1877	0.1864	0.0014	0.7848	0.7848
H_2O	0.0041	0.3314	0.8099	0.0315	0	0.1334	0.1334
DME	0.99	0.015	0	0.0164	0.0155	0.0194	0.0194
Methane	0	0	0	0.0301	0.0393	0.0005	0.0005
Hydrogen	0	0	0	0.465	0.6087	0.0003	0.0003
CO	0	0	0	0.0052	0.0068	0	0
Ethane	0	0	0	0	0	0	0
Propane	0	0	0	0	0	0	0
n-Butane	0	0	0	0	0	0	0
CO_2	0.005	0	0.0019	0.2653	0.3283	0.0616	0.0616
Oxygen	0	0	0	0	0	0	0

CONDITIONS	51	53	Gas	Methanol	Water.out	CO_2	DME
Vapour/Phase Fraction	1	0	1	1	0	1	0.7845
Temperature [C]	260	-25	-25	196.2	233.7	-5.668	95.2
Pressure [bar]	30	30	30	29.95	30.05	29.8	29.9
Molar Flow [kgmole/h]	848.3	873.6	2799	791.9	2852	1566	2627
Mass Flow [kg/h]	26430	38850	49870	23904	51580	67640	120300
Std Ideal Liquid Volume Flow [m3/h]	32.8	51.95	109	29.53	51.8	83.19	179.3
COMPOSITION (Mole Fraction)							
Methanol	0.7848	0.000639	0.000001	0.845551	0.005	0	0.003799
H_2O	0.1334	0.001836	0.000013	0.142975	0.995	0	0.007025
DME	0.0194	0.410219	0.020232	0.002929	0	0.00554	0.988099
Methane	0.0005	0.005752	0.038664	0.000001	0	0.00863	0
Hydrogen	0.0003	0.004056	0.596503	0.000018	0	0.011757	0
CO	0	0.000271	0.006684	0.000001	0	0.000573	0
Ethane	0	0	0	0	0	0	0
Propane	0	0	0	0	0	0	0
n-Butane	0	0	0	0	0	0	0
CO_2	0.0616	0.577227	0.337902	0.008526	0	0.970268	0.001076
Oxygen	0	0	0	0	0	0	0

Stream Condition – Indirect Method

CONDITIONS	Methanol	2	3	4	5	6	7
Vapour/Phase Fraction	0	0	0	0	0.3439	1	1
Temperature [C]	25	25.3	49.97	142.9	160.7	250	352.2
Pressure [bar]	1	15.5	15.2	14.9	14.9	14.7	14.7
Molar Flow [kgmole/h]	5426	5426	5426	5426	7905	7905	7905
Mass Flow [kg/h]	173133.67	173133.67	173133.67	173133.67	233432.44	233432.44	233433.21
Std Ideal Liquid Volume Flow [m3/h]	217.3	217.3	217.3	217.3	286.9	286.9	303.1
COMPOSITION (Mole Fraction)							
Methanol	0.990465	0.990465	0.990465	0.990465	0.820947	0.820947	0.164189
H_2O	0.009535	0.009535	0.009535	0.009535	0.179053	0.179053	0.507432
DME	0	0	0	0	0	0	0.328379

CONDITIONS	8	9	10	11	12	13	14
Vapour/Phase Fraction	1	1	0	0.0429	0	1	0
Temperature [C]	180	175.1	169.3	155.7	139	154.4	165.9
Pressure [bar]	14.4	10.4	10.4	7.4	7.4	7.3	7.6
Molar Flow [kgmole/h]	7905	7905	5296	5296	5296	2551	2745
Mass Flow [kg/h]	233433.21	233433.21	113430.39	113430.39	113430.39	62061.95	51368.43
Std Ideal Liquid Volume Flow [m3/h]	303.1	303.1	124.1	124.1	124.1	71.55	52.59
COMPOSITION (Mole Fraction)							
Methanol	0.164189	0.164189	0.242606	0.242606	0.242606	0.44979	0.05
H_2O	0.507432	0.507432	0.757394	0.757394	0.757394	0.55021	0.95
DME	0.328379	0.328379	0	0	0	0	0

CONDITIONS	15	16	17	18	DME	Water	
Vapour/Phase Fraction	1	1	1	1	1	0	
Temperature [C]	154	241.3	241.3	241.3	47.6	70	
Pressure [bar]	7.3	15.5	15.5	15.5	10.3	7.3	
Molar Flow [kgmole/h]	2555	2555	2479	76.66	2609	2745	
Mass Flow [kg/h]	62163.68	62163.68	60298.77	1865	120002.8	51368.43	
Std Ideal Liquid Volume Flow [m3/h]	71.67	71.67	69.52	2.15	178.9	52.59	
COMPOSITION (Mole Fraction)							
Methanol	0.449881	0.449881	0.449881	0.449881	0.005	0.05	
H_2O	0.550119	0.550119	0.550119	0.550119	0	0.95	
DME	0	0	0	0	0.995	0	

APPENDIX B

Kinetics[1]

Several sources were studied to obtain the most plausible kinetics for the DME-reactor. The choice of kinetics is supported by the fact that most of the sources contained errors that made it impossible to obtain any DME. The chosen source included a reasonable reaction mechanism, with rate expressions and rate constants that are well documented. This documentation made it possible to double check the equations to make sure that they did not contain any errors. For the direct method three reactions take place in the syngas-to-DME reactor, namely:

Methanol synthesis:

$$CO2 + 3H2 \leftrightarrow CH3OH + H2O \qquad \Delta H = -56.33\ kJ/mol \qquad (B.1)$$

Methanol dehydration:

$$2CH3OH \leftrightarrow CH3OCH3 + H2O \qquad \Delta H = -21.255\ kJ/mol \qquad (B.2)$$

Water gas shift:

$$CO + H2O \leftrightarrow H2 + CO2 \qquad \Delta H = -40.9 kJ/mol \qquad (B.3)$$

Overall reaction

$$3CO + 3H2 \leftrightarrow CH3OCH3 + CO2 \qquad \Delta H = -256.615\ kJ/mol \qquad (B.4)$$

All tree reactions, as well as the overall reaction, are reversible and exothermic. The catalyst that is used is the dual catalyst Cu–ZnO–Al_2O_3/HZSM-5, manufactured by co-precipitation deposition method. The component for methanol synthesis is Cu–ZnO–Al_2O_3, and that for methanol dehydration is HZSM-5.

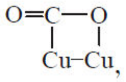
The reaction mechanism that the rate expressions are based on is described below. The reaction mechanisms for CO_2 hydrogenation to methanol and water gas shift reaction are as follows:

---

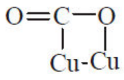
[1] Wen-Zhi Lu, Li-Hua Teng and Wen-De Xiao, "Simulation and experiment study of dimethyl ether synthesis from syngas in a fluidized-bed reactor", Chemical Engineering Science 59 (2004) 5455 – 5464.

$$2Cu_2 + H_2 \rightleftharpoons 2Cu_2H, \qquad (a)$$

$$CO_2 + Cu_2 \rightleftharpoons$$



(b)



$$+ 2Cu_2H \rightleftharpoons Cu_2CH_2O + Cu_2O + Cu_2, \qquad (c)$$

$$Cu_2CH_2O + Cu_2H \rightleftharpoons Cu_2CH_3O + Cu_2, \qquad (d)$$

$$Cu_2CH_3O + Cu_2H \rightleftharpoons Cu_2CH_3OH + Cu_2, \qquad (e)$$

$$Cu_2CH_3OH \rightleftharpoons Cu_2 + CH_3OH(a), \qquad (f)$$

$$Cu_2O + 2Cu_2H \rightleftharpoons 2Cu_2 + Cu_2H_2O, \qquad (g)$$

$$Cu_2H_2O \rightleftharpoons Cu_2 + H_2O(a), \qquad (h)$$

$$H_2O(a) + Cu_2 \rightleftharpoons Cu_2O + H_2, \qquad (i)$$

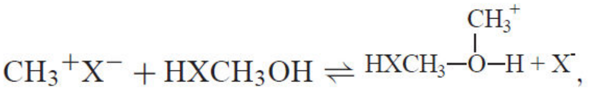
$$CO + Cu_2O \rightleftharpoons Cu_2 + CO_2. \qquad (j)$$

Reaction (c) and (i) are assumed to be the rate determining steps individually

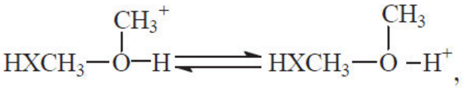
The reaction mechanism for the formation of DME is as follows:

$$CH_3OH(a) + HX \rightleftharpoons HXCH_3OH, \qquad (k)$$

$$HXCH_3OH \rightleftharpoons CH_3{}^+X^- + H_2O(a), \qquad (l)$$



$$CH_3{}^+X^- + HXCH_3OH \rightleftharpoons HXCH_3-\overset{CH_3^+}{\overset{|}{O}}-H + X^-, \qquad (m)$$



$$HXCH_3-\overset{CH_3^+}{\overset{|}{O}}-H \rightleftharpoons HXCH_3-\overset{CH_3}{\overset{|}{O}}-H^+, \qquad (n)$$

$$HXCH_3-\overset{CH_3}{\overset{|}{O}}-H^+ \rightleftharpoons HXCH_3-O-CH_3 + H^+, \qquad (o)$$

$$HXCH_3-O-CH_3 \rightleftharpoons CH_3OCH_3 + HX, \qquad (p)$$

$$H^+ + X^- \rightleftharpoons HX. \qquad (q)$$

Here reaction (m) is assumed to be the rate determining step. Based oh these kinetics one could obtain the following rate expressions:

The reaction rate for the methanol formation reaction is:

$$r_1 = K_1 \cdot \frac{\left(P_{CO2} P_{H2} - \frac{P_W P_M}{K_{P,1} {P_{H2}}^2} \right)}{\left(1 + K_{CO2} P_{CO2} + K_{CO} P_{CO} + \sqrt{K_{H2} P_{H2}} \right)^3} \tag{B.5}$$

The reaction rate for the methanol dehydration reaction is:

$$r_2 = K_2 \cdot \left(\frac{{P_M}^2}{P_W} - \frac{P_D}{K_{P,2}} \right) \tag{B.6}$$

The reaction rate for the water gas shift reaction is:

$$r_3 = K_3 \cdot \frac{\left(P_W - \frac{P_{CO2} P_{H2}}{K_{P,3} P_{CO}} \right)}{\left(1 + K_{CO2} P_{CO2} + K_{CO} P_{CO} + \sqrt{K_{H2} P_{H2}} \right)} \tag{B.7}$$

The constants K_1, K_2, K_3 (kinetic parameters), $K_{CO2,}$ K_{CO}, K_{H2} (adsorption constants), $K_{P,1}$, $K_{P,2}$ and $K_{P,3}$ (equilibrium constants) are defined as:

$$K_1 = 35.45 \exp(-1.7069 \times 10^4 / RT),$$

$$K_2 = 8.2894 \times 10^4 \exp(-5.2940 \times 10^4 / RT),$$

$$K_3 = 7.3976 \exp(-2.0436 \times 10^4 / RT),$$

$$K_{H_2} = 0.249 \exp(3.4394 \times 10^4 / RT),$$

$$K_{CO_2} = 1.02 \times 10^{-7} \exp(6.7400 \times 10^4 / RT),$$

$$K_{CO} = 7.99 \times 10^{-7} \exp(5.8100 \times 10^4 / RT),$$

$$\ln K_{P,1} = 4213/T - 5.752 \ln T - 1.707 \times 10^{-3} T + 2.682 \times 10^{-6} T^2 - 7.232 \times 10^{-10} T^3 + 17.6$$

$$\ln K_{P,2} = 4019/T + 3.707 \ln T - 2.783 \times 10^{-3} T + 3.8 \times 10^{-7} T^2 - 6.561 \times 10^4 / T^3 - 26.64,$$

$$\ln K_{P,3} = 2167/T - 0.5194 \log T + 1.037 \times 10^{-3} T - 2.331 \times 10^{-7} T^2 - 1.2777.$$

Inserting these equations into UniSim we have to use the following nomenclature.
The rate expressions in Unisim have to be in the form as described in equation B.7:

$$rate = \frac{Numerator}{Deno\min ator} \tag{B.7}$$

Where the numerator and denominator is in the form described in eq. B.6 and B.7:

$$Numerator = k \cdot f(basis) - k^{'} \cdot f^{'}(basis) \tag{B.8}$$

$$Deno\min ator = (1 + K1 \cdot f1(basis) + K2 \cdot f2(basis) + Kn \cdot fn(basis))^{n} \tag{B.9}$$

n is the denominator exponent. f, f', f1 and f2 are functions of the basis used in Unisim. When projecting the data from the rate expressions into Unisim the functions are partial pressures of the components in the reactions to the power of the specified components. The rate constants k and k' is for the forward and backward reaction respectively. From rate expression to Unisim it will be k = K_1, K_2, K_3 and k`= $\frac{K_1}{K_{P,1}}$, $\frac{K_2}{K_{P,2}}$, $\frac{K_3}{K_{P,3}}$. The constants in Unisim for the reversible reaction is defined below:

$$k = A \cdot \exp[\frac{-E}{RT}] \cdot T^{\beta} \qquad k^{'} = A' \cdot \exp[\frac{-E^{'}}{RT}] \cdot T^{'\beta} \tag{B.10}$$

$$K1 = A1 \cdot \exp[\frac{-E1}{RT}] \qquad K2 = A2 \cdot \exp[\frac{-E2}{RT}] \tag{B.11}$$

The constants K, A and E have indexes which indicates the numbers in the denominator term in the rate expression. The equations describes the dependence of the rate constants on temperature and activation energy E, which is defined as the Arrehenius equation. The term $\exp[\frac{-E}{RT}]$ will be the probability that any given collision will result in a reaction.

APPENDIX C

The McCabe-Thiele method

How to construct a McCabe-Thiele diagram is explained below and to find the operating lines the reflux ratio must be set. Total reflux means that R goes to infinity, and this gives the operating line in equation C.3 and is a 45° straight line.

$$y_{n+1} = \frac{R}{R+1} X_n + \frac{X_D}{R+1} \tag{C.1}$$

$$y_{n+1} = \frac{\infty}{\infty} X_n + \frac{X_D}{\infty} \tag{C.2}$$

$$y_{n+1} = X_n \tag{C.3}$$

In a column, the feed enters the column at the top as liquid and flows down the column to the boiler before the distillation begins. Liquid and vapor streams enter a tray, are equilibrated, and leave, see figure C.1:

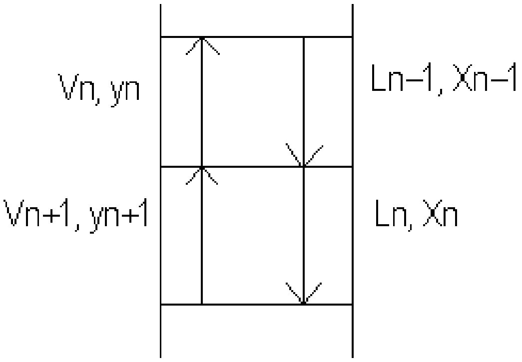


Figure C.1, A Principe sketch over what happens in the column.

Liquid and vapour streams enter a tray, are equilibrated, and leave, see figure C.1. The stripping line and the enriching line were not calculated only drawn with respect to the equilibrium line.

McCabe Thiele Diagram

For the separation we needed several distillation columns or the simulation would not run. Since we have multi components and not only a binary mixture the molar basis composition for the light key component and the heavy key component were plotted. Figure C.2 - Figure C.6 shows the equilibrium composition including the operating lines, enriching and stripping lines for each distillation column.

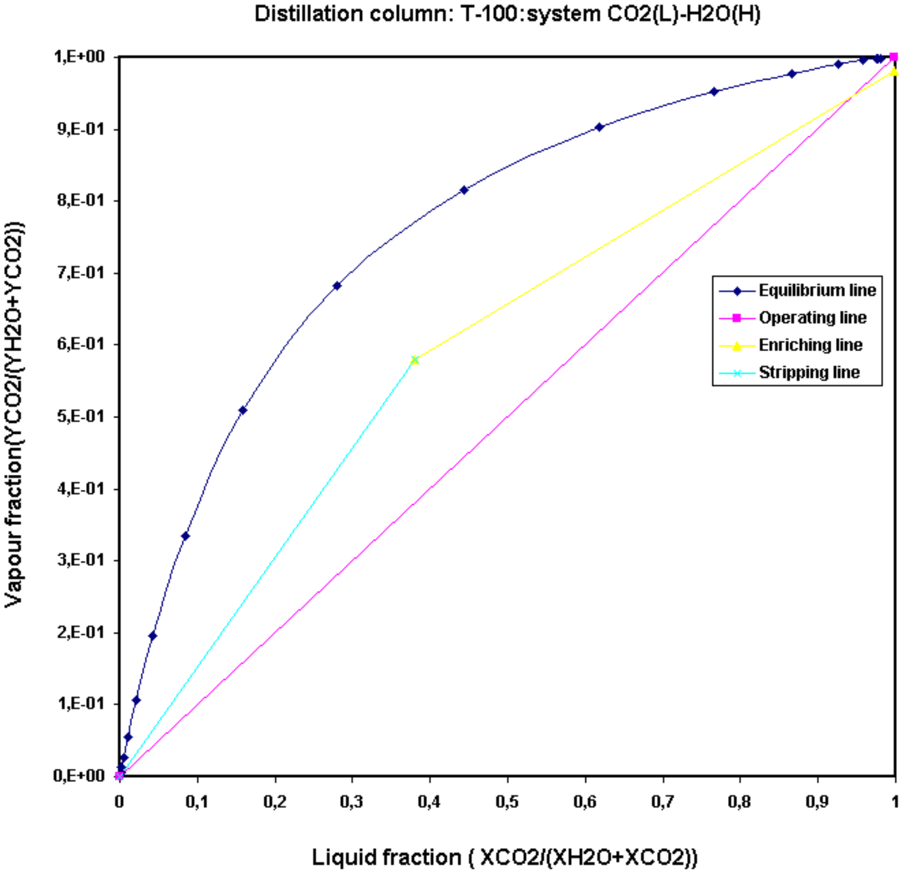


Figure C.2: McCabe Thiele diagram for CO_2(L)-H_2O(H)

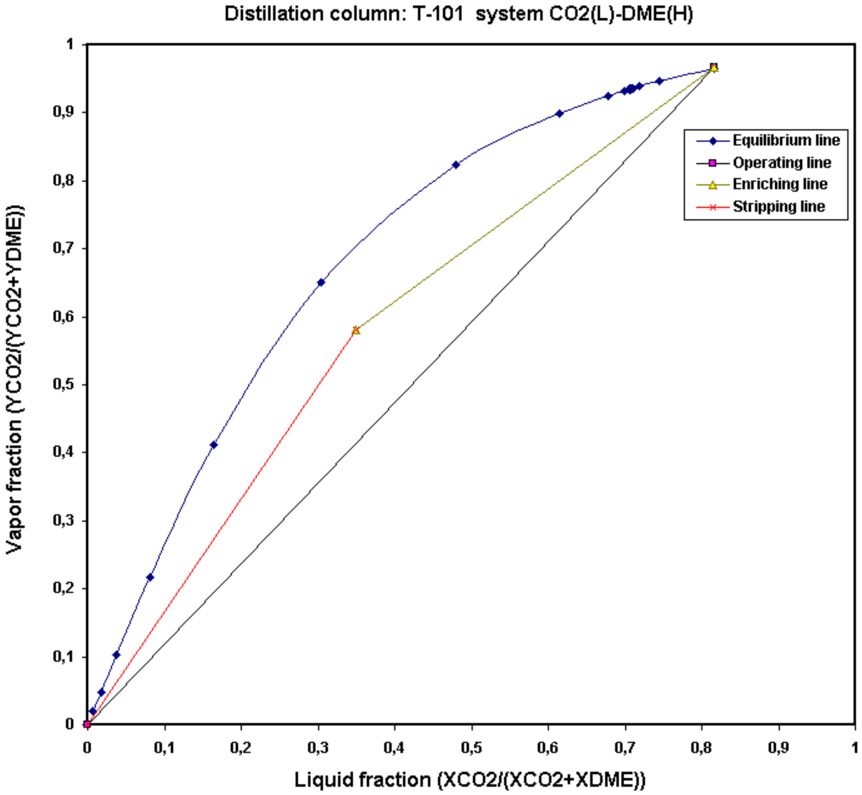


Figure C.3: McCabe Thiele diagram for CO_2(L)-DME(H)

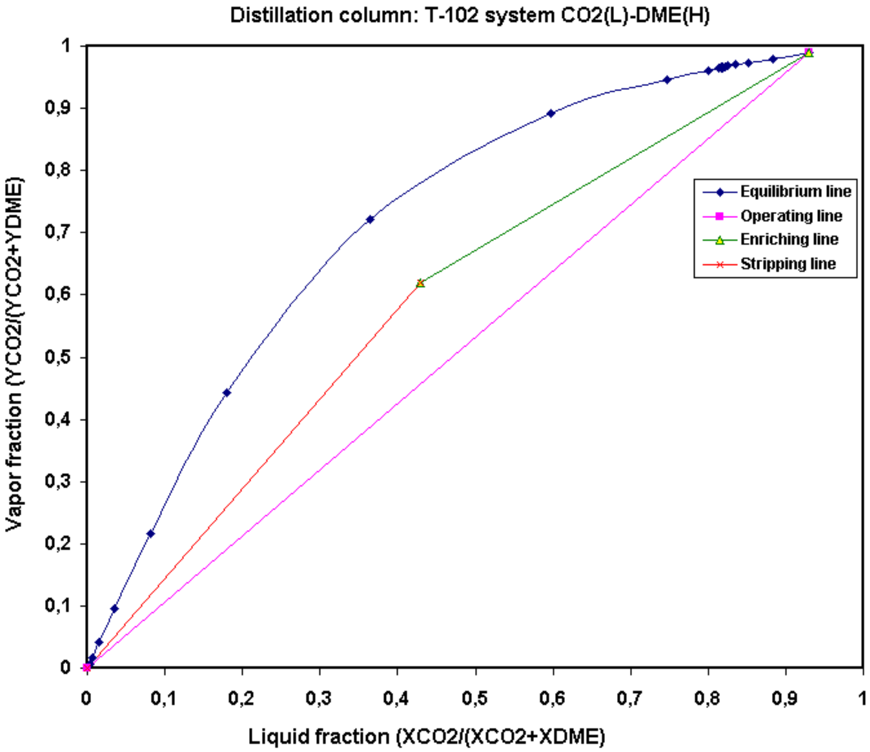


Figure C.4: McCabe Thiele diagram for CO_2(L)-DME(H)

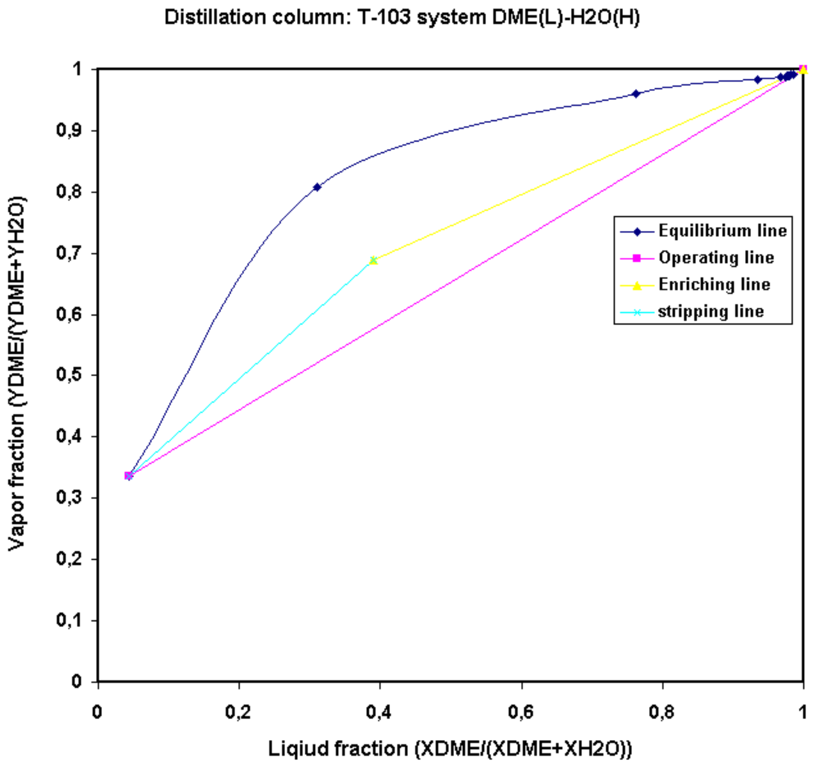


Figure C.5: McCabe Thiele diagram for DME(L)-H_2O(H)

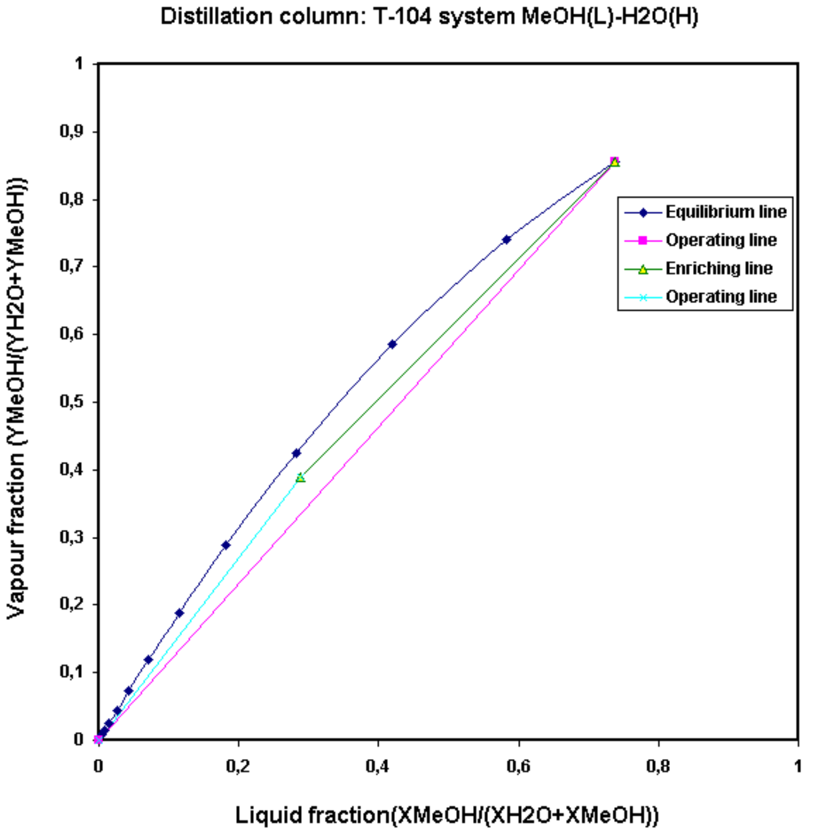
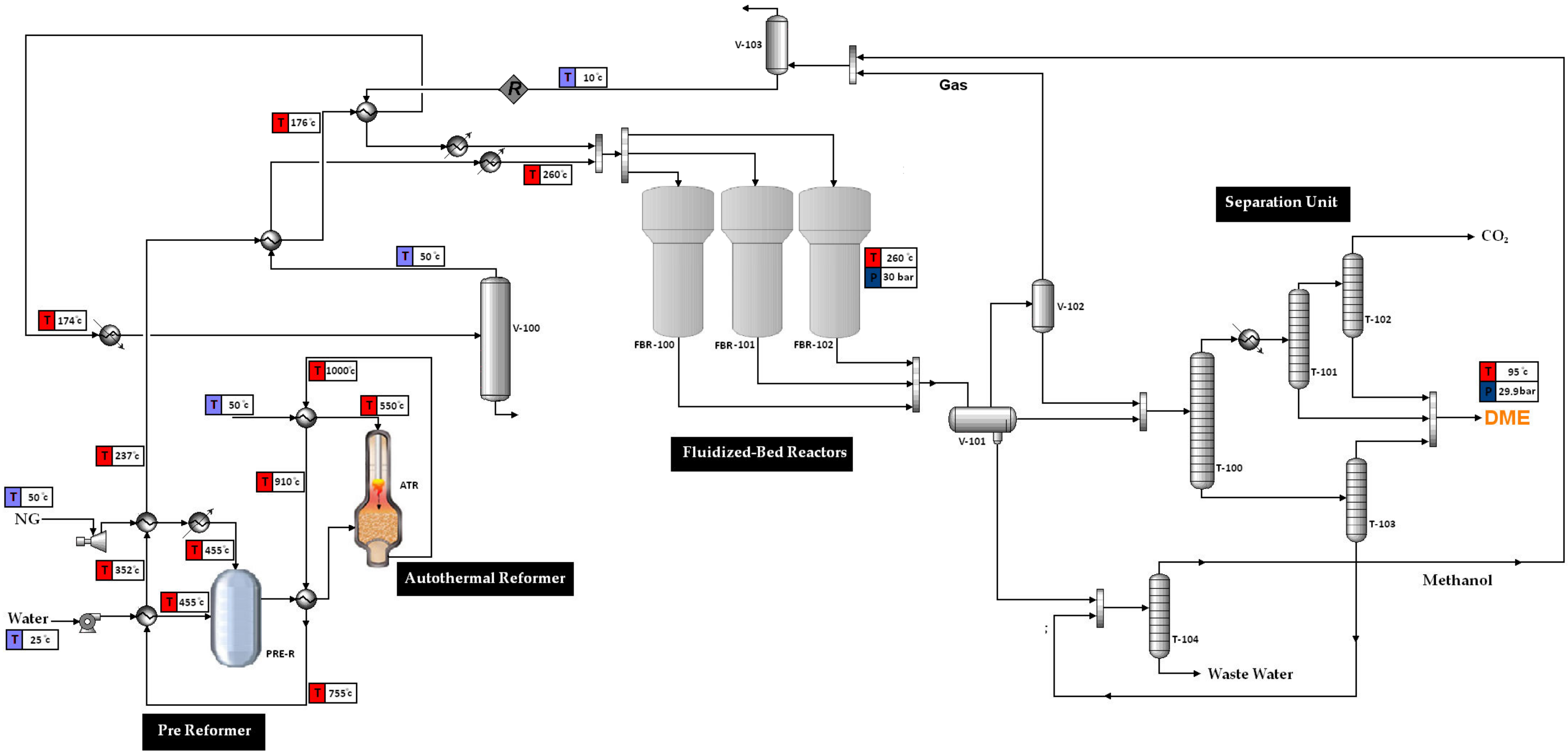


Figure C.6: McCabe Thiele diagram for MeOH(L)-H_2O(H)

APPENDIX D – Flowsheet with heat integration



APPENDIX E

Economical equipment study of DME plants

To obtain an estimate of the capital cost of the plants, the costs associated with major plant equipment must be known. The most accurate estimate of the purchased cost of a piece of major equipment is provided by a current price quote of a suitable vendor. The method that was used for the plants in this project is a good alternative when the cost data on previously purchased equipment of the same type are used.

Module costing technique

The equipment module costing technique was used to estimate the total equipment cost. This is a common technique to estimate the cost of a new chemical plant. This costing technique relates all costs back to the purchased costs of equipment evaluated for some base conditions. Deviations from these base conditions are handled by using multiplying factors that depend on the specific equipment type, the specific system pressure and the specific materials of construction.

Equation 2 is used to calculate the bare module cost, $C_{BM,}$ which includes both direct and indirect costs for each piece of equipment.

$$C_{BM} = C_p^0 F_{BM} \tag{E.1}$$

C_p^0 is the purchased cost for base condition, which means condition where equipment is made of the most common material, usually carbon steel and operating at near ambient pressure. F_{BM} is the bare module cost factor, which is a multiplying factor for: Direct project expenses (equipment free on board costs, materials required for installation and labor to install equipment and material), indirect project expenses (freight insurance, taxes, construction overhead and contractor engineering expenses), contingency and contractor fee and auxiliary facilities (site development, auxiliary buildings, off – sites and utilities) plus the specific materials of construction and operating pressure.

Purchased equipment cost

Data for the purchased cost of the equipment, at ambient operating pressure and using carbon steel construction, C_p^0 were fitted to following equation E.2:

$$\log_{10} C_p^0 = K_1 + K_2\log_{10}(A) + K_3[\log_{10}(A)]^2 \quad \text{(E.2)}$$

Where A is the capacity or the size parameter for the equipment and K_1, K_2 and K_3 are some constants dependent on the equipment type and the size of the capacity.

Pressure factors:

As the pressure at which a piece of equipment operates increases, the thickness of the walls of the equipment will also increase.

Process vessels

The relationship between cost of a vessel and its operating pressure is a complex one. With all other things being constant, the cost of the vessel is approximately proportional to the weight of the vessel, which in turn is proportional to the vessel thickness. Equation 4 give the pressure factor for horizontal and vertical process vessels and is based on diameter D meters, operating at pressure P barg (1 barg = 100 kPa) and carbon steel construction.

$$F_{p,vessel} = \frac{\dfrac{(P+1)D}{2[850-0,6(P+1)]}+0,00315}{0,0063} \quad \text{for } t_{vessel} > 0,0063m \quad \text{(E.3)}$$

For $F_{p,\ vessel}$ less than 1, then $F_{p,vessel} = 1$

Other process equipments

The pressure factors from the other equipments are given by equation 5 on its general form:

$$\log_{10} F_P = C_1 + C_2 \log_{10} P + C_3(\log_{10} P)^2 \quad \text{(E.4)}$$

The units of pressure P is barg. The constants C_1, C_2 and C_3 are dependent on the equipment type and pressure range.

The value predicted from this equation gives values of F_p much smaller than those for vessels at the same pressure. This difference arises from the fact that for other equipment, the internals of equipment make up the major portion of the cost.

Some equipments, like for example tower trays and packing, is unaffected by pressure. Tower trays and packing is not subjected to significant differential pressure because it is surrounded by process fluid. Compressors do not have corrections for pressure because such data is not available.

Bare module and material factors

The costs of equipment change with the change of different material of construction.

The choice of which materials of construction to use depends on the chemicals that will contact the walls of the equipment, and the operating temperature and operating pressure.

To account for the cost of different materials of construction, it is necessary to use the appropriate material factor, F_m, in the bare module factor. This material factor is not simply the relative cost of the material of interest to that of carbon steel. The reason is that the cost to produce a piece of equipment is not directly proportional to the cost of the raw materials.

Heat exchangers, process vessels and pumps

The material factors, F_M for heat exchangers, process vessels and pumps are given in a figure (Richard Turton, 2009) with the appropriate identification number listed in a table in the same book (Richard Turton, 2009). The bare module costs C_{BM} are given by the following equation:

$$C_{BM} = C_P^0 F_{BM} = C_P^0 (B_1 + B_2 F_M F_P) \tag{E.5}$$

B_1 and B_2 are some constants (Richard Turton, 2009).

$B_1 = F^0_{BM} - 1 - f_{P\&I}$ and $B_2 = 1 + f_{P\&I}$ (E.6)

Where $f_{P\&I}$ are modified values that accounts for the fraction of the installation cost that is associated with piping and instrumentation.

Since it probably is desirable to separate the equipment costs and the costs that have to be considered in the evaluation of the total capital cost of a chemical plant, equation E.5 becomes:

$$C_{BM} = C^0_P F_M F_P \tag{E.6}$$

Where only the operating pressure and the specific material of constructions are taken into account. First we calculated the equipment cost by using equation E.5. Then the costs for some of the pieces became unreasonably large. Then we removed the B1, B2 and the FBM factor. This reduced the costs equipment by 60 %. As mentioned above F_{BM} is the bare module cost factor, which is a multiplying factor for: Direct project expenses (equipment free on board costs, materials required for installation and labour to install equipment and material), indirect project expenses (freight insurance, taxes, construction overhead and contractor engineering expenses), contingency and contractor fee and auxiliary facilities (site development, auxiliary buildings, off – sites and utilities) plus the specific materials of construction and operating pressure. This factor could be removed, because all of this equipment related costs are calculated as a percentage of the total fixed capital. Therefore we use equation E.6 instead of equation E.5 to calculate the equipment cost.

Fired heaters

Equation E.7 gives the module cost for fired heaters:

$$C_{BM} = C^0_P F_{BM} F_P F_T \tag{E.7}$$

Where F_T is the superheated correction factor for non-reactive fired heaters is 1

Equation E.9 with only the operating pressure, the superheated correction factor and the specific material of construction taken into account is given below:

$$C_{BM} = C_P^0 F_M F_P F_T \tag{E.8}$$

Sieve trays

The bare module costs of the sieve trays are given in the equation below:

$$C_{BM} = C_P^0 N F_{BM} F_q \tag{E.9}$$

Where N is the number of trays and F_q is quantity factor given by equation E.10:

$$\log_{10} F_q = 0,4771 + 0,085161 \log_{10} N - 0,3473 (\log_{10} N)^2 \text{ for N} < 20 \tag{E.10}$$

$F_q = 1$ for $N \geq 20$

Equation E.9 with only the operating pressure and the specific material of construction taken into account is given below:

$$C_{BM} = C_P^0 N F_M F_q \tag{E.11}$$

Towers

Equation E.12 gives the module cost for towers:

$$C_{BM} = C_p^0 F_{BM} \tag{E.12}$$

Equation E.12 with only the operating pressure and the specific material of construction taken into account is given below:

$$C_{BM} = C_p^0 F_M F_P \tag{E.13}$$

The bare module factors were found in a figure (Turton book, year 2009) with the appropriate identification number listed in a table (Turton book, year 2009). Then the F_{BM} factors were removed for reasons discussed above.

Storage tanks

The volume of the storage tank for water in the indirect process was too small to be calculated the same way as the other tanks. It had to be scaled up by using one of the other tanks as a basis and the equation:

$$C_A = C_B \left(\frac{V_A}{V_B} \right)^n \tag{E.14}$$

where n was given as 0,6[mehdi], C_A the cost of the tank for water, C_B the cost of the basis tank, V_A the volume of the tank for water and V_B the volume of the basis tank.

Effect of time on purchased equipment cost

All cost-estimating methods use historical data, and are themselves forecasts of future costs. The method usually used to update historical cost data makes use of published cost indices. These relate present costs to past costs by taking the economic conditions into account. This following equation:

$$C_{BM,2008} = C_{BM,2001} \left(\frac{I_{2008}}{I_{2001}} \right) \tag{E.15}$$

Where C_{BM} = purchased bare module cost and I = Cost index.

Subscripts: 2001 refers to base time when cost is known. 2008 refer to time when cost is desired.

APPENDIX F

Mass and Energy balance

- Mass balance for the direct method

It is important to check that the mass balances from the flowsheet in Unisim are correct. The mass balances are correct when the follow the equation F.1 given below:

$$mass_{in} - mass_{out} = 0 \qquad \text{(F.1)}$$

Below gives an overwiev over the mass streams coming in and out for the different processes and for the total process. The stream error is also given.

PRE REFORMER		
STREAM		**ton/day**
IN	NG	3019.76
	Water	3242.72
OUT	7	6262.63
STREAM ERROR		0.0024%

ATR		
STREAM		**ton/day**
IN	Oxygen	4992
	7	6262.63
OUT	8	11254.33
STREAM ERROR		0.0026%

FBR		
STREAM		**ton/day**
IN	23	6885.63
	49	634.44
OUT	33	7519.96
STREAM ERROR		0.0014%

V-100		
STREAM		**ton/day**
IN	15	11254.33
OUT	18	4368.7
	12	6885.63
STREAM ERROR		0

V-101		
STREAM		**ton/day**
IN	33	7519.96
OUT	34	2129.06
	35	3640.47
	36	1750.43
STREAM ERROR		0

V-102		
STREAM		**ton/day**
IN	34	2129.06
OUT	53	932.28
	Gas	1196.78
STREAM ERROR		0

V-103		
STREAM		**ton/day**
IN	47	1770.34
OUT	50	634.43
	48	1135.9
STREAM ERROR		0

T-100		
STREAM		**ton/day**
IN	37	4572.75
OUT	41	2309.98
	38	2262.76
STREAM ERROR		0

T-101

STREAM		ton/day
IN	39	2262.76
OUT	44	603.1
	40	1659.67
STREAM ERROR		0

T-102

STREAM		ton/day
IN	40	1659.67
OUT	43	36.25
	CO_2	1623.42
STREAM ERROR		0

T-103

STREAM		ton/day
IN	41	2309.99
OUT	45	61.13
	42	2248.86
STREAM ERROR		0

T-104

STREAM		ton/day
IN	46	1811.56
OUT	Water.out	1238.
	Methanol	573.56
STREAM ERROR		0

TOTAL MASS BALANCE

STREAM		ton/day
IN	NG	3019.76
	Water	3242.72
	Oxygen	4992
OUT	DME	2888.2
	48	1135.9
	CO_2	1623.42
	Water.out	1238.
	18	4368.7
STREAM ERROR		0.002%

- Energy balance for the direct method

It is also important to control that the energy balances from the flowsheet in Unisim is correct. The energy balances are correct when the follow equation F.2 below:

$$Energy_{in} - Energy_{out} = 0 \tag{F.2}$$

Below gives an overwiev over the energy streams coming in and out for the total process

TOTAL ENERGY BALANCE			
IN			
STREAM		KJ/h	MW
IN	**Q-102**	518633.1969	0.144065
IN	**Q-103**	0	0
IN	**Q-104**	0	0
IN	**Q-105**	178212995,8	49,50361
IN	**Q-106**	40569260.34	11.26924
IN	**Q-107**	-1122281319,44	-311,7448
IN	**Q-108**	1607271.638	0.446464
IN	**Q-109**	315827.2245	0.08773
IN	**Q-110**	696036.8196	0.193344
IN	**Q-111**	-8.38E-07	-2.3E-13
IN	**Q-112**	133420845.6	37.06135
IN	**Q-113**	-194142936	-53.9286
IN	**Q-114**	-194142936	-53.9286
IN	**Q-115**	-194142936	-53.9286
IN	**Q-116**	-350765795	-97.4349
IN	**Q-117**	-18664380.9	-5.18455
IN	**Q-120**	58211887.8	16.16997
IN	**Q-122**	26060870.22	7.239131
IN	**Q-124**	2894420.543	0.804006
IN	**Q-126**	31539077.88	8.760855
IN	**Q-128**	2159905444	599.9737
IN	**Q-129**	-39313815.4	-10.9205
IN	**Q-130**	47072878.81	13.0758
IN	**13**	-1944511269	-540.142
IN	**16**	-1304391451	-362.331
IN	**19**	-4387680450	-1218.8
IN	**21**	-1720478069	-477.911
IN	**22**	-649848844.2	-180.514
IN	**NG**	-568412498.5	-157.892
IN	**Water**	-2141996179	-594.999
IN	**Oxygen**	3203961.418	0.889989

TOTAL ENERGY BALANCE			
OUT			
STREAM		KJ/h	MW
OUT	**Q-101**	10295538.36	2.859872
OUT	**Q-118**	30229652.11	8.397126
OUT	**Q-119**	1569170.143	0.435881
OUT	**Q-121**	3388405.375	0.941224
OUT	**Q-123**	3517547.635	0.977097
OUT	**Q-125**	6853537.768	1.90376
OUT	**Q-127**	2064154384	573.3762
OUT	**18**	-2866242405	-796.178
OUT	**25**	-2157410065	-599.281
OUT	**32**	-819356302.8	-227.599
OUT	**48**	-375258090.4	-104.238
OUT	**DME**	-2141996179	-594.999
OUT	**HPS**	-1543279817	-428.689
OUT	**MPS**	-1033415971	-287.06
OUT	**LPS**	-3609663120	-1002.68
OUT	**Gas**	-398484813.2	-110.69
OUT	**CO_2**	-606142681.9	-168.373
OUT	**Water.out**	-767461818.3	-213.184

Mass and Energy balance for the indirect method

- Mass balance

Below gives an overwiev over the mass streams coming in and out for the total process

R-101		
STREAM		**ton/day**
IN	6	5602.37856
OUT	7	5602.39704
STREAM ERROR		0.0003%

T-100		
STREAM		**ton/day**
IN	9	5602.39704
OUT	10	2722.32936
	DME	2880.0672
STREAM ERROR		0

T-101		
STREAM		**ton/day**
IN	12	2722.32936
OUT	13	1489.4868
	14	1232.84232
STREAM ERROR		0

TEE-100		
STREAM		**ton/day**
IN	16	1491.92832
OUT	17	1447.17048
	18	44.76
STREAM ERROR		0.0001%

TOTAL MASS BALANCE		
STREAM		**ton/day**
IN	Methanol	4155.20808
OUT	DME	2880.0672
	Water	1232.84232
	18	44.76
STREAM ERROR		0.004%

- Energy balance

Below gives an overwiev over the energy streams coming in and out for the total process

TOTAL ENERGY BALANCE			
STREAM		KJ/h	MW
IN	**Q-101**	531668.5246	0.147686
IN	**Q-102**	201571100.6	55.99197
	Q-103	0	0
OUT	**Q-104**	7527602195	2091.001
IN	**Q-105**	7309172577	2030.326
OUT	**Q-106**	17849461.63	4.958184
OUT	**Q-107**	2055394.708	0.570943
IN	**Q-108**	105903045.3	29.41751
IN	**Q-109**	9132653.055	2.536848
	2	-1344307593	-373.419
	3	-1322446221	-367.346
	4	-1236625378	-343.507
	5	-1770554572	-491.821
	6	-1568983471	-435.829
	7	-1568999039	-435.833
	8	-1654819882	-459.672
	9	-1654819882	-459.672
	10	-1393417926	-387.061
	11	-1393417926	-387.061
	12	-1411267387	-392.019
	13	-558692496.6	-155.192
	14	-748727650.6	-207.98
	15	-559575120.9	-155.438
	16	-550442467.8	-152.901
	17	-533929193.8	-148.314
OUT	**18**	-16513274.04	-4.58702
OUT	**DME**	-479859335.3	-133.294
OUT	**Water**	-770589022.2	-214.053
IN	**Methanol**	-1344839261	-373.566

APPENDIX G - **Major equipment cost-direct method**

Vessels	V [m3]	K1	K2	K3	logCP,0	CP,0 [$]	D [m]			P [barg]		Fp,vessel	Fm	B	B2	FBM	Cbm [$]
V-100 Separator 1 (PV, vertical, SS)	91.2	3.4974	0.4485	0.1074	4.78904	61523.83	2.7			29		8.3	3.1	0	1		1588667
V-101 Separator 2 (PV, vertical, SS)	73.7	3.4974	0.4485	0.1074	4.70971	51251.89	2.2			29		6.8	3.1	0	1		1085268
V-102 Separator 3 (PV, vertical, SS)	38.0	3.4974	0.4485	0.1074	4.47415	29795.65	1.1			29		3.8	3.1	0	1		347675
V-103 Separator 4 (PV, vertical, SS)	16.4	3.4974	0.4485	0.1074	4.20076	15876.81	0.5			29		1.9	3.1	0	1		93907
Pumps	Shaft power [kW]	K1	K2	K3	logCP,0	CP,0 [$]	C1	C2	C3	P [barg]	logFp	Fp	Fm	B1	B2	FBM	Cbm [$]
P-1 (Centrifugal, ED, SS)	156.4	3.3892	0.0536	0.1538	4.24731	17672.9	-0.3935	0.3957	-0.00226	29	0.18034	1.5	2.25	0	1	1	60232
P-100 (HPS) (Centrifugal, ED, SS)	458.4	3.3892	0.0536	0.1538	4.62109	41791.6	-0.3935	0.3957	-0.00226	99	0.38717	2.4	2.25	0	1	1	229321
P-101 (MPS) (Centrifugal, ED, SS)	88.3	3.3892	0.0536	0.1538	4.07584	11908.1	-0.3935	0.3957	-0.00226	29	0.18034	1.5	2.25	0	1	1	40585
P-102 (LPS) (Centrifugal, ED, SS)	183.0	3.3892	0.0536	0.1538	4.29772	19848.2	-0.3935	0.3957	-0.00226	19	0.10881	1.3	2.25	0	1	1	57373
Turbins	Shaft power [kW]	K1	K2	K3	logCP,0	CP,0 [$]	C1	C2	C3	P [barg]	logFp	Fp	Fm	B1	B2	FBM	Cbm [$]
K-1 (Axial gas tubine, SS)	2859.9	-21.77	13.218	-1.528	5.66126	458417.1	0	0	0	29	0	1.0				1	458417.1
Heat exchangers	A [m2]	K1	K2	K3	logCP,0	CP,0 [$]	C1	C2	C3	P [barg]	logFp	Fp	Fm	B1	B2	FBM	Cbm [$]
E-108 (FH, S&T, SS)	1885	4.8306	-0.8509	0.3187	5.46254	290097.7	0.03881	-0.1127	0.08183	99	0.13975	1.4	2.8	0	1	1	1120617
E-101 (FH, S&T, SS)	1150	4.8306	-0.8509	0.3187	5.21179	162851.9	0.03881	-0.1127	0.08183	29	0.04897	1.1	2.8	0	1	1	510413
E-107 (FH, S&T, SS)	1050	4.8306	-0.8509	0.3187	5.16883	147513.3	0.03881	-0.1127	0.08183	29	0.04897	1.1	2.8	0	1	1	462339
E-103 (FH, S&T, SS)	447	4.8306	-0.8509	0.3187	4.81404	65169.37	0.03881	-0.1127	0.08183	29	0.04897	1.1	2.8	0	1	1	204255
E-105 (MPS) (FH, S&T, SS)	122	4.8306	-0.8509	0.3187	4.44258	27706.7	0.03881	-0.1127	0.08183	29	0.04897	1.1	2.8	0	1	1	86839
E-106 (LPS) (FH, S&T, SS)	975	4.8306	-0.8509	0.3187	5.13457	136323	0.03881	-0.1127	0.08183	29	0.04897	1.1	2.8	0	1	1	427266
E-104 (HPS) (FH, S&T, SS)	143	4.8306	-0.8509	0.3187	4.47714	30001.08	0.03881	-0.1127	0.08183	99	0.13975	1.4	2.8	0	1	1	115891
E-109 (FH, S&T, SS)	35	4.8306	-0.8509	0.3187	4.27658	18905.14	0.03881	-0.1127	0.08183	29	0.04897	1.1	2.8	0	1	1	59253

Continue - Major equipment cost-direct method

Heat exchangers	A [m2]	K1	K2	K3	logCP,0	CP,0 [$]	C1	C2	C3	P [barg]	logFp	Fp	Fm	B1	B2	FBM	Cbm [$]
Heat exchanger ATR (FH, S&T, SS)	2000	4,8306	-0,8509	0,3187	5,49456	312293,8	0,03881	-0,1127	0,08183	29	0,04897	1,1	2,8	0	1	1	978796
Heat exchanger FBR-1 (FH, S&T, SS)	1500	4,8306	-0,8509	0,3187	5,34297	220276,4	0,03881	-0,1127	0,08183	29	0,04897	1,1	2,8	0	1	1	690394
Heat exchanger FBR-2 (FH, S&T, SS)	1500	4,8306	-0,8509	0,3187	5,34297	220276,4	0,03881	-0,1127	0,08183	29	0,04897	1,1	2,8	0	1	1	690394
Heat exchanger FBR-3 (FH, S&T, SS)	1500	4,8306	-0,8509	0,3187	5,34297	220276,4	0,03881	-0,1127	0,08183	29	0,04897	1,1	2,8	0	1	1	690394
E-108 (FH, S&T, SS)	1067	4,8306	-0,8509	0,3187	5,17634	150087,2	0,03881	-0,1127	0,08183	29	0,04897	1,1	2,8	0	1	1	470406
Fired Heater	**Q [m3]**	**K1**	**K2**	**K3**	**logCP,0**	**CP,0 [$]**	**C1**	**C2**	**C3**	**P [barg]**	**logFp**	**Fp**	**FBM**	**B1**	**B2**	**FT**	**Cbm [$]**
Pre-reformer (Reformer furnace, SS)	454722	3,068	0,6597	0,0194	7,42141	26388271	0,1405	-0,2698	0,1293	29	0,02247	1,1	2,8			1	77810102,8
E-102 (Non-reactive fired heater, SS)	24272	7,3488	-1,1666	0,2028	6,13281	1357720	0,1347	-0,2368	0,1021	29	0,00676	1,0	2,8			1	3861216,19
Reactor vessels	**V [m3]**	**K1**	**K2**	**K3**	**logCP,0**	**CP,0 [$]**	**D [m]**			**P [barg]**		**Fp,vessel**	**Fm**	**B1**	**B2**	**FBM**	**Cbm [$]**
FBR-100 (PV, vertical, SS)	2400	3,4974	0,4485	0,1074	6,24056	1740038	4			29		11,9	3,1	0	1		64442904
FBR-101 (PV, vertical, SS)	2400	3,4974	0,4485	0,1074	6,24056	1740038	4			29		11,9	3,1	0	1		64442904
FBR-102 (PV, vertical, SS)	2400	3,4974	0,4485	0,1074	6,24056	1740038	4			29		11,9	3,1	0	1		64442904
ATR (PV, vertical, SS)	434,2	3,4974	0,4485	0,1074	5,42763	267691,5	4			29		11,9	3,1	0	1		9914047
PRE- E&C (PV, vertical, SS)	460,9	3,4974	0,4485	0,1074	5,45401	284452,1	4			29		11,9	3,1	0	1		10534784
Towers	**V [m3]**	**K1**	**K2**	**K3**	**logCP,0**	**CP,0 [$]**	**D [m]**	**Nid [tray]**	**Nac [tray]**	**P [barg]**		**Fp,vessel**	**Fm**	**B1**	**B2**	**FBM**	**Cbm [$]**
T-104 (tray and packed) N = 10+2	25,3	3,4974	0,4485	0,1074	4,33776	21765	1,5	12	24	29,00		4,8	3,1	1	1		345128
T-101 (tray and packed) N = 30+2	64,1	3,4974	0,4485	0,1074	4,65868	45569,76	1,5	32	64	29,00		4,8	3,1	1	1		722600
T-100 (tray and packed) N = 40+2	83,6	3,4974	0,4485	0,1074	4,75628	57052,72	1,5	42	84	29,00		4,8	3,1	1	1		904685
T-102 (tray and packed) N = 30+2	64,1	3,4974	0,4485	0,1074	4,65868	45569,76	1,5	32	64	29,00		4,8	3,1	1	1		722600
T-103 (tray and packed) N = 30+2	64,1	3,4974	0,4485	0,1074	4,65868	45569,76	1,5	32	64	29,00		4,8	3,1	1	1		722600

Continue - Major equipment cost-direct method

Tower trays		Area/tray [m2]	K1	K2	K3	logCP,0	CP,0 [$]	D [m]	Nid [tray]	Nac [tray]	P [barg]		Fq	Fm	B1	B2	FBM	Cbm [$]
T-104 (ST, SS) N = 10+2		1,8	2,9949	0,4465	0,3961	3,12938	1347,053	1,5	12	24	29,00		1	1,7			1	16165
T-101 (ST, SS) N = 30+2		1,8	2,9949	0,4465	0,3961	3,12938	1347,053	1,5	32	64	29,00		1	1,7			1	43106
T-100 (ST, SS) N = 40+2		1,8	2,9949	0,4465	0,3961	3,12938	1347,053	1,5	42	84	29,00		1	1,7			1	56576
T-102 (ST, SS) N = 30+2		1,8	2,9949	0,4465	0,3961	3,12938	1347,053	1,5	32	64	29,00		1	1,7			1	43106
T-103 (ST, SS) N = 30+2		1,8	2,9949	0,4465	0,3961	3,12938	1347,053	1,5	32	64	29,00		1	1,7			1	43106
Storage tanks	Flow [m3/h]	V [m3]	K1	K2	K3	logCP,0	CP,0 [$]	C1	C2	C3	P [barg]	logFp	Fp	Fm	B1	B2	FBM	Cbm [$]
NG (API fixed roof, SS)	411	1382	4,8509	-0,3973	0,1445	5,0284	106757,4	0	0	0	29	0	1	3,1	0	1		330948
Oxygen (API fixed roof, SS)	183	614	4,8509	-0,3973	0,1445	4,86655	73543,9	0	0	0	29	0	1	3,1	0	1		227986
CO2 (API fixed roof, SS)	83,9	282	4,8509	-0,3973	0,1445	4,74491	55578,6	0	0	0	29	0	1	3,1	0	1		172294
DME (API fixed roof, SS)	164	549	4,8509	-0,3973	0,1445	4,84709	70321,8	0	0	0	29	0	1	3,1	0	1		217997
H2 (API fixed roof, SS)	124	416	4,8509	-0,3973	0,1445	4,80167	63338,5	0	0	0	29	0	1	3,1	0	1		196349
Gas recycle (API fixed roof, SS)	9	31	4,8509	-0,3973	0,1445	4,57979	38000,2	0	0	0	29	0	1	3,1	0	1		117801
TOTAL$_{2001}$			I$_{2001}$	397										**310800606**				
TOTAL$_{2008}$			I$_{2008}$	575,4										**450465160**				

Major equipment cost-indirect method

Pumps		**Q [kW]**	**K1**	**K2**	**K3**	**logCP,0**	**CP,0 [$]**	**C1**	**C2**	**C3**	**P [barg]**	**logFp**	**Fp**	**Fm**			**Cbm 2001 [$]**	**I 2001**	**I 2008**	**Cbm 2001 [$]**
P-100 (Centrifugal/electric drive, SS)		147,7	3,3892	0,0536	0,1538	4,2293	16954	-0,394	0,3957	-0,00226	15,5	0,0743	1,2	2,15			43253	397,0	575,4	62689
Heat exchangers		**A [m2]**	**K1**	**K2**	**K3**	**logCP,0**	**CP,0 [$]**	**C1**	**C2**	**C3**	**P [barg]**	**logFp**	**Fp**	**Fm**			**Cbm 2001 [$]**			
E-101(floating head, shell and tube, SS)		1032	4,8306	-0,851	0,3187	5,1608	144803	0,0388	-0,113	0,0818	15,3	0,0201	1,05	2,8			424674	397,0	575,4	615510
E-102 (floating head, shell and tube, SS)		1122	4,8306	-0,851	0,3187	5,2001	158509	0,0388	-0,113	0,0818	13,9	0,0169	1,04	2,8			461414	397,0	575,4	668760
E-103 (floating head, shell and tube, SS)		1200	4,8306	-0,851	0,3187	5,2322	170700	0,0388	-0,113	0,0818	13,9	0,0169	1,04	2,8			496901	397,0	575,4	720194
E-104 (floating head, shell and tube, SS)		1530	4,8306	-0,851	0,3187	5,3531	225468	0,0388	-0,113	0,0818	13,9	0,0169	1,04	2,8			656328	397,0	575,4	951263
Reactor	**Flow [m3/h]**	**V [m3]**	**K1**	**K2**	**K3**	**logCP,0**	**CP,0 [$]**	**C1**	**C2**	**C3**	**P [barg]**	**D**	**Fp**	**Fm**			**Cbm 2001 [$]**			
CRV-101 (Process vessels, vertical, SS)	303,1	151,5	3,4974	0,4485	0,1074	4,9860	96831	0	0	0	15,1	2,52	4,3	3,1			1301712	397,0	575,4	1886663
Towers		**V [m3]**	**K1**	**K2**	**K3**	**logCP,0**	**CP,0 [$]**	**C1**	**C2**	**C3**	**P [barg]**	**D**	**Fp**	**Fm**	**Nid**	**Nact**	**Cbm 2001 [$]**			
T-100 (25 SS sieve trays plus reboiler and condenser)		50,54	3,4974	0,4485	0,1074	4,5732	37428	0	0	0	7,6	1,5	1,7	3,1	25	50	198620	397,0	575,4	287873
T-101 (20 SS sieve trays plus reboiler and condenser)		40,82	3,4974	0,4485	0,1074	4,4986	31519	0	0	0	10,5	1,5	2,1	3,1	20	40	207520	397,0	575,4	300773
Trays in towers		**A [m2]**	**K1**	**K2**	**K3**	**logCP,0**	**CP,0 [$]**	**C1**	**C2**	**C3**	**P [barg]**	**logFp**	**Fp**	**Fm**	**N**	**Fq**	**Cbm 2001 [$]**			
Trays for T-100 (25 SS trays)		1,7671	2,9949	0,4465	0,3965	3,1296	1348	-	-	-	-	-	-	1,7	25	1	57272	397,0	575,4	83008
Trays for T-101 (20 SS trays)		1,7671	2,9949	0,4465	0,3965	3,1296	1348	-	-	-	-	-	-	1,7	20	1	45817	397,0	575,4	66406
Compressors		**V [kW]**	**K1**	**K2**	**K3**	**logCP,0**	**CP,0 [$]**	**C1**	**C2**	**C3**	**P [barg]**	**logFp**	**Fp**	**Fm**			**Cbm 2001 [$]**			
K-100 (centrifugal, SS)		2536,8	2,2897	1,3604	-0,103	5,7307	537885	0	0	0	15,5	0	1,0	-			537885	397,0	575,4	779594
Storage tanks	**Flow [m3/h]**	**V [m3]**	**K1**	**K2**	**K3**	**logCP,0**	**CP,0 [$]**	**C1**	**C2**	**C3**	**P [barg]**	**logFp**	**Fp**	**Fm**			**Cbm 2001 [$]**			
methanol (API fixed roof, SS)	220,0	739	4,8509	-0,397	0,1445	4,9003	79496	0	0	0	29	0,0	1,0	3,1			246439	397,0	575,4	357181
Water (API fixed roof, SS)	54,1	182	-	-	-	-	-	-	-	-		-	-	-			106168	397,0	575,4	153877
DME(API fixed roof, SS)	178,9	601	4,8509	-0,397	0,1445	4,8628	72906	0	0	0	29	0,0	1	3,1			226008	397,0	575,4	327570
Total equipment cost																	**4966757**			**7261360**

APPENDIX H

Basis and operating cost for the DME-direct method(Richard Turton, 2009)

1$ = 5,626 NOK	Capacity	unit	Price	Unit	cost at full production capacity	unit
Basis						
Fixed capital cost			*2 057 000 000*	[$]		
Working capital			*61 710 000*	[$]		
Production capacity	1054120	[tonne/ yr]				
Sales revenue for DME			948	[$/tonne]	9,99E+08	[$/yr]
Sales revenue for HPS	622398	[tonne/yr]	30	[$/tonne]	18671940	[$/yr]
Sales revenue for LPS	2424768	[tonne/yr]	30	[$/tonne]	72743040	[$/yr]
Sales revenue for Hydrogen	719800	[kg/yr]	3,87	[$/kg]	2785626	[$/yr]
Sales revenue total					**1094**	[M$/yr]
1. Manufactoring cost						
raw materials						
Natural gas	1012656	[tonne/yr]	225	[$/tonne]	2,28E+08	[$/yr]
Oxygen	182208	[tonne/yr]	190	[$ pr yr/tonne]	34564858	[$/yr]
catalyst						
NiO						
Ruthenium	1383391	[kg]	18	[$/kg]	6225260	[$/yr]
Cu-ZnO-Al2O3	2416974	[kg]	18	[$/kg]	10876383	[$/yr]
	6423300	[kg]	18	[$/kg]	28904850	[$/yr]
Utilities						
Cost for stream (MPS)	1775177	[tonne/yr]	30	[$/tonne]	53255310	[$/yr]
Natural gas for heaters	1513202	[GJ/yr]	11	[$/GJ]	18662825	[$/yr]
Cooling water	2847481	[GJ/yr]	0,354	[$/GJ]	1008008	[$/yr]
Electricalpower	53325	[kW]	0,06	[$/kWh]	31141800	[$/yr]
product cost						
Packaging per tonne DME			11	[$/tonne DME]	11384496	[$/yr]
Packing and storage			11	[$/tonne DME]	11384496	[$/yr]
Royalties 5 % of sales revenue for DME					49965288	[$/yr]
Total manufactoring cost					**485**	[M$/yr]
2. Fixed cost						
Annual maintenance: 5% of fixed capital cost			102850000	[$/yr]		
Salary, incl. social expences			51546	[$/yr]		
Operators: 5.5 shifts à 174 operators			49329522	[$/yr]		
Foremen and daymen: 50 % of operator cost			24664761	[$/yr]		
Laboratory cost: 20 % of operator cost			9865904	[$/yr]		
Administration			98659044	[$/yr]		
sales cost			0	[$/yr]		
Total fixed costs			**285**	[M$/yr]		
Operating costs			**771**	[M$/yr]		

Basis and operating cost for the DME-indirect method(Richard Turton, 2009)

1$ = 5,626 NOK	Capacity	unit	Price	Unit	cost at full production capacity	unit
Basis						
Fixed capital cost			*33 000 000*	[$]		
Working capital			*990 000*	[$]		
Production capacity	1022000	[tonne/ yr]				
Sales revenue for DME			948	[$/tonne]	969	[M$/yr]
Sales revenue for electrical power	29148	[kW]	0,06	[$/kWh]	17	[M$/yr]
Sales revenue total					**986**	[M$/yr]
1. Manufactoring cost						
raw materials						
methanol	1516651	[tonne/ yr]	294	[$/tonne]	445895394,00	[$/yr]
catalyst(Amorphous alumina catalyst)	2461274	[kg]	18	[$/kg]	10934209,75	[$/yr]
product cost						
Packaging per tonne DME			11	[$/tonne DME]	11037600,00	[$/yr]
Packing and storage			11	[$/tonne DME]	11037600,00	[$/yr]
Royalties 5 % of sales revenue for DME			47	[$/tonne DME]	48442800,00	[$/yr]
Total manufactoring cost					**527,35**	[M$/yr]
2. Fixed cost						
Annual maintenance: 5% of fixed capital cost			1650000	[$/yr]		
Salary, incl. social expences			51546	[$/yr]		
Operators: 5.5 shifts à 31 operators			8788593	[$/yr]		
Foremen and daymen: 50 % of operator cost			4394297	[$/yr]		
Laboratory cost: 20 % of operator cost			1757719	[$/yr]		
Administration			17577186	[$/yr]		
sales cost			9690000	[$/yr]		
Total fixed costs			**44**	[M$/yr]		
Operating costs			***571***	[M$/yr]		

APPENDIX I

Direct method Year →	Basic data	-1	0	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**	**15**	
Fixed capital cost	2 057																		
Working capital	62																		
Alt 1: Fixed rate of depreciation, 10 %	0	*The fixed rate of depreciation is 10, and the reducing balance rate is 0*																	
Alt 2: Reducing balance method of depreciation 20 %	20	*The fixed rate of depreciation is 0, and the reducing balance rate is 20*																	
Depreciation factor, reducing balance method		a*(1-a)^(i-1)		0.2	0.1600	0.1280	0.1024	0.0819	0.0655	0.0524	0.0419	0.0336	0.0268	0.0215	0.0172	0.0137	0.0110	0.0088	
Fixed capital cost			-2057																
Working capital			-61.71																
Recovered working capital													61.71						
Annual sales revenue	1 094			1094	1094	1094	1094	1094	1094	1094	1094	1094	1094	1094	1094	1094	1094	1094	
Annual operating cost	771			771	771	771	771	771	771	771	771	771	771	771	771	771	771	771	
Gross operating profit				323	323	323	323	323	323	323	323	323	323	323	323	323	323	323	
Depreciation				411	329	263	211	169	135	108	86	69	55	44	35	28	23	18	
Profit before tax				-88	-6	60	112	154	188	215	237	254	268	279	288	295	300	305	
Tax. precentage = 28%	28			0	0	17	31	43	53	60	66	71	75	78	81	83	84	85	
Net profit				-88	-6	43	81	111	135	155	170	183	193	201	207	212	216	220	
Depreciation				411	329	263	211	169	135	108	86	69	55	44	35	28	23	18	
Net cash flow (NFW)			-2057.00	323	323	306	292	280	270	263	257	252	248	245	242	240	239	238	NFW
Cumulative net cash flow		0	-2118.71	-1796	-1473	-1166	-875	-595	-325	-62	195	447	756	1001	1244	1484	1723	1961	
Rent of interest(%)/Discount factor	10.00		1.00	0.91	0.83	0.75	0.68	0.62	0.56	0.51	0.47	0.42	0.39	0.35	0.32	0.29	0.26	0.24	
Discounted net cash flow		0	-2057	294	267	230	199	174	153	135	120	107	96	86	77	70	63	57	68.7
Internal rate of return		0	-2057.00	-1763.36	-1496.42	-1266.31	-1067.18	-893.48	-740.90	-606.07	-486.31	-379.48	-283.86	-198.01	-120.76	-51.10	11.81	68.69	
Net present worth (NPW)	**68.69101**																		

Indirect method Year →	Basic data	-1	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	
Fixed capital cost	33																		
Working capital	1																		
Alt 1: Fixed rate of depreciation, 10 %	0	*The fixed rate of depreciation is 10, and the reducing balance rate is 0*																	
Alt 2: Reducing balance method of depreciation 20 %	20	*The fixed rate of depreciation is 0, and the reducing balance rate is 20*																	
Depreciation factor, reducing balance method		a*(1-a)^(i-1)		0,2	0,1600	0,1280	0,1024	0,0819	0,0655	0,0524	0,0419	0,0336	0,0268	0,0215	0,0172	0,0137	0,0110	0,0088	
Fixed capital cost			-33																
Working capital			-0,99																
Recovered working capital													0,99						
Annual sales revenue	986			986	986	986	986	986	986	986	986	986	986	986	986	986	986	986	
Annual operating cost	571			571	571	571	571	571	571	571	571	571	571	571	571	571	571	571	
Gross operating profit				415	415	415	415	415	415	415	415	415	415	415	415	415	415	415	
Depreciation				7	5	4	3	3	2	2	1	1	1	1	1	0	0	0	
Profit before tax				408	410	411	412	412	413	413	414	414	414	414	414	415	415	415	
Tax, precentage = 28%	28			114	115	115	115	115	116	116	116	116	116	116	116	116	116	116	
Net profit				294	295	296	296	297	297	298	298	298	298	298	298	298	299	299	
Depreciation				7	5	4	3	3	2	2	1	1	1	1	1	0	0	0	
Net cash flow (NFW)			-33,00	301	300	300	300	300	299	299	299	299	299	299	299	299	299	**299**	**NFW**
Cumulative net cash flow		0	-33,99	267	567	867	1167	1466	1766	2065	2364	2663	2963	3262	3561	3860	4159	4458	
Rent of interest(%)/Discount factor	10,00		1,00	0,91	0,83	0,75	0,68	0,62	0,56	0,51	0,47	0,42	0,39	0,35	0,32	0,29	0,26	0,24	
Discounted net cash flow		0	-33	273	248	225	205	186	169	154	140	127	115	105	95	87	79	72	2245,8
Internal rate of return		0	-33,00	240,32	488,48	713,86	918,59	1104,59	1273,60	1427,18	1566,75	1693,61	1808,90	1913,70	2008,96	2095,54	2174,25	2245,80	
Net present worth (NPW)	**2245,805**																		

APPENDIX J

Profitability analysis

ROI (Return on investment)

Determining projects profitability implies also to evaluate the investment by comparing the magnitude and timing of expected gains to the investment cost. ROI can be improved by reducing cost and increasing gains. Return on investment refers to how much money you get back per invested dollar. The equation J.1 below shows how ROI was calculated.

$$\text{ROI} = \frac{\text{sales revenue - operating costs}}{\text{Total investment}} \tag{J.1}$$

If an investment does not have a positive ROI, or if there are other opportunities with a higher ROI, then the investment should be rejected.

Payback time

Payback time is a useful criterion for judging the profitability of projects with a short lifetime. It defines the time required after the start of the project to pay off the initial investment from income. Calculation of payback time is shown in eqn J.2:

$$T = \frac{Investment}{(\text{Sales revenue - Operating cost}) \cdot (1 - s) + Depreciation \cdot s} \tag{J.2}$$

Where s is the tax rate of 28% of the taxable income. The depreciation is given below in eqn.J.3:

$$\text{Depreciation} = \text{C}_0\text{a} \cdot \left(1 - \text{a}\right)^{\text{n}-1} \tag{J.3}$$

Where a is declining balance rate of 20 % p.a. for the not discounted capital, C_0 is the investment and n is the lifetime of the plant.

NFW (Net future worth)

Net Future worth (NFW) is the total future worth of all cash flows for n years. Net Future Worth is an estimate of what the investment cost will be in the future. A positive Net Future Worth indicates a profitable investment. However, given that future cash flows are estimates, the NFW is only as accurate as the estimated future cash flows.

The future value of an investment after n years is given in equation J.4:

$$NFW = (\text{Present worth}) \cdot (1+i)^n \tag{J.4}$$

Where i is the annual interest rate.

NPW (Net Present Worth)

Net present worth is the future worth of the net cash flow in year, n. The money earned in any year can be put to work (reinvested) as soon as it is available and start to earn a return. Money earned in the early years of the project is more valuable than that earned in later years. The net cash flow in each year of the project is brought into its "present worth" at the start of the project by discounting it at some chosen compound interest rate. The total NPW of project is given in equation J.5:

$$\text{Total NPW of a project} = \sum_{n=1}^{n=t} \frac{NFW}{(1+r)^n} \tag{J.5}$$

Where r is the discount rate.

DCFRR (Discounted cash flow rate of return)

The discounted cash flow analysis, that we used to calculate the present worth of future earnings, is sensitive to the interest rate assumed. By calculating the NPW for various interest rates, it is possible to find an interest rate at which the cumulative net present worth at the end of the project is zero. This particular rate is called the "discounted cash flow rate of return" and is a measure of the maximum rate that the project could pay and still breakeven by the end of the project life.

$$\sum_{n=1}^{n=t} \frac{NFW}{(1+r')^n} = 0 \tag{J.6}$$

Where r' is the discounted cash flow rate of return, NFW is the future worth of net cash flow in year n, and t is the life time of the project.