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Techno-economic comparison between Dimethyl-ether and Methanol synthesis processes

TESI DI LAUREA MAGISTRALE IN
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INGEGNERIA CHIMICA

Author: **Eleonora Alberghina**

Student ID: 10636405
Advisor: Flavio Manenti
Co-advisor: Kristiano Prifti, Matteo Fedeli
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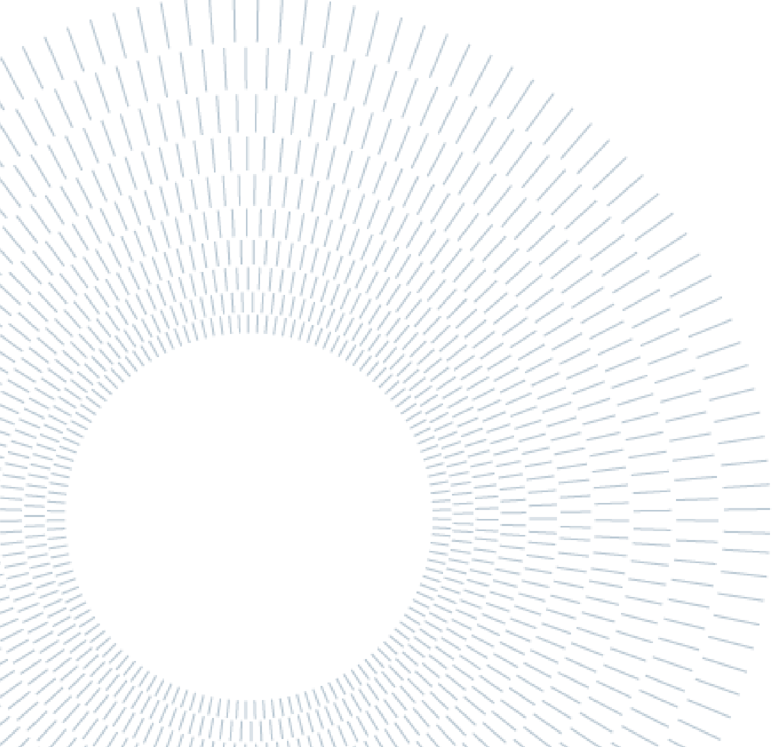


Abstract

The proposed M.Sc. thesis work investigates the more profitable way to exploit a syngas stream produced from renewable sources, which is a very important topic considering the urgent climate crisis. The chemical industry is one of the main contributors of the greenhouse emissions and needs to be redesigned including concepts like the circular economy and the waste-to-product.

The first alternative analyzed is methanol production and direct sale; the second possibility consist, instead, in the production of methanol and successive use within the plant to produce a more valuable chemical: dimethyl-ether (DME).

The engineering study conducted throughout steady-state simulations implemented on Aspen HYSYS, is then accompanied by an economic assessment of these two process alternatives, in order to determine which is the best economic choice.

Biogas has been assumed as feedstock to produce syngas.

Dimethyl-ether is produced in a two-steps process: methanol production from syngas then followed by methanol dehydration. Therefore, the first part of the DME plant is equal to the methanol plant, followed by a section for the methanol conversion to dimethyl-ether and successive purification.

Refitted Graaf kinetics set was used for methanol synthesis on CZA catalyst and Bercic and Levec kinetics was studied for methanol dehydration on γ-alumina.

In order to be more comprehensive, the design of the cold and hot utility sections is also performed and included in the following economic appraisal.

This work aims to determine if it is more convenient for small scale plants that can’t exploit economy of scale to manufacture commodities such as methanol or higher value goods like DME that however require bigger investments. Results of simulations confirmed what was expected: since few additional units and utilities are required to convert methanol into DME, the higher costs are completely paid off by the higher revenues.

Considering the same amount of syngas used in the plant, the addition of the dimethyl-ether module to the methanol plant increased the net present value by more than three times after ten years.

Other analyses are conducted in order to understand how the profitability of the two plant alternatives changed according to variation in: size of the plant, cost of the investment, production expenses, production volume and selling price. An analysis on the plant in different markets is also executed. The outcomes of these additional comparisons have not impacted enough the result to affect the more profitability of the dimethyl-ether over the methanol plant.

Key-words: Methanol, Dimethyl-ether, process simulation, economic appraisal.

Abstract in italiano

La seguente tesi indaga il modo più redditizio per sfruttare un flusso di syngas prodotto da fonti rinnovabili, un argomento molto importante considerata l'urgente crisi climatica. L'industria chimica è uno dei principali settori che contribuisce alle emissioni di gas serra e dovrebbe essere riprogettata tenendo conto di concetti come l'economia circolare e il waste-to-product.

La prima alternativa analizzata è la produzione di metanolo e la conseguente vendita diretta; la seconda possibilità consiste, invece, nella produzione di metanolo e nel suo successivo utilizzo all'interno dell'impianto per produrre un composto chimico di maggior valore: il dimetiletere (DME).

Lo studio ingegneristico condotto attraverso simulazioni dello stato stazionario, implementate su Aspen HYSYS, è successivamente accompagnato da una valutazione economica di queste due alternative di processo, al fine di determinare quale sia la migliore scelta da un punto di vista economico.

Come materia prima per la produzione di syngas è stato considerato il biogas.

Il dimetiletere viene prodotto in un processo in due fasi: prima avviene la produzione di metanolo dal syngas e in seguito la disidratazione del metanolo. Pertanto, la prima parte dell'impianto di DME è identico all'impianto del metanolo, dal quale segue una sezione per la conversione del metanolo a dimetiletere e la sua successiva purificazione.

Per la sintesi del metanolo su un catalizzatore CZA è stata utilizzata una versione modificata della cinetica proposta da Graaf, mentre per la disidratazione del metanolo su γ-allumina è stata studiata la cinetica proposta da Bercic e Levec.

Per completezza è stata anche eseguita la progettazione delle sezioni di utenza, sia fredda che calda, che viene inserita, quindi, anche nella seguente analisi economica.

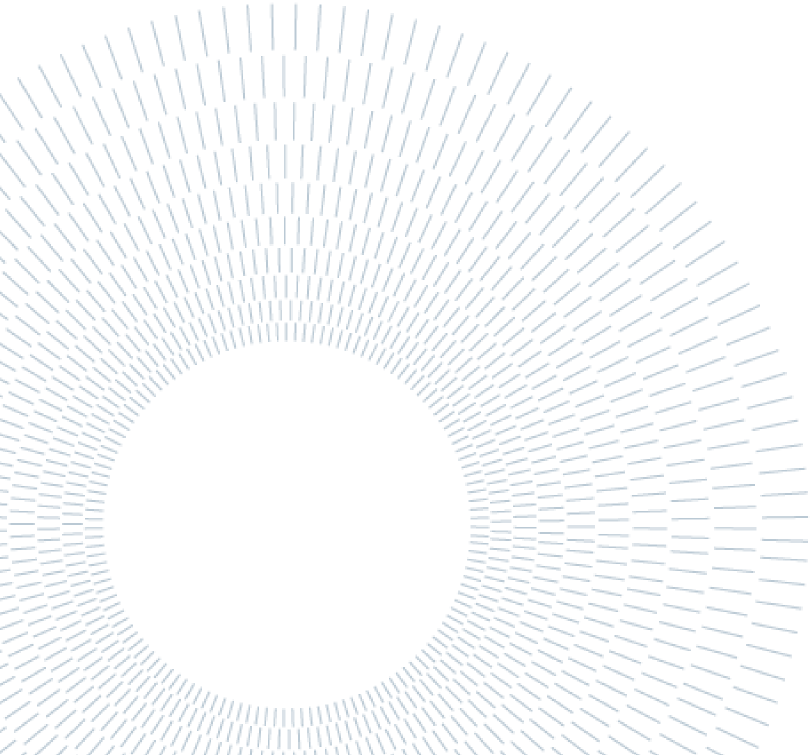
Questo lavoro mira a determinare se sia più conveniente, per impianti di piccola taglia che non possono sfruttare l'economia di scala, produrre metanolo o un composto di valore superiore come il DME, che tuttavia richiede maggiori investimenti.

I risultati delle simulazioni hanno confermato quanto previsto: poiché sono necessarie poche unità e utenze aggiuntive per convertire il metanolo in DME, i maggiori costi sono completamente ripagati dai maggiori ricavi.

A parità di syngas utilizzato nell'impianto, l'aggiunta del modulo del dimetiletere all'impianto del metanolo ha più che triplicato il suo valore attuale netto dopo dieci anni.

Altre analisi sono state condotte per comprendere come la redditività delle due alternative impiantistiche cambi al variare di: dimensione dell'impianto, costo dell'investimento, spese di produzione, volume di produzione e prezzo di vendita. È stata eseguita anche un'analisi sull'impianto in diversi mercati. Gli esiti di questi ulteriori confronti non hanno impattato abbastanza i risultati da compromettere la maggiore redditività dell'impianto del dimetiletere rispetto all'impianto del metanolo.

Parole chiave: Metanolo, dimetiletere, simulazione di processo, valutazione economica.



Contents

Introduction

Global emissions problem

Climate change is one of today's major issues. Greenhouse gases (GHG) are responsible for trapping the sun's energy in the atmosphere. In balanced proportions, heat-trapping gases act like a blanket surrounding Earth, keeping temperatures within a range where life can thrive on a planet with liquid water. Unfortunately, anthropogenic factors are to blame for the accumulation of these gases at increasing concentrations in the atmosphere. Human activities, such as the burning of fossil fuels in cars and power plants, and the deforestation for agriculture or development, are causing global warming. GHGs include carbon dioxide (CO_2), nitrous oxide (N_2O), and methane (CH_4). Even if methane and nitrous oxide are estimated to have Global Warming Potential (GWP) higher than CO_2, carbon dioxide is more abundant and remains in the climate system for much longer. 40% stays in the atmosphere for 100 years, 20% will remain for 1000 years, while the last 10% takes 10,000 years to turn over [1].

Antarctic ice core records clearly illustrate that current atmospheric CO_2 levels are higher than levels recorded over the past 800,000 years. Atmospheric CO_2 levels have increased by 40% between 1750 and 2011. Half of human-related CO_2 emissions have occurred only in the last 40 years. In 2013, atmospheric CO_2 levels exceeded 400 million ppm for the first time in human history [2]. In March 2023 atmospheric CO_2 reaches 421.85 ppm [3].

The severity of the problem was globally recognized with the Paris agreement signed in 2015 by UNFCCC (United Nations Framework Convention on Climate Change), where countries committed to limit the global temperature rise below 2°C with respect to pre-industrial levels and to pursue efforts to limit the temperature increase even below 1.5°C [4].

Figure 0.1 reports the global energy consumption divided by the source. Fossil fuels hegemony goes back to the second industrial revolution; and in the figure it can be seen how fossil fuels (coal, oil and natural gas) continue to dominate the market with 77% of the total. The energy sector is the source of around three-quarters of greenhouse gas emissions; being fossil fuel the most spread energy source it is not a surprise that global carbon dioxide emissions from fossil fuels reached 36.6 Gt of CO_2 emitted in 2022 [5].

In order to reduce global carbon dioxide emissions to net zero by 2050 a complete transformation of how energy is produced, transported and consumed is inevitable. Net zero implies a huge decline in the use of fossil fuels and a switch towards renewable energy. According to International Energy Agency, two-thirds of total energy supply in 2050 will be coming from wind, solar, bioenergy, geothermal and hydro energy and the global energy demand will be around 8% smaller than today, while serving an economy more than twice as big and a population with 2 billion more people [6].

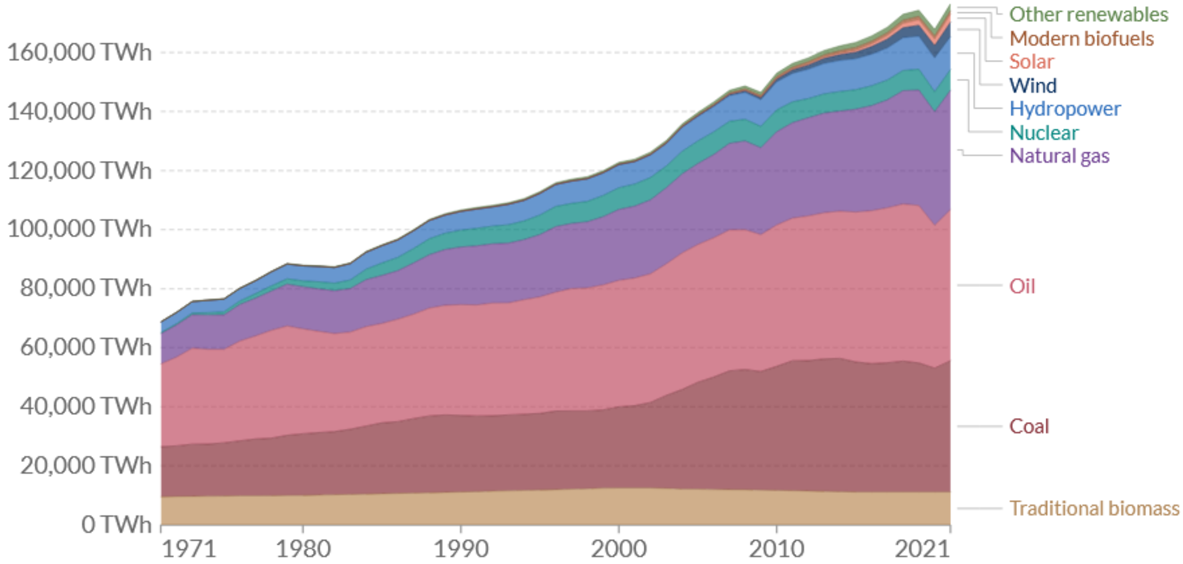


Figure 0.1 Global primary energy consumption by source. Primary energy is calculated based on the 'substitution method' which takes account of the inefficiencies of fossil fuel production by converting non-fossil energy into the energy inputs required if they had the same conversion losses as fossil fuels [7].

Figure 0.2 shows energy consumption of the last decade and its projection for the next years. It divides the consumption of the OECD countries (Organization for Economic Co-operation and Development) and those which are not part of it. It can be seen that non-OECD countries are those which consume more energy now and that they will increase their consumption. It is also visible that the industrial sector is the most energy consuming, and it is estimated that it will be responsible for more than half of the estimated growth. Transportation, instead, represents the second largest GHG emissions sector. Road transport constitutes the highest proportion of overall transport emissions: in 2020 it emitted 77% of all European transport GHGs [8].

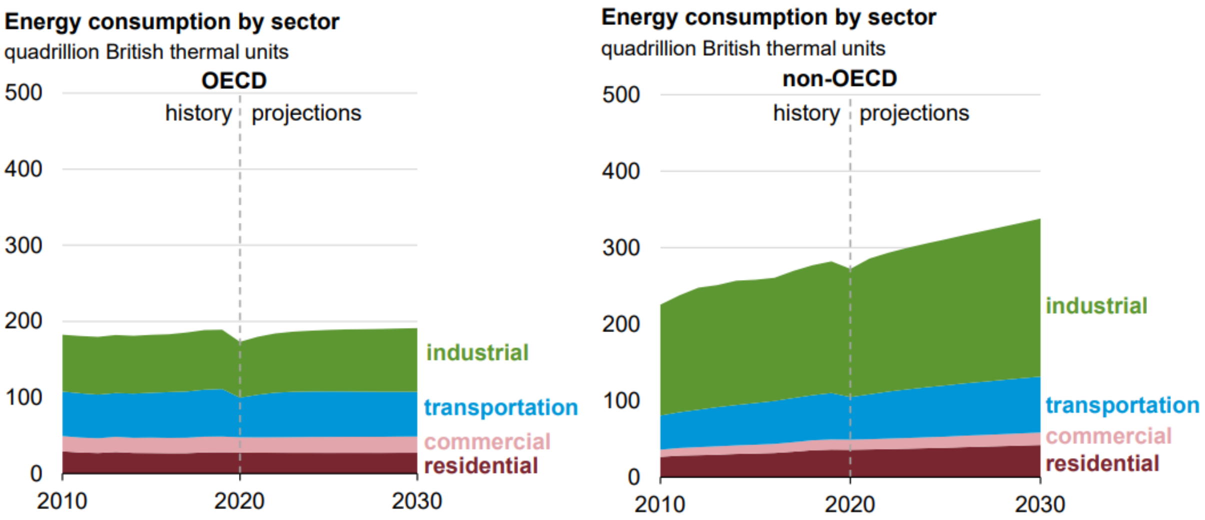


Figure 0.2 Energy consumption forecast by sector for OECD and non-OECD countries [9].

Bioenergy opportunities

To face the presented problem and to reduce fossil fuel dependency, new renewable routes to produce energy and goods must be found.

Bioenergy accounts roughly for one-tenth of world total primary energy supply today. Modern bioenergy is an important source of renewable energy, its contribution to final energy demand across all sectors is five times higher than wind and solar photovoltaic combined, even when the traditional use of biomass is excluded [10].

Key potential biomass feedstocks include forestry and agricultural waste and by-products, biogas from landfill, sewage, municipal solid waste (MSW) and black liquor from the pulp and paper industry [11].

All above presented renewable feedstocks may be used to produce renewable syngas. Syngas is an extremely important building block to produce several chemicals and fuels, such as the two studied in this Thesis: methanol and dimethyl-ether.

In this work the considered feedstock for syngas production is biogas.

Biogas

Biogas is a mixture of methane, CO_2 and small quantities of other gases produced by anaerobic digestion of organic matter in an oxygen-free environment. The composition of biogas depends on the type of feedstock and the production pathway. Methane content typically ranges from 45% to 75% by volume, with most of the remainder being CO_2. This variation means that the energy content of biogas can vary; the lower heating value (LHV) is between 16 and 28 MJ/m^3. Biogas can be used directly as an energy source to produce electricity and heat, or to produce other chemicals. A wide variety of feedstocks can be used to produce biogas, which can be classified according to four categories: crop residues, animal manure, MSW organic fraction (including industrial waste), and wastewater sludge.

During its growth, biomass has captured a certain amount of CO_2 from the atmosphere in order to do photosynthesis. The CO_2 captured is returned to the atmosphere during the combustion of biogas or its derivatives, and then captured again by the newly growing biomass. This implies that the combustion of biogas does not increase the amount of CO_2 present in the atmosphere, but it makes it circulate in short carbon cycles [12]. This is the reason why it can be stated that biogas is a renewable energy source with no carbon emissions.

Figure 0.3 reports a schematic graph of biogas production and fields of application.

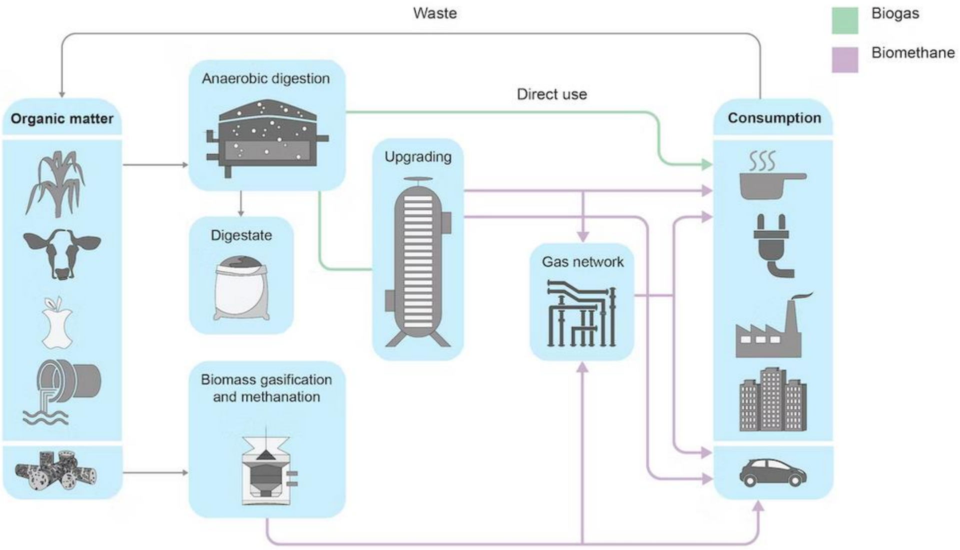


Figure 0.3 Biogas production and utilization scheme [13].

China has the largest number of biogas plants and the largest annual biogas production (72000 TWh) followed by Germany (120 TWh) [14].

The European Union is a leading region in the biogas sector. Germany is by far the largest market, and home to two-thirds of Europe's biogas plant capacity. Energy crops were the primary choice of feedstock that underpinned the growth of Germany's biogas industry, but policy has recently shifted more towards the use of crop residues, sequential crops, livestock waste and the capture of methane from landfill sites. Other countries such as Denmark, France, Italy and the Netherlands have actively promoted biogas production [13]. Figure 0.4 shows the amount of power produced from biogas in several counties. Italy is one of the major users of biogas, the development of this technology is due to an environmental campaign back in 2010 that introduced incentives for electric energy generation from biogas [15]. Since incentives decrease in time other production routes like synthesis of chemicals are more favorable.

Biogas is typically used as fuel in Combined Heat and Power plants (CHP) to generate heat and electricity. This type of use of biogas do produce carbon emissions, therefore an interesting alternative is to use biogas as raw material in chemical synthesis, allowing to fix carbon in a chemical molecule like methanol and dimethyl-ether and avoid its release as carbon dioxide. This is the basic idea of Combined Heat Power and Chemical plants (CHPC) [16].

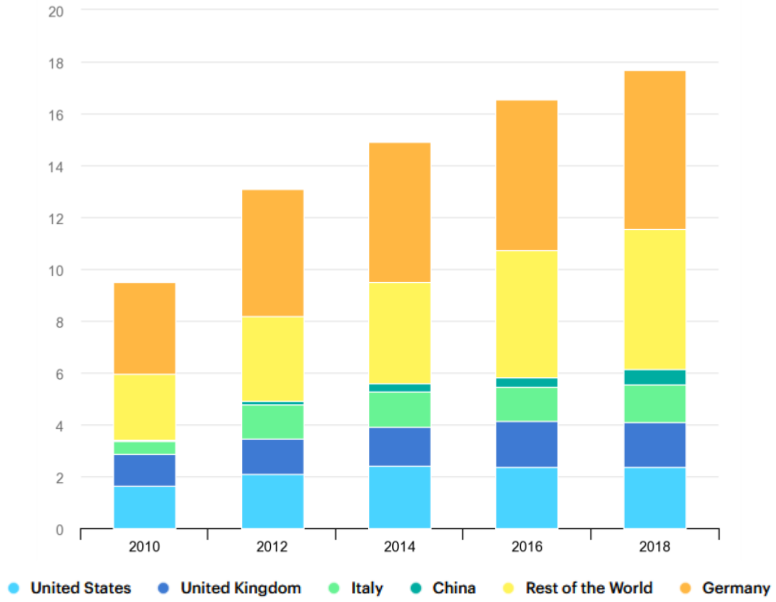


Figure 0.4 Biogas installed power generation capacity expressed in GW, 2010-2018 divided by country [13]

Biogas production technologies are part of the 2030 Agenda for Sustainable Development, which was accepted by all United Nation Member States in 2015. Humans directly or indirectly generate over 105 Gt of organic waste globally each year, all of which release harmful methane and other greenhouse gas emissions directly into the atmosphere as they decompose. Today only 2% of these are treated and recycled. By simply managing these important bioresources more effectively global GHG emissions can be reduced by 10% by 2030 [17].

Methanol

Methanol synthesis is the most studied route to use biogas for chemical production. Methanol is an organic chemical and the simplest aliphatic alcohol, with the formula CH_3OH. It is a light, volatile, colourless, flammable liquid. It has a wide range of applications, the most important are listed here below and reported in Figure 0.5:

- Production of formaldehyde, acetic acid, and methyl tert-butyl ether: methanol is mainly converted to formaldehyde, which is widely used in polymers, or to acetic acid. Methyl tert-butyl ether (MTBE), an important octane booster for gasoline, is obtained combining methanol and isobutene.

- Production of hydrocarbons, olefins, and gasoline: condensation of methanol to produce hydrocarbons and aromatic systems is the basis of several technologies related to gas-to-liquids. These include methanol-to-hydrocarbons (MtH), methanol-to-gasoline (MtG), methanol-to-olefins (MtO), and methanol-to-propylene (MtP).
- Gasoline additive: the European Fuel Quality Directive allows fuel producers to blend up to 3% methanol.
- Other chemicals: methanol is the precursor of most simple methylamines, methyl halides, and methyl ethers.
- Energy carrier: methanol is a promising energy carrier because, being a liquid, it is easier to store than hydrogen or natural gas. Its massive energy density is, however, lower than methane, but it has the advantages of being highly biodegradable and less toxic for the environment.
- Fuel: methanol is sometimes used as a fuel for internal combustion engines. It burns to carbon dioxide and water. The main advantage is that it can be adapted to gasoline internal combustion engines with minimal changes to the engine and to the infrastructure that delivers and stores the liquid fuel, but the main disadvantage is the low cetane number. Methanol is an alternative fuel for ships that helps the shipping industry to meet increasingly stringent emissions regulations. It significantly reduces sulphur oxides (SO_x), nitrogen oxides (NO_x) and particulate matter emissions. In China, industrial boilers burn with methanol. Its use is replacing coal, which is under pressure from increasingly stringent environmental regulations.
- Other applications.

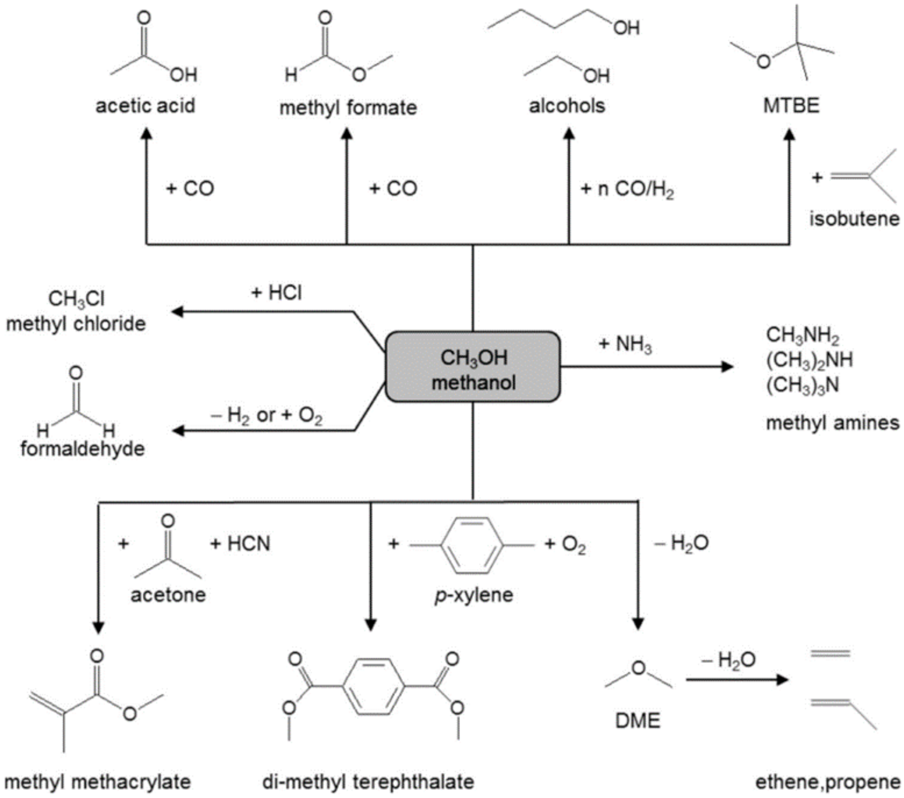


Figure 0.5 Main chemical routes for methanol [18].

In the 1990s, the Nobel prize George A. Olah proposed the concept of a methanol economy. The methanol economy is a suggested future economy in which methanol and dimethyl-ether will replace fossil fuels as energy storage, ground transportation fuel, and feedstock for synthetic hydrocarbons and their successive products.

Methanol can be produced from a several sources such as fossil fuels, agricultural products, municipal waste, wood, and various biomasses. It can also be synthetized from the chemical recycle of carbon dioxide. Today the majority of methanol is produced from methane through syngas [19].

Market

Methanol production across the globe has been on a continual increase during the last few years. In 2022, methanol production reached over 111 million metric tons, an increase of nearly 4% with respect to the previous year. Since 2017, global production of methanol grew by roughly 22.6 million metric tons [20]. In Figure 0.6 the principal methanol applications are represented with the respective market shares.

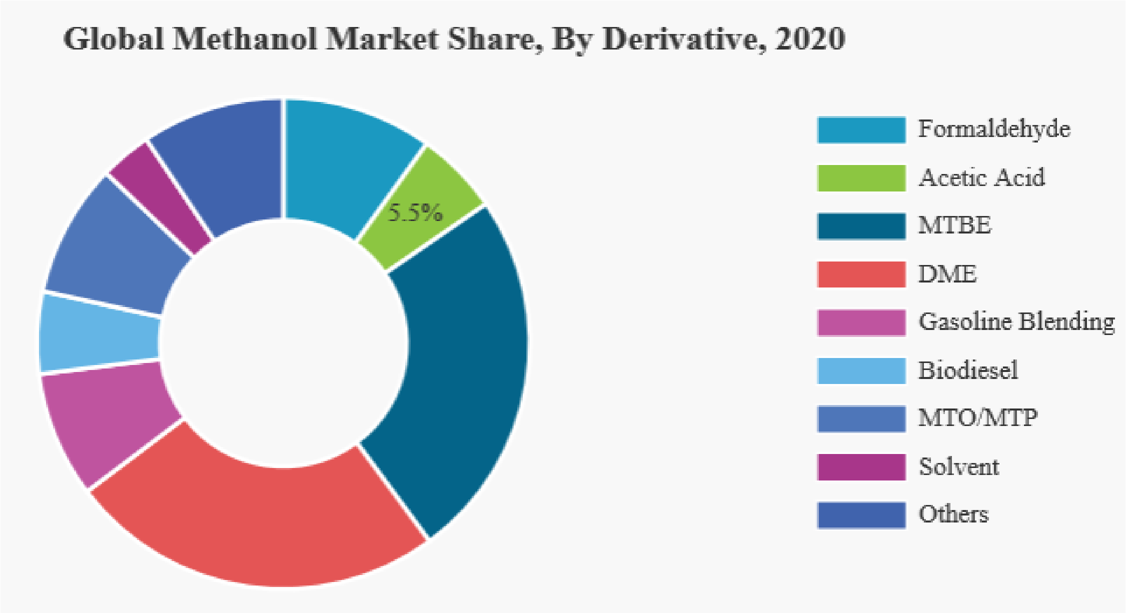


Figure 0.6 Global methanol market share, by derivative, 2020 [21].

It can be observed that methanol is mainly used to produce chemicals in various fields, from paints and resins to plastics and adhesives. The use of methanol in the fuel sector is increasing, and it can be seen, for example, from the share of MTBE, used for gasoline blending.

Dimethyl-ether

Dimethyl-ether is an important alternative fuel for vehicle engines, especially to replace diesel. It is a fuel additive and can also be used for household cooking gas instead of LPG. It is also widely recommended as environmentally friendly aerosol and green refrigerant because it has zero ozone depletion potential and a lower GWP compared with traditional chlorofluorocarbons. DME is also an important intermediate for the manufacture of many value-added chemicals such as lower olefins, methyl acetate, and dimethyl sulphate. Therefore, the production and utilization of DME has suddenly gained attention because of the need for environmental protection and the increased price of crude oil [22].

DME has received an increased attention as sustainable alternative fuel for Diesel engines (blended with gasoil) due to its high cetane number (>55) and to the important reduction of NO_x, SO_x, and PM emissions in exhaust gases. Hence, its high oxygen content also reduce the number of by-products and it does not produce soot since no C-C bonds are present [23], but at the same time, it results having a lower LHV with respect to gasoil.

Due to DME physical and chemical properties similarity to LPG, blending 15-20% of DME with LPG increases the LHV to efficiently use the mix for domestic needs [24].

Figure 0.7 reports dimethyl-ether production subdivided with respect to field of application.

Figure 0.7 Global dimethyl-ether market share by application, 2020 [25].

It is possible to produce dimethyl-ether from fossil origins; it can be derived from CO_2 capture and utilization (CCU), or it can be produced from biomasses. The last two routes manage the problem of high GHG emissions.

Market

The dimethyl-ether market size was valued at 5.05 billion USD in 2022. The Fortune Business Insights report [26] has estimated that dimethyl-ether industry is projected to grow from 6.02 billion USD in 2023 to 12.83 billion USD by 2030, exhibiting a compound annual growth rate (CAGR) of 12.35% during the forecast period (2023-2030). Figure 0.8 shows the DME expected grow rate for each geographic region.

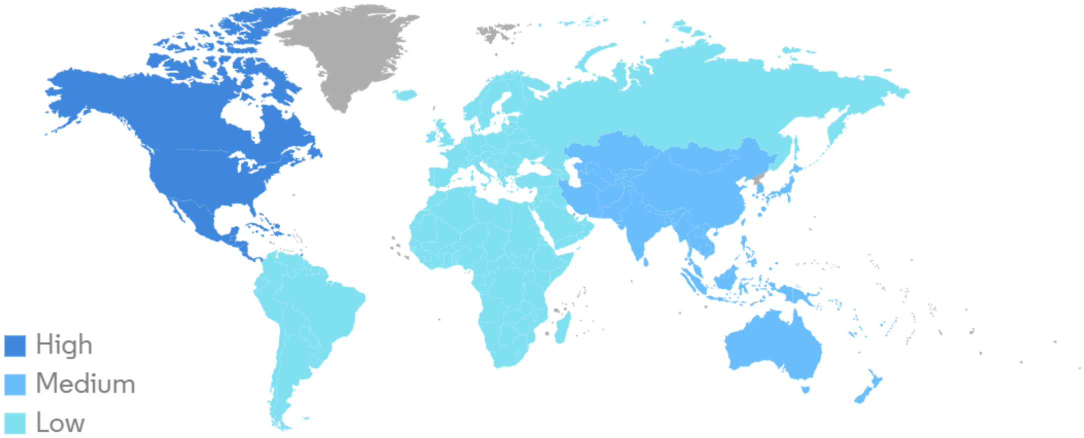


Figure 0.8 Global Dimethyl-ether grow rate by geographic region (2022-2025) [27]

The DME global demand is expected to grow with its increasing utilization in the transportation sector as fuel.

Asia-Pacific region has the largest share of the DME market. Being the most dominant regional market, Asia Pacific will account for the maximum growth over the coming years, as can be appreciated in Figure 0.9. China alone consumes more than 85% of the worldwide demand for DME [28]. This is mainly due to the use as domestic fuel and the constantly growing automobile industry in this region. Moreover, other countries such as Japan, India and South Korea are expected to be the fastest growing countries. This growth is due to regulatory conditions in these countries which promote the use of DME [29].

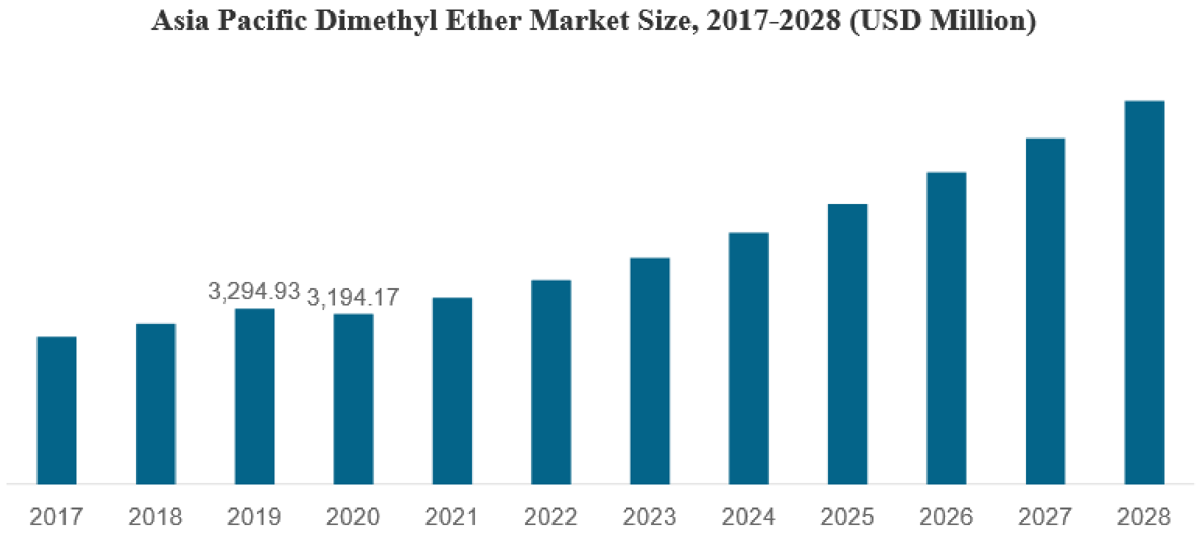


Figure 0.9 Expected size growth of Asia Pacific dimethyl-ether market from 2017 to 2028 [25].

Europe has a significant smaller part in the market where the key contributors are Germany, U.K. and Italy, with a major utilization in the automobile industry [29].

Aim of the thesis

This thesis work aims to determine the most profitable chemical synthesis from renewable syngas, produced with biogas. Doing so, renewable materials can be valorised to give advanced biofuels. The production of chemicals is analysed since several decrees, as the one in Italy [30], promote the usage of alternative fuels in the transportation sector with the introduction of governmental incentives. The two possibilities investigated are the production of methanol and the production of dimethyl-ether. The best investment is determined by an economic evaluation of the two plant alternatives and the calculation of helpful indexes. The constraining limit present in the design is the capacity of the plant, which is limited by the amount of available syngas coming from the syngas plant. In fact, while for syngas from fossil fuels big plants are feasible, biogas plants have limited capacity. The syngas production plant is not designed for this analysis, since the focus is put on the process plant that shows differences. The research, therefore, comprise only the methanol and dimethyl-ether plants from syngas.

Before explaining the process configurations and operating conditions in detail, a literature review is conducted on syngas production as background, syngas conversion to methanol and methanol conversion to dimethyl-ether.

1 State of the art

In this first Chapter, a literature review on the consolidated production processes is delivered. Figure 1.1 shows the chain of processes involved and how the transformations are connected between themselves for the production of methanol and dimethyl-ether.

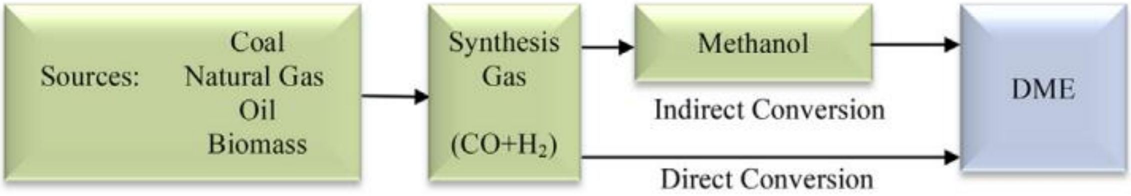


Figure 1.1 Processes schematization [29].

1.1. Syngas

Syngas, or synthesis gas, is a gas mixture which main components are H_2 and CO. Small quantities of CH_4 and CO_2 are also present. It is one of the main raw materials for chemicals production, and its optimal composition depends on the application. One of the most important parameters to express the composition is the H_2/CO ratio.

As already stated in the Introduction, syngas can be produced starting from several raw materials.

Fossil source

Syngas is usually produced from the steam reforming of methane (natural gas). Indeed, after World War II, natural gas replaced coal as the main feedstock for syngas production. It is more energy efficient, has a higher hydrogen content, a lower amount of contaminants, such as nitrogen, sulphur, halogenated chemicals, and heavy metals.

The main production routes for syngas production are:

- Steam reforming of natural gas or light hydrocarbons and steam, optionally in presence of oxygen or carbon dioxide. In the last case the reaction is called dry reforming. It is a catalytic endothermic reaction.

- Partial oxidation of hydrocarbons in presence of steam or oxygen/air or both. Complete oxidation would lead to carbon dioxide and water, not syngas. It is a non-catalytic exothermic reaction.
- Partial oxidation (gasification) of coal where the gasifying agent is oxygen/air and steam. It is a gas-solid reaction.

The combination of the steam reforming and the partial oxidation, in which the endothermicity of one reaction is coupled with the exothermicity of the other one, is referred to as autothermal reforming. Figure 1.2 shows the general flow scheme of the main processes for syngas production.

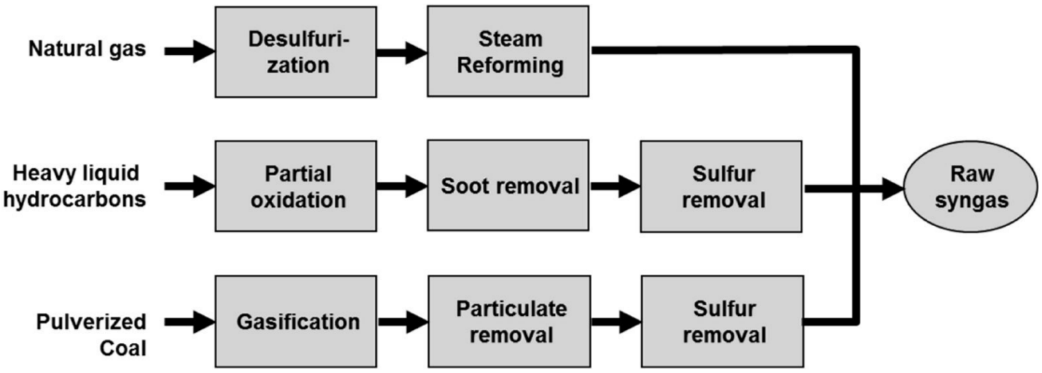


Figure 1.2 General process flow diagrams for syngas production [18].

Most syngas today is produced by natural gas steam reforming.

Partial oxidation is not suitable for light feedstock since it would require a cryogenic separation with extremely high operative costs. It is preferable with respect to steam reforming if the cost of a heavy feedstock is lower than the one of light feedstocks or if the desired syngas composition requires more CO.

Steam reforming

As it can be seen from Figure 1.2, the feed has to be de-sulphurised as the first step. Sulphur is a poison for metal catalyst, as the one used for steam reforming and/or in successive reactors, because it can block the active sites. If sulphur is only present as hydrogen sulphide, adsorption is sufficient for sulphur removal, but if more stable sulphur compounds are present hydrotreating is required.

Although natural gas is a mixture of several compound, for simplicity, it is assumed that it consists of methane only. Reactions from (1.1) to (1.9) represent the main reactions during methane conversion. When converting methane in presence of steam the most important reactions are steam reforming (1.1) and the water-gas shift (1.2). In case CO_2 is used, the main reaction is the dry reforming (1.3). Methane decomposition (1.4) and CO disproportionation (1.5) are responsible for coke formation, which leads to the deactivation of the catalyst and eventually in blockage of the reformer tubes.

Carbon formations can be suppressed by adding excess steam which also enhances hydrocarbon conversion due to their lower partial pressure.

$$CH_4 + H_2O \leftrightarrow CO + 3H_2 \qquad \Delta H_{298K} = +206\, kJ/kmol \tag{1.1}$$

$$CO + H_2O \leftrightarrow CO_2 + H_2 \qquad \Delta H_{298K} = -41.0\, kJ/kmol \tag{2.13}$$

$$CH_4 + CO_2 \leftrightarrow 2CO{+}2H_2 \qquad \Delta H_{298K} = +247\, kJ/kmol \tag{1.3}$$

$$CH_4 \leftrightarrow C{+}2H_2 \qquad \Delta H_{298K} = +75\, kJ/kmol \tag{1.4}$$

$$2CO \leftrightarrow C{+}CO_2 \qquad \Delta H_{298K} = -173\, kJ/kmol \tag{1.5}$$

$$CH_4 + {}^1/_2\, O_2 \leftrightarrow CO{+}2H_2 \qquad \Delta H_{298K} = -36.0\, kJ/kmol \tag{1.5}$$

$$CH_4 + 2O_2 \leftrightarrow CO_2{+}2H_2O \qquad \Delta H_{298K} = -803\, kJ/kmol \tag{1.6}$$

$$CO + {}^1/_2\, O_2 \leftrightarrow CO_2 \qquad \Delta H_{298K} = -284\, kJ/kmol \tag{1.7}$$

$$H_2 + {}^1/_2\, O_2 \leftrightarrow H_2O \qquad \Delta H_{298K} = -242\, kJ/kmol \tag{1.9}$$

Reforming reactions are highly endothermic; therefore, a significant amount of heat needs to be provided, usually by burning a fuel. The steam reforming reaction require temperature higher than 700°C so typical temperature range for reforming reactor is 800-900°C. Reforming reactions are hindered at high pressure, due to the increase in the number of moles, but typical operating pressure is set around 15-25 atm taking into consideration a cost-benefit analysis (lower syngas compression cost and smaller reformer size). The syngas composition may be modified in additional process steps as a secondary reforming and/or shift reactors that reduce the CO concentration.

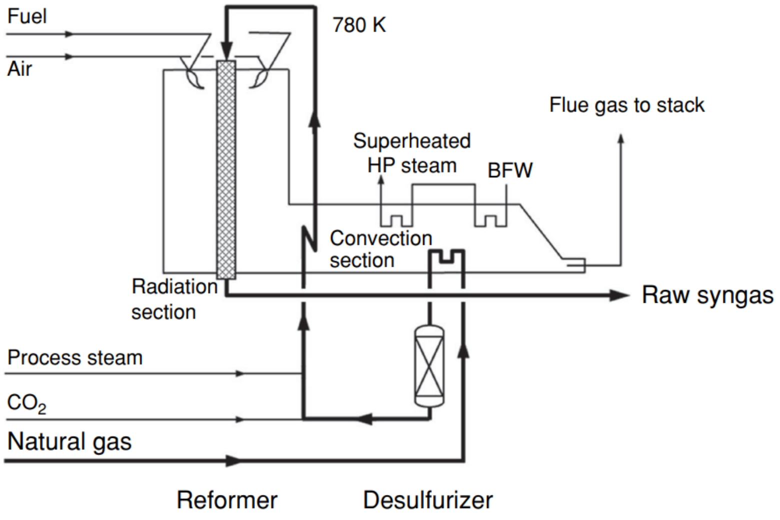


Figure 1.3 Simplified flow scheme of the steam reforming process [18].

Alumina supported nickel catalyst is very efficient, so the reactions go to equilibrium and the process is governed by thermodynamics. Figure 1.3 shows a simplified scheme of the reforming process. The upper region of the reformer is characterized by a convective heat exchange in which reactants are preheated. Reactions occur in the lower region, characterized by radiative heat exchange, that allows to reach the high temperature required.

Renewable source: Biogas

Normally, biogas composition is 35-75% methane, 25-65% carbon dioxide, 1-5% hydrogen, and traces of water vapor, ammonia, and hydrogen sulphide.

Therefore, it is possible to feed biogas instead of methane in the steam reforming reactor. In this case since CO_2 is present in the feed dry reforming reaction occurs as well as the steam reforming and the WGS reaction.

Biomass can also be used instead of coal for gasification, helping to reduce the greenhouse gas emissions that are present in the fossil source pathway.

1.2. Methanol

As already mentioned in the Introduction, methanol is the simplest aliphatic alcohol. It is a polar compound, very soluble in water and also in alcohols and esters. It is flammable and also toxic. In Table 1.1 some properties of methanol are reported.

Table 1.1 Methanol physical and chemical properties.

Chemical formula	CH_4O
Molar mass	32.04 g/mol
Density	1.062 kg/m^3 (gas, 100 °C, 1013 mbar) 0.786 g/mL (liquid, 25°C)
Boiling point at 1 atm	64.6 °C
Melting point	-97.6 °C
Flammability limits	6.7-36.5%

History

The decisive step in the large-scale industrial production of methanol was made in 1923 with the development of a sulphur resistant zinc oxide-chromium oxide catalyst, used by BASF Leuna Works. This, as well as other process plants at the time, worked at high pressure (23-35 MPa) and 320-450°C. High-pressure methanol production dictated the scene until ICI developed in the 1960s a new highly selective copper oxide catalyst. This so-called low-pressure process was characterized by milder reaction conditions: 5-10 MPa and 200-300°C.

Thermodynamics

The production of methanol from synthesis gas can be described by the following equilibrium reactions:

$$CO + 2H_2 \leftrightarrow CH_3OH \qquad \Delta H_{298K} = -90.8\, kJ/kmol \tag{1.9}$$

$$CO_2 + H_2 \leftrightarrow CO + H_2O \qquad \Delta H_{298K} = +41.0\, kJ/kmol \tag{2.13}$$

$$CO_2 + 3H_2 \leftrightarrow CH_3OH + H_2O \qquad \Delta H_{298K} = -49.6\, kJ/kmol \tag{1.10}$$

Reactions (1.9) and (1.10)are, respectively, CO and CO_2 hydrogenation reactions. Both reactions are exothermic and accompanied by a decrease in the number of moles. Methanol production is thus favoured by low temperature and high pressure, with the maximum conversion limited by equilibrium composition.

Due to the simultaneous presence of CO_2 and H_2 in the reaction mixture, also the reverse water gas shift (reaction (2.13)) occurs.

Reaction (1.10) is the overall result of the other two equations, and the equilibrium constant K_2 can be described as K_2=K_1 K_3.

Methanol synthesis is strongly affected by thermodynamics. The spontaneity of a reaction is determined by Gibbs free energy: a system is thermodynamically favoured when the Gibbs free energy is at a minimum. The minimization of the Gibbs free energy can be used to predict the equilibrium composition of the system. Looking at Figure 1.4 it can be observed that the reaction is thermodynamically favoured at temperatures lower than 135°C, temperature for which K_{eq} is equal to 1. In the desired temperature region, however, methanol synthesis is not the only reaction present; other reactions are thermodynamically more favoured: methanation, formation of higher alcohols and other hydrocarbons. Furthermore, at this low temperature kinetics is strongly penalized, resulting in a very slow reaction rate. This situation requires to use a catalyst to enhance selectivity, but no catalyst is active at a temperature this low. Thus, working at higher temperature is required.

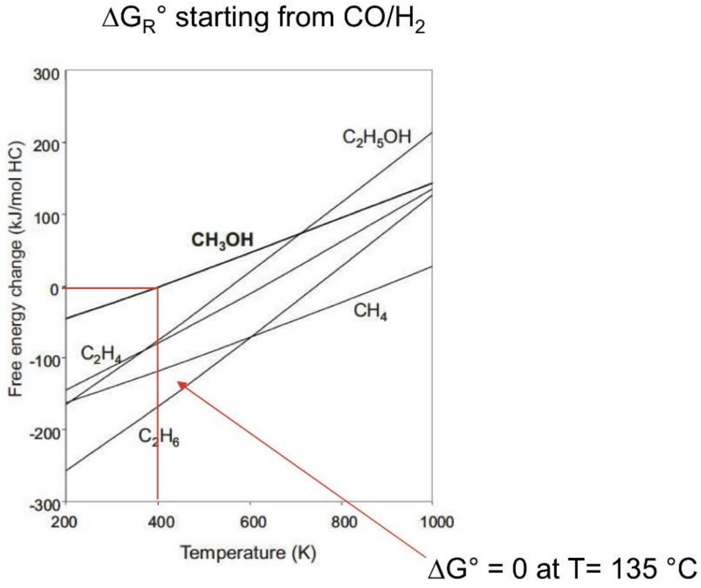


Figure 1.4 Products from CO H_2; standard free energy of formation [18].

To increase the conversion, an increase of the operating pressure is possible, considering also the cost and technological limitations associated with working at high pressure. Typical values of operating temperature and pressure are reported in Figure 1.5.

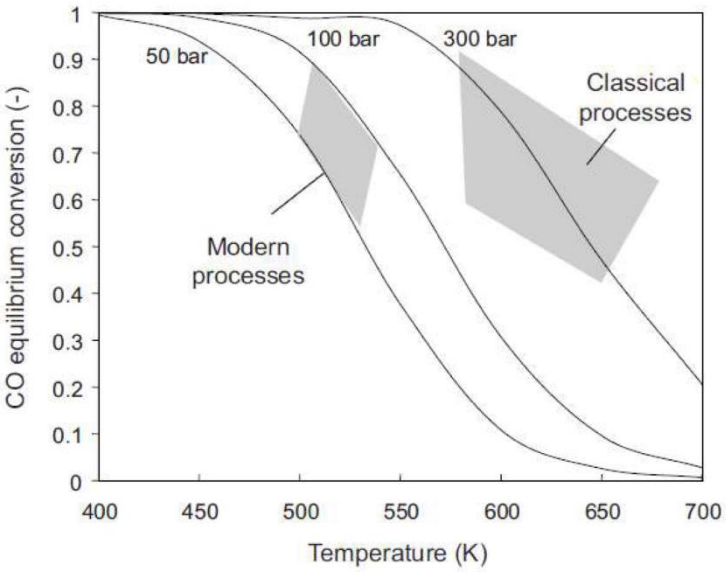


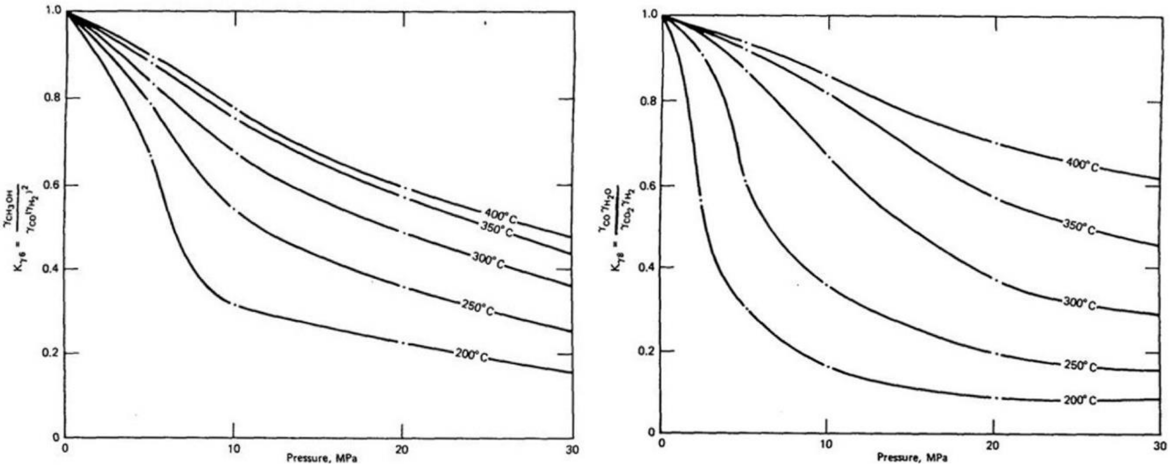
Figure 1.5 Equilibrium CO conversion to methanol (feed H_2/CO = 2 mol/mol) [18].

Methanol synthesis happens with a gaseous phase contacting a solid catalyst. Working at high pressure enlarges the non-idealities of the mixture. The equilibrium constant of reaction (1.9) and (2.13)) are expressed as the ratio of fugacity, as in equation (1.11) and (1.12).

$$K_{eq}^{1} = \left[\frac{f_{CH_3OH}}{f_{CO} f_{H_2}^{2}}\right] = \left[\frac{\varphi_{CH_3OH}}{\varphi_{CO} \varphi_{H_2}^{2}}\right]\left[\frac{p_{CH_3OH}}{p_{CO} p_{H_2}^{2}}\right] = K_{\varphi}^{1} K_{p}^{1} \tag{1.11}$$

$$K_{eq}^2 = \left[\frac{f_{CO} f_{H_2O}}{f_{CO_2} f_{H_2}}\right] = \left[\frac{\varphi_{CO} \varphi_{H_2O}}{\varphi_{CO_2} \varphi_{H_2}}\right]\left[\frac{p_{CO} p_{H_2O}}{p_{CO_2} p_{H_2}}\right] = K_\varphi^2 K_p^2 \tag{1.12}$$

Where K_φ represent the non-ideality of the gas mixture. As it can be seen in Figure 1.6, the non-ideality brings an advantage since K_φ is always smaller than 1, and therefore, methanol partial pressure must be higher.



a) b)

Figure 1.6 Values for K_φ for a) reaction (1.9), and b) reaction (2.13)).

Reaction pathway

Even if the catalyst chosen is selective, parallel and consecutive reactions still occur. Hereafter, some examples of undesired side reactions are reported:

$$CO + 3H_2 \leftrightarrow CH_4 + H_2O \tag{1.13}$$

$$2CH_3OH \leftrightarrow CH_3OCH_3 + H_2O \tag{2.13}$$

$$2CO + 4H_2 \leftrightarrow C_2H_5OH + H_2O \tag{1.14}$$

$$CH_3OH + CO \leftrightarrow HCOOCH_3 \tag{1.15}$$

From all reactions presented it can be noted the significative amount of water produced. Water is a fatal by-product that need to be separated from methanol. The separation is expensive because the two compounds form an azeotrope.

Reaction (1.13) is the methanation reaction. It is not problematic from the separation point of view, since methane is gaseous at separation condition, but being an inert it will accumulate in the recycle. Another problem is the exothermicity of the reaction, that will increase the reactor temperature, and the reagent (hydrogen) consumption.

Reaction (2.13) is the dehydration reaction to dimethyl-ether. If the desired product is methanol, this reaction is undesired, and it also consume the product. The other two side reaction are the formation of higher alcohols (reaction (2.13)) and the formation of oxygenates from methanol carbonylation (reaction (1.14)).

Stoichiometry asks for a ratio $H_2/CO = 2$, if lower there is an increase by-product formation while if higher means working in excess of hydrogen. Nevertheless, it is chosen to work with excess of hydrogen to have a better control on temperature and to keep the catalyst in a reducing environment. Stoichiometric number SN (equation (1.16)) for commercial applications can also arrive to 3 [31].

$$SN = \frac{[H_2] - [CO_2]}{[CO] + [CO_2]} \tag{1.16}$$

Catalysts

Classical processes use high-temperature catalysts which operate around 300 bar and 380-400°C. These catalysts are constituted of $ZnO\text{-}Cr_2O_3$ (Zn/Cr=70/30).

Modern processes, which use $Cu\text{-}ZnO\text{-}Al_2O_3$ (CZA) catalysts, are able to work at lower pressure and temperature between 200-250°C.

Modern heterogeneous catalysts are more active and selective, but less resistant to sintering and to poisoning.

Kinetics

The nature of the active centres in the CZA catalyst used in industrial condition is still a subject of discussion. The feed gas composition also plays a role in determining the activity and selectivity of the catalyst. Different mechanisms have been proposed. An example is the Graaf et al. [32].

Reactors

The major problem for the reactor design is temperature control. The optimal temperature profile is decrescent along the reactor. Therefore, a simple adiabatic reactor is not suitable. In Figure 1.7 three of the most common reactor configurations for methanol synthesis and the corresponding temperature profile are reported. The picture on the left shows a multitubular pseudo-isothermal reactor, in which the temperature increase is controlled by boiling water. The other two pictures illustrate two different adiabatic multi-stage reactors, which control the temperature increase by splitting the catalytic bed into multiple catalytic beds between which reactants are cooled. Cooling can be performed in a direct way (injecting cold reactants) or indirect one (with heat exchange between reacting beds).

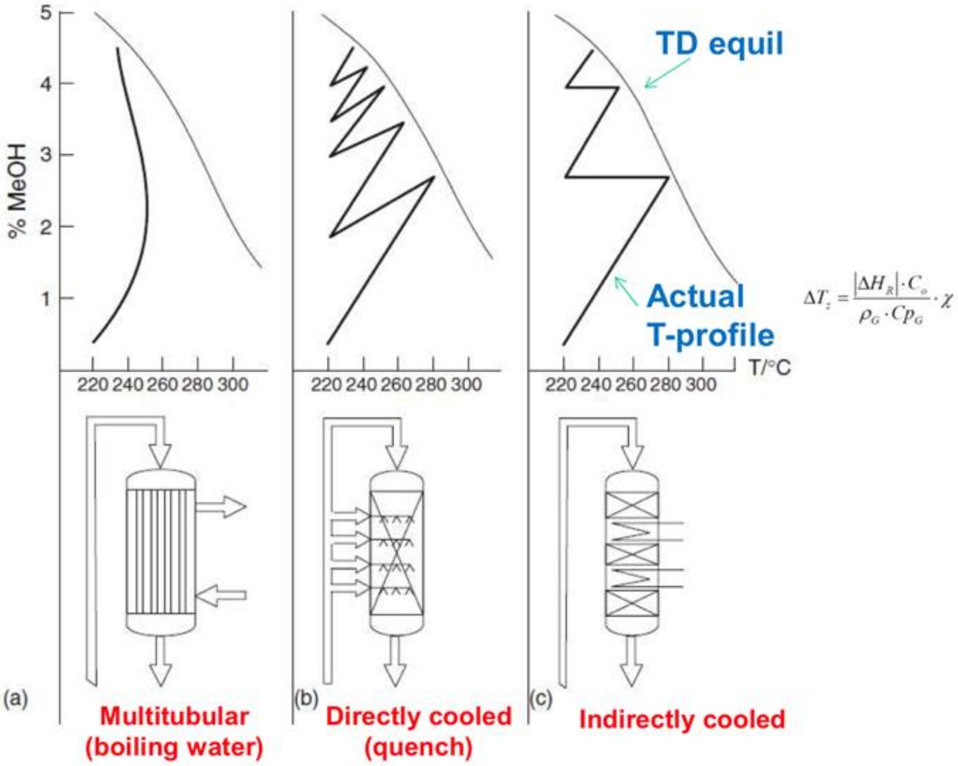


Figure 1.7 Different reactor configurations and relative temperature profile.

Process

The typical methanol synthesis plant is divided into the following sections:

- Syngas production;
- Methanol synthesis;
- Methanol purification.

A PFD for low-pressure methanol production by ICI can be found in Figure 1.8 while Figure 1.9 represent low-pressure methanol process by Lurgi.

These two configurations mainly differ in reactor design, catalyst configuration and purification section. After being compressed and heated the syngas is sent to the reactor. In ICI configuration, the reactor is adiabatic with a single catalytic bed. The temperature is controlled by adding cold gas at several points. The Lurgi reactor, instead, is a tubular reactor with the catalyst inside the tubes and cooled by boiling water. The product mixture is then sent in the separation section. The first separator separates the gas which are purged and recycled back and crude methanol that needs to be purified. Different distillation approaches can be adopted. A first possibility is to remove the light ends from the top of a column and then remove the wastewater from the bottom of a second column. Another possibility is to adopt a single column in which light ends are separated from the top, wastewater from the bottom, and the purified methanol from a side draw.

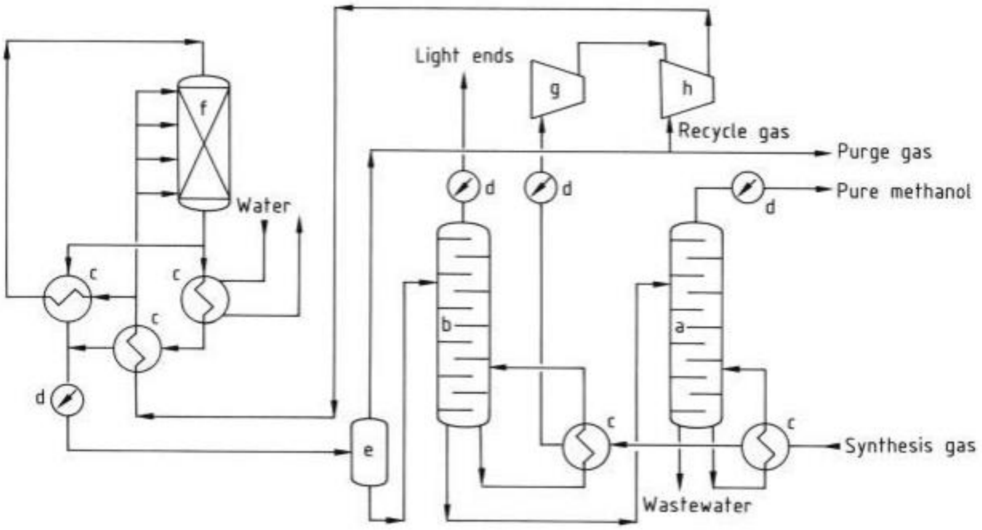


Figure 1.8 The ICI low-pressure methanol process. a) Pure methanol column; b) Light ends column; c) Heat exchanger; d) Cooler; e) Separator; f) Reactor; g) Compressor; h) Compressor recycle stage [33].

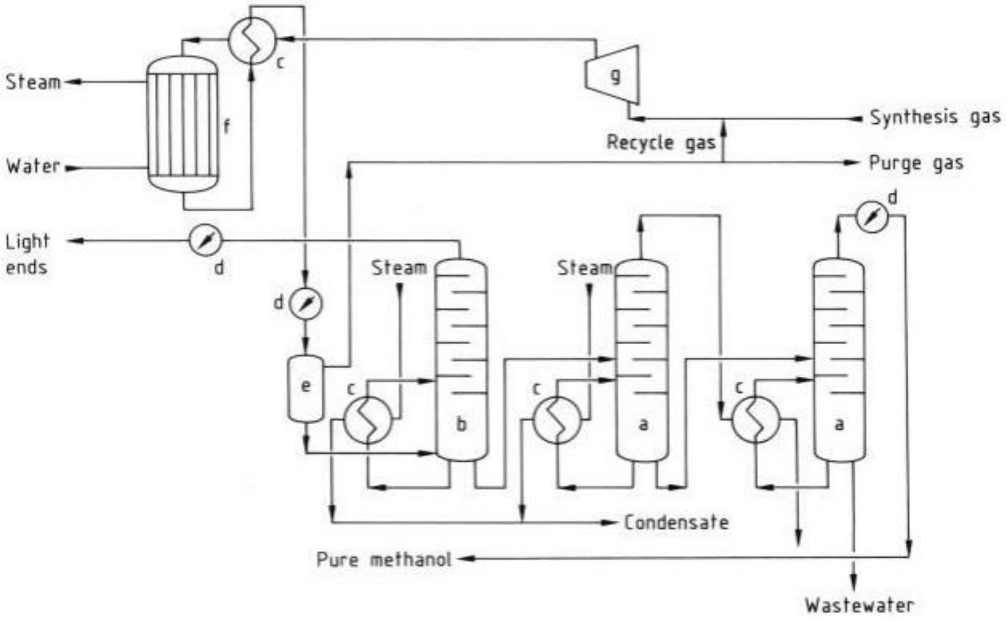


Figure 1.9 Lurgi low-pressure methanol process. a) Pure methanol columns; b) Light ends column; c) Heat exchanger; d) Cooler; e) Separator; f) Reactor; g) Compressor recycle stage [33].

Lurgi also proposed a new reactor approach called Megamethanol, in which the reactor configuration changes. The reactor is divided into two vessels: the first one cooled by non-reacted syngas which then enters the second vessel, and the second vessel cooled by boiling water.

CO_2 to methanol

In the context of methanol economy [34], another route of methanol production to reduce GHGs emissions is the reductive oxygenation of CO_2. Carbon dioxide can be taken from several sources, including other industrial plants or the atmosphere itself.

According to thermodynamics, methanol reaction from CO_2 is less favourite than from CO, as it can be noted in Figure 1.10.

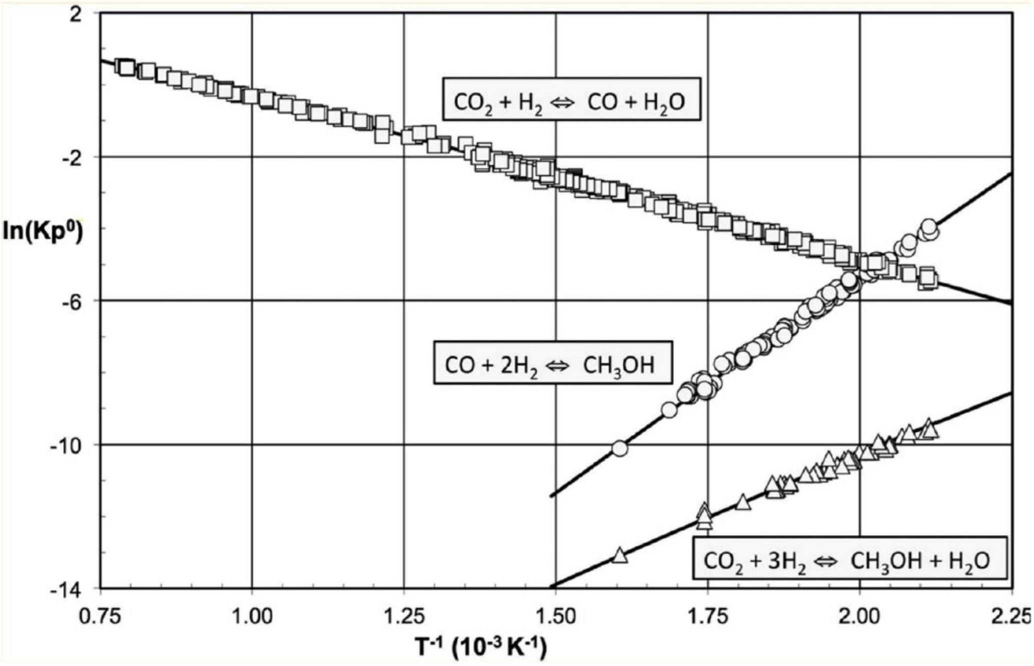


Figure 1.10 Trend of methanol synthesis reaction equilibrium constant versus temperature.

In order to consider the process as carbon-free, hydrogen has to be generated from renewable sources, for example from water electrolysis, which is an expensive process. It is reminded that a higher amount of hydrogen is necessary since this route consumes more hydrogen than the traditional one. Another remark is that at high CO_2 partial pressure the presence of water became relevant leading to worse performances and deactivation of traditional catalysts. Methods to improve conventional catalyst for this purpose are shown in [35] and [36].

1.3. Dimethyl-ether

Colourless, non-toxic, non-corrosive, non-carcinogenic and environmentally friendly compound, DME is the simplest ether, with a normal boiling point of −25°C, which can be liquefied above 0.5 MPa at room temperature. Chemical and physical properties are similar to LPG and this may represent a strategic advantage as the storage and transport facilities of LPG can be easily converted to distribute DME. Table 1.2 reports the main physical and chemical properties of methanol.

Table 1.2 Dimethyl-ether physical and chemical properties.

Chemical formula	C_2H_6O
Molar mass	46.069 g/mol
Density	2.098 kg/m^3 (gas, 0 °C, 1013 mbar) 0.671 g/mL (liquid, -25°C)
Boiling point at 1 atm	-24.8 °C
Melting point	-141.5 °C

History

Until about 1975 dimethyl-ether was obtained as a by-product in the high-pressure production of methanol. In this process up to 3-5 wt % dimethyl-ether is formed. Dimethyl-ether can be recovered in pure form by distillation of crude methanol. The development of the low-pressure methanol synthesis, particularly by Lurgi and ICI, resulted in the almost complete replacement of all high-pressure plants by 1980. The low-pressure processes, which require less severe conditions, produce only very small amounts of dimethyl-ether. As a result, special catalytic processes have been developed for the production of dimethyl-ether. The preparation of dimethyl-ether from a methanol in presence of acidic catalysts on a laboratory scale has been known for many years. Numerous methods have been discussed in patent literature. For instance, aliphatic ethers can be prepared by heating alcohols in the presence of zinc chloride. Aluminum oxide and aluminum silicate, with or without doping, are the most important catalysts for industrial use. **Error! Reference source not found.** illustrates the process developed by Union Rheinische Braunkohlen Kraftstoff AG (now DEA Mineraloel AG, Wesseling) for the production of high purity dimethyl-ether (purity>99.99%).

The catalytic dehydration of pure, gaseous methanol is carried out in a pipe reactor. The product is cooled in two stages and subsequently distilled to yield pure dimethyl-ether. Small amounts of dimethyl-ether are recovered from the off gas in a scrubber and recycled to the reactor. Unreacted methanol is separated from water in a second column and also recycled. Very pure dimethyl-ether is obtained by special rectification processes [33].

Thermodynamics

The production of dimethyl-ether from methanol can be described by the reversible reaction (1.17) which represent methanol dehydration reaction.

$$2CH_3OH \rightarrow CH_3OCH_3 + H_2O \qquad \Delta H_{298K} = -32.4\, kJ/kmol \tag{1.17}$$

The dehydration reaction is exothermic, and it is not accompanied by a change in the number of moles. Dimethyl-ether production is thus favored by low temperature, while is thermodynamically insensitive toward the operating pressure. The maximum conversion is limited by equilibrium composition. DME synthesis is affected by thermodynamics. Diep [37] has performed a thermodynamics analysis on the methanol-dimethyl ether-water system at temperature from 498 to 623°C to derive equilibrium conversion and to determine the thermodynamic equilibrium constant, which expression is reported in Equation (1.18).

$$\ln K_{eq} = \frac{2835.2}{T} + 1.65 \ln T - 2.39 \cdot 10^{-4} T - 2.39 \cdot 10^{-6} T^2 - 13.360 \tag{1.18}$$

The methanol dehydration to DME is a gas-phase reaction conducted typically at 1.0-2.0 MPa with an inlet temperature of about 220-250 °C and outlet temperature of about 300-350 °C [24].

Catalyst

The commonly employed catalysts for dimethyl-ether synthesis from methanol are solid-acid types like γ-alumina catalysts. Alumina is very attractive since it is cost effective and exhibits high surface area, excellent thermal and mechanical stability, high mechanical resistance, and high selectivity toward DME. Furthermore, it has high catalytic activity toward DME formation due to its low content of highly acidic sites which are mostly of the Lewis type. Although its activity, it tends to strongly adsorb water thereby losing activity [29].

Kinetics

Methanol dehydration reaction takes place on pure γ-alumina and γ-alumina slightly modified with phosphates or titanates. Bercic et al. [38] proposed a kinetic mechanism over γ-alumina at temperature between 290-360°C which is able to describe with reliability experimental results.

Reactors

Being the reaction exothermic, the optimal temperature profile is high at the beginning of the reactor to have a high reaction rate and low at the exit to reach higher conversion. A decreasing temperature profile cab be obtained controlling the spontaneous temperature increase with a cooling medium in a direct or indirect way.

Owing to simplicity and lower costs, the reactors most commonly used either at laboratory or pilot scale are fixed beds.

An innovative reactor design, instead, is the coupled reactor. In this type of reactors, the exothermic reaction becomes the heat source for the endothermic reaction(s). In the work of Khademi et al. [39], optimal operation conditions for a thermally coupled reactor in which DME synthesis and cyclohexane dehydration occurred simultaneously have been evaluated. The reactor, as depicted in Figure 1.11, consisted of two separate sides for exothermic and endothermic reactions. Catalytic dehydrogenation of cyclohexane to benzene took place in the shell side, whereas methanol dehydration occurred inside the tube with fixed bed of different catalysts on both sides. Heat is transferred continuously from the exothermic to the endothermic reaction zone. It was shown that suitable amount of initial molar flow rate and inlet temperature of both sides could provide the necessary heat to heat up the mixtures and to drive the endothermic process at the same time. In addition, the short distance of heat transfer increased the efficiency of the process.

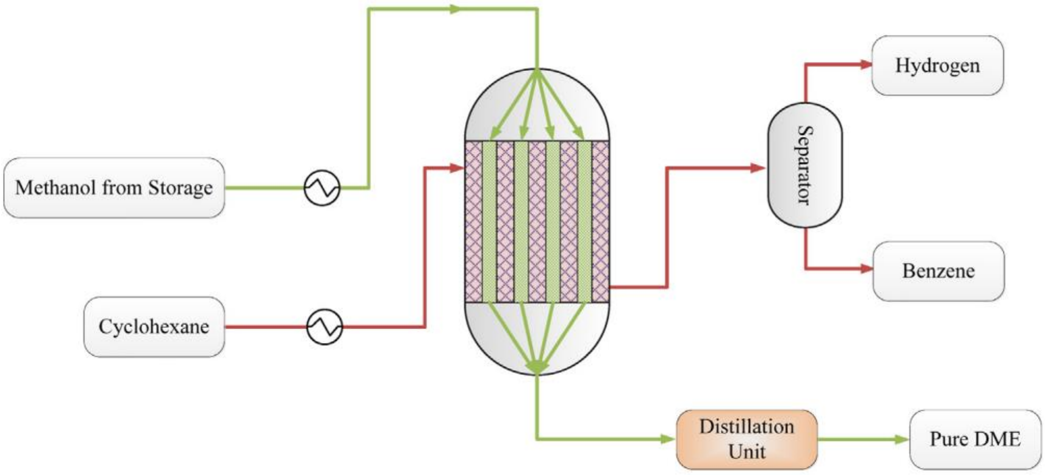


Figure 1.11 Thermally coupled reactor configuration [29].

Process

Traditionally, DME is produced in two steps: the first consists in methanol production from syngas, while the second is methanol dehydration to dimethyl-ether. Before being fed to the reactor methanol is separated from the product mixture. The dehydration reactor is filled with a solid acidic catalyst that catalyses reaction (1.17).

The two-step process is also called the indirect route for dimethyl-ether production, and it is a simple conversion process, industrially mature. Figure 1.12 shows an example of DME production plant from methanol. Methanol may be procured by an external supply or produced upstream in the same facility.

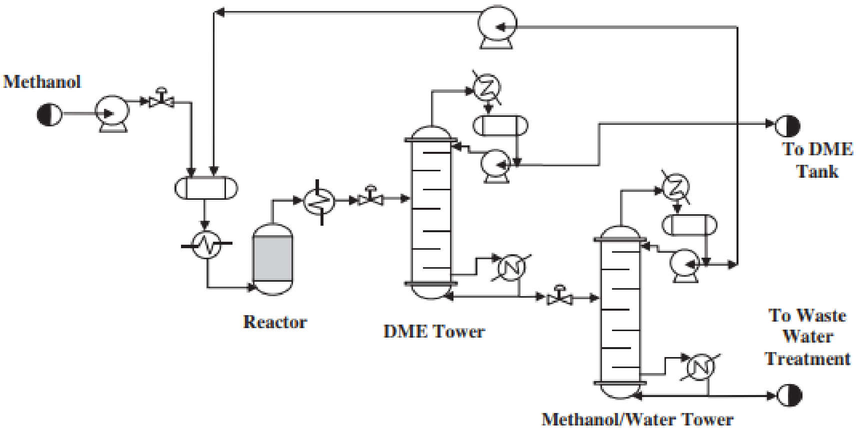


Figure 1.12 Scheme of the DME indirect synthesis process [40].

Between DME, methanol and water, the three species present in the outlet stream of the reactor, dimethyl-ether is the more volatile one. A solution for the distillation layout may consist in a first distillation column with separate DME from the top, and a second distillation that separate methanol form the top and wastewater from the bottom. Since the conversion per pass of the reactor is not complete the methanol stream recovered in the separation section can be recycled back to the reactor to increase the yield of the process.

Direct synthesis

The direct route is characterized by the presence of a single reactor where both methanol and DME synthesis occur. The occurring reactions require a bi-functional catalyst, that is able to catalyze both synthesis reactions at the same time. The two functionalities are a metal one to produce methanol from syngas, for example a CZA catalyst, and an acid one to dehydrate methanol to DME, such as γ-Al_2O_3. In a direct process reactor four reactions occur: CO hydrogenation, CO_2 hydrogenation, r-WGS and methanol dehydration, already presented in the previous sections. The introduction of the last reaction helps to overcome the equilibrium constraint of the methanol synthesis reactions, since it consumes methanol in order to produce DME. Direct synthesis is favored at temperatures between 240-260 °C and pressure between 3-5 MPa.

Figure 1.13 report a scheme for the direct synthesis of dimethyl-ether from syngas.

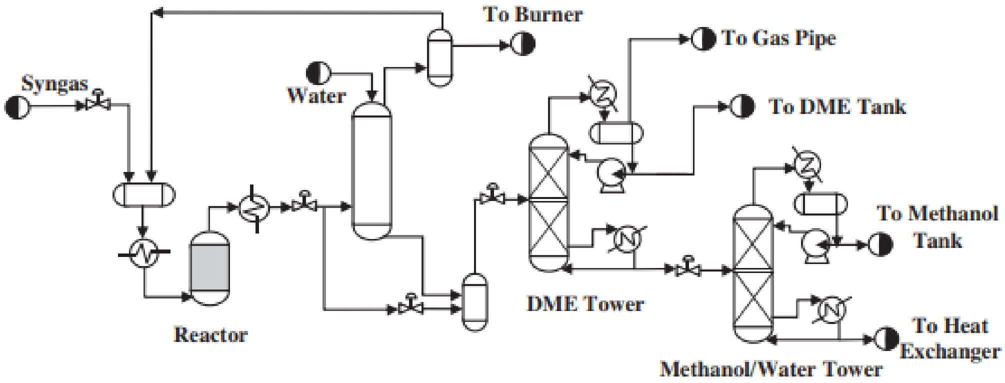


Figure 1.13 Scheme of the DME direct synthesis process [40].

The separation section for the direct DME synthesis is more complicated in comparison to the indirect DME production since it has to account for a more complex mixture. Unreacted syngas, methanol, carbon dioxide are present other than the dimethyl-ether produced in the reactor, with CO_2 being the most challenging chemical to handle in the separation section. Even with the development of new catalyst to intensify CO_2 consumption, the separation will still be consisting in several units and be energy demanding [41].

Literature studies shows that the direct process allows a higher CO conversion, higher DME selectivity and an easier reactor design, but at the same time the separation section becomes more complex.

2 Methods and tools

The tool used to perform the simulations is described in this chapter, along with those used for the economic evaluations.

The implementation of the process simulations described in this work required the use of software such as Aspen HYSYS. To partially automatize the calculation of the information needed to perform the economic comparison a software developed by Prifti et al. [42], called CORO (CAPEX OPEX Robust Optimizer), has been used. Other simpler tools, such as Excel, have also been used.

2.1. Aspen HYSYS

Aspen HYSYS is a commercial chemical process simulator developed by AspenTech. It is used to mathematically model chemical processes ranging from single unit operations to complete plants. Thanks to its user-friendly graphical interface, it is possible to easily model many chemical engineering core operations, such as heat exchangers, columns, reactors, tanks, etc., already implemented on the software from the point of view of the mathematical model and numerical resolution. Once the degrees of freedom of a unit are saturated, the software is able to perform all the relative mass and energy balances, thermodynamic equilibriums, reaction kinetics and so on. The software provides robust and reliable results, based on standard thermodynamic methods and physical data included in property databases. HYSYS is used extensively in industry and academia for steady-state and dynamic simulation, process design, performance modelling, and optimization [43].

2.2. Property methods

A property method is a specialized collection of property calculation routes. All unit operation models require property calculations in Aspen HYSYS to solve them and produce results. Thermodynamic properties include fugacity coefficient, enthalpy, entropy, Gibbs energy and volume; while transport properties comprehend viscosity, thermal conductivity, diffusion coefficient and surface tension. Fugacity is the most requested property for thermodynamic equilibrium (flash calculation) and enthalpy calculation is also frequently requested. A mass and heat balance, indeed, can frequently be calculated using fugacities and enthalpies only. Moreover, additional thermodynamic properties (and transport properties, if required) are calculated for all process streams. Property calculation highly impacts on the calculation result. Hence, it is important to choose the proper property method for the specific application. The property models fall into the following categories:

- Thermodynamic property methods;
- Transport property methods;
- Nonconventional component enthalpy calculation.

The category of thermodynamic property methods includes two methods calculating the vapor-liquid equilibrium (VLE): the equation-of-state method and the activity coefficient method. Using the equation-of-state method, all properties can be derived from the equation of state, for both phases. Using the activity coefficient method, the vapor phase properties are derived from an equation of state, exactly as in the equation-of- state method. However, the properties of the liquid are determined from the sum of the pure component properties to which a mixing term or an excess term is added. The program generates accurate and trustworthy predictions based on conventional thermodynamic methodologies and physical data found in property databases. Cubic Equation of State models have proven to be very reliable in predicting the properties of most hydrocarbons over a wide range of operating conditions [44]. The property package used in this study is SRK, which uses the Soave-Redlich-Kwong (SRK) cubic equation of state for all thermodynamic properties with the option of improving liquid molar volume through volume correction.

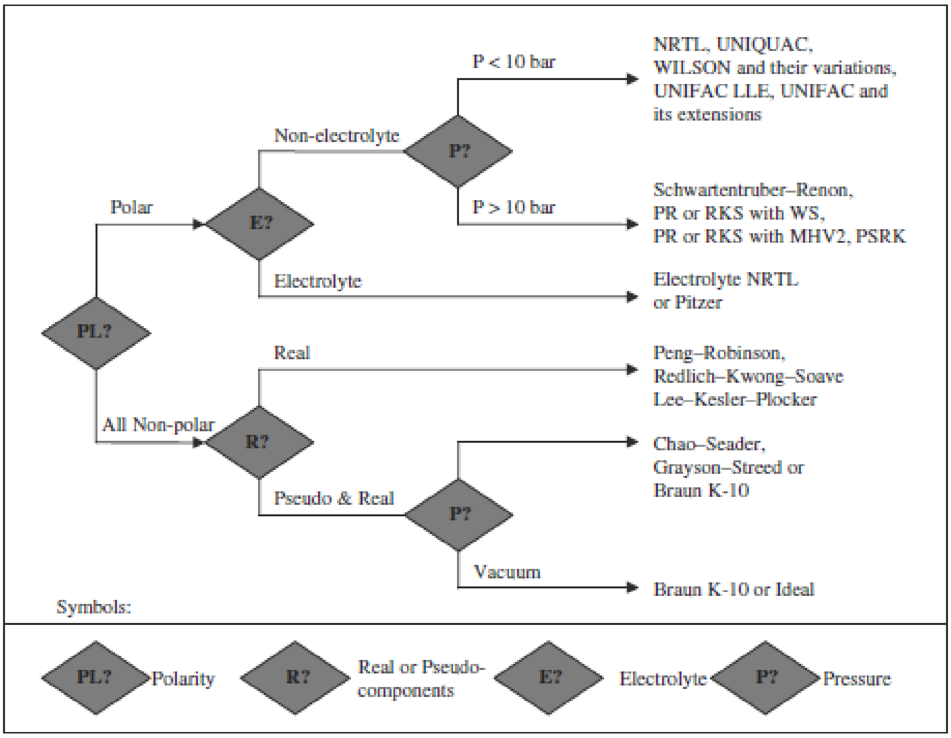


Figure 2.1 Available thermodynamic models in commercial process simulators and an example of a selection tree for choosing appropriate thermodynamic model depending on the type of compounds involved.

Looking at Figure 2.1 from Kontogeorgis et al. [45], in fact, the decision on the appropriate property method can be related to the fact that DME, methanol and water make a polar, non-electrolytical mixture and that the pressure is higher than 10 bar. SRK is chosen among the possible adequate alternatives. This property package is recommended for gas-processing, refinery, and petrochemical applications since reasonable results at all temperatures and pressures can be expected. Indeed, the SRK property method is consistent in the critical region, while results in the region close to the mixture critical point are least accurate. Therefore, unlike the activity coefficient property methods, it does not exhibit anomalous behavior.

2.3. Kinetic model

Two kinetic models are considered in this study: one for methanol synthesis and one for dimethyl-ether synthesis.

2.3.1. Methanol synthesis kinetics

The methanol synthesis kinetics is derived from an article written by Bisotti et al [31] in which they refitted the kinetics parameters of the models presented by Graaf et al. [32] and Bussche et al. [46] in order to overcome theirs shortcomings in particular operating conditions.

The kinetic model is represented by reactions (2.1), (2.2) and (2.3).

$$CO + 2H_2 \leftrightarrow CH_3OH \qquad \Delta H_{298K} = -90.8\, kJ/kmol \tag{2.1}$$

$$CO_2 + H_2 \leftrightarrow CO + H_2O \qquad \Delta H_{298K} = +41.0\, kJ/kmol \tag{2.13}$$

$$CO_2 + 3H_2 \leftrightarrow CH_3OH + H_2O \qquad \Delta H_{298K} = -49.6\, kJ/kmol \tag{2.3}$$

In Table 2.1, the rates of the three reactions reported above are presented.

Table 2.1 kinetic model for methanol synthesis on CZA catalyst.

reactions	**rates**
$CO_2 + 3H_2 \leftrightarrow CH_3OH + H_2O$	$r_{CO_2/MeOH} = \dfrac{k_1 K_{CO_2}\left(f_{CO_2} f_{H_2}^{3/2} - \dfrac{f_{MeOH} f_{H_2O}}{f_{H_2}^{3/2} K_{eqCO_2}}\right)}{DEN}$
$CO_2 + H_2 \leftrightarrow CO + H_2O$	$r_{RWGS} = \dfrac{k_2 K_{CO_2}\left(f_{CO_2} f_{H_2} - \dfrac{f_{H_2O} f_{CO}}{K_{eqRWGS}}\right)}{DEN}$
$CO + 2H_2 \leftrightarrow CH_3OH$	$r_{CO/MeOH} = \dfrac{k_3 K_{CO}\left(f_{CO} f_{H_2}^{3/2} - \dfrac{f_{MeOH}}{f_{H_2}^{1/2} K_{eqCO}}\right)}{DEN}$
$DEN = \left(1 + K_{CO} f_{CO} + K_{CO_2} f_{CO_2}\right)\left(f_{H_2}^{1/2} + \left(K_{H_2O}/K_{H_2}^{1/2}\right) f_{H_2O}\right)$	

While the kinetic parameters and adsorption constants introduced are reported in

Table 2.2.

Table 2.2 kinetic parameters and adsorption constant of the kinetic model for methanol synthesis on CZA catalyst

Kinetic parameters	Adsorption constants
$k_1 = 9.205 \times 10^1 e^{-45889/RT}$	$K_{CO_2} = 1.540 \times 10^{-3} e^{14936/RT}$
$k_2 = 4.241 \times 10^{13} e^{-149856/RT}$	$K_{CO} = 8.206 \times 10^{-9} e^{76594/RT}$
$k_3 = 2.240 \times 10^7 e^{-106729/RT}$	$K_{H_2O/K_{H_2}^{1/2}} = 3.818 \times 10^{-9} e^{97350/RT}$

Where activation energies are expressed in [J/mol].

2.3.2. Dimethyl-ether synthesis kinetics

For the dimethyl ether synthesis, the kinetic model on alumina catalyst derived by Bercic et al. [38] was analyzed. The kinetics of the reaction include only the methanol dehydration to DME as represented in reaction (2.4).

$$2CH_3OH \rightarrow CH_3OCH_3 + H_2O \qquad \Delta H_{298K} = -32.4\, kJ/kmol \tag{2.4}$$

Reaction (2.5) Table 2.1describe the rate of the methanol dehydration reaction reported above (2.4).

$$r_M(T, C_i) = \frac{k_s K_M^2 (C_M^2 - C_W C_E / K)}{\left(1 + 2\sqrt{K_M C_M} + K_W C_W\right)^4} \tag{2.5}$$

Parameters for the kinetics introduced are reported in Table 2.3

Table 2.2.

Table 2.3 kinetic parameters and adsorption constant of the kinetic model for methanol synthesis on CZA catalyst

k_s	$5.35 \cdot 10^{13} exp\left(\frac{-17280}{T}\right)$
K_M	$5.39 \cdot 10^{-4} exp\left(\frac{8487}{T}\right)$
K_W	$8.47 \cdot 10^{-2} exp\left(\frac{5070}{T}\right)$

In the simulation, however, this kinetics behaved numerically unstable: the conversion of the reaction dropped down to zero when the operating conditions were slightly adjusted. Hence, the decision to model the reactor with a Gibbs Reactor was made. The Gibbs Reactor calculates the exiting compositions so that the phase and chemical equilibria of the outlet streams are achieved. The condition that the Gibbs free energy of the reacting system is minimal at equilibrium is used to calculate composition of the product mixture. Therefore, it is not necessary to use a specified reaction stoichiometry to compute the outlet stream composition. The methodology used in this work to size this type of reactor will be presented in Section 0.

2.4. CAPEX OPEX Robust Optimizer

CORO is a software that collects economic libraries such as the Turton handbook library [47], used for the economic comparison, and uses Aspen HYSYS as the simulation package to estimate the input variable of the economic correlations. Excel, instead, is used both as graphical user interface and as a data extraction tool from Aspen HYSYS [42]. The correctness of the algorithm was validated by a parallel manual calculation of those same parameters for the Methanol plant. Since the CORO's results were in accordance with the manuals one, the Dimethyl-ether plant values were calculated only by the program.

2.5. Economic analysis

The aim of this work is to compare methanol production and DME production. To do this, an economic evaluation of the two processes was conducted. The methodology used to develop the economic analysis is presented in this section and uses the Turton handbook [47] as a reference to estimate the cost of the plants, which are divided into:

- capital expenditure (CAPEX);
- operational expenditure (OPEX).

CAPEX, or capital costs, are the costs concerning the construction of the physical plant and must take into consideration many costs other than the purchased cost of the equipment. OPEX, instead, are the operating costs needed to run a plant including raw materials, utilities, catalyst replacement, wages, and all administrative costs.

2.5.1. CAPEX

The Module Costing Technique introduced by Guthrie is often regarded as one of the most appropriate methods to estimate the cost of a new chemical plant, so it was chosen as the method to evaluate the capital expenditure of the two plants.

The cost of a plant includes the cost of purchasing the equipment and the expenditure associated with making the units operative (i.e., installation, civil works, instrumentation, insulation, etc.).

This costing technique relates all costs to the purchased cost of equipment evaluated for some base conditions. Deviations from these conditions are handled by applying specific multiplicative factors depending on:

1. The specific equipment type;
2. The specific system pressure;

3. The specific construction material.

The first step of the procedure requires the use of Equation (2.6) to evaluate the purchased cost for base conditions c_p^0.

$$\log_{10} c_p^0 = K_1 + K_2 \log_{10}(A) + K_3[\log_{10}(A)]^2 \tag{2.6}$$

Where K_1, K_2 and K_3 are parameters specific of each equipment and A is the capacity or size parameter of the equipment. The term "base conditions" refers to a near-ambient operating pressure and the most common base material, usually carbon steel (CS).

Equation (2.7) allows the calculation of the bare module cost C_{BM} for each single unit.

$$C_{BM} = F_{BM} C_p^0 \tag{2.7}$$

Where F_{BM} is the bare module cost factor, a multiplication factor that accounts for the items in Table 2.4 and the specific materials of construction and operating pressure. Therefore, the bare module cost considers both direct and indirect costs related to the project.

Table 2.4: Factors Affecting the Costs Associated with Evaluation of Capital Cost of Chemical Plants [47].

Direct project expenses	
Equipment free on-board cost	C_P
Materials required for installation	C_M
Labor to install equipment and material	C_L
Indirect project expenses	
Freight, insurance and taxes	C_{FIT}
Construction overhead	C_O
Contractor engineering expenses	C_E
Contingency and fee	
Contingency	C_{Cont}
Contractor fee	C_{Fee}
Auxiliary facilities	
Site development	C_{Site}
Auxiliary buildings	C_{Aux}
Off-sites and utilities	C_{Off}

As the pressure at which a piece of equipment operates increases, so does the thickness of the walls of the equipment, resulting in a more expensive unit.

The pressure factor F_P for process vessels is evaluated using Equation (2.8)(2.8).

$$F_{P,vessel} = \frac{\frac{(P+1)D}{2[850-0.6(P+1)]}+0.00315}{0.0063} \tag{2.8}$$

It is also assumed that the vessel is designed with a minimum wall thickness of 6.3 mm (1/4 inch), imposing 1 as the minimum pressure factor. A minimum wall thickness is required to ensure that the vessel does not buckle under its own weight or when being transported.

Pressure factors for different equipment such as heat exchangers are presented by Equation (2.9):

$$\log_{10} F_P = C_1 + C_2 \log_{10}(P) + C_3[\log_{10}(P)]^2 \tag{2.9}$$

Where the pressure P is expressed in bar gauges.

Finally, some equipment is unaffected by pressure. Examples are tower packing and trays.

To account for the cost of different materials, it is necessary to use the appropriate material factor, F_M, in the bare module factor reported in [47].

For heat exchangers, process vessels, and pumps the bare module cost is evaluated with equation (2.10).

$$C_{BM} = F_{BM}C_p^0 = C_p^0(B_1 + B_2F_MF_P) \tag{2.10}$$

Where B_1 and B_2 are specific for each piece of equipment.

For other units the bare module cost correlations are listed in Table 2.5Table 2.4.

Table 2.5: Equations for Bare Module Cost for some Equipment

Compressors and blowers without drives	$C_{BM} = C_p^0F_{BM}$
Sieve trays	$C_{BM} = C_p^0NF_{BM}F_q$ Where N is the number of trays and F_q is a quantity factor for trays only given by $\log_{10} F_q = 0.4771 + 0.08516\log_{10}(N) - 0.3473[\log_{10}(N)]^2$ for N<20 $F_q = 1$ for N $\geq$ 20
Tower packing	$C_{BM} = C_p^0F_{BM}$

When the size parameter A of an equipment falls outside the validity range of its correlation present in [47], it is not possible to extrapolate the relationship to evaluate the purchased cost for base conditions. Instead, what can be done is to use Equation (2.11) to establish a valid relationship between the purchased cost C and an attribute of the equipment related to units of capacity A.

$$\frac{C_a}{C_b} = \left(\frac{A_a}{A_b}\right)^n \tag{2.11}$$

Where a and b represent the two different sizes of the unit while n is the cost exponent.

The equipment cost attribute represents the parameter used to correlate the capital cost of each piece of equipment. The cost exponent may vary between equipment, but in this study the value of $n = 0.6$ is adopted for each piece of equipment that need this calculation. This value is the typical one used in Chemical engineering since most of the equipment has a cost exponent close to it.

This equation shows a concept known as the economy of scale, which leads to the generalization: the larger the equipment, the lower the cost of it per unit of capacity.

The purchased cost is evaluated with correlations for price information from [47], which use parameters fitted using values updated to 2001. Therefore, it is necessary to update them to take changing economic conditions, like inflation, into account. Equation (2.12) can be used to achieve this:

$$C_2 = C_1\left(\frac{I_2}{I_1}\right) \tag{2.12}$$

Where I represent the cost index, C the purchased cost and 1, 2 the different time instants.

There are several cost indices used by the chemical industry, in this case the Chemical Engineering Plant Cost Index (CEPCI) is used to adjust for the effects of inflation.

The CEPCI index is a composite value that reflects inflation in a combination of goods and services related to the chemical process industry. In Table 2.6 the CEPCI values for 2001 and 2017 are listed.

Table 2.6: 2001 and 2017 CEPCI indexes

2001	397
2017	607.5

Year 2017 is chosen as the year of the comparison because a complete overview of the cost of all the utilities and prices was available and trustable and was also the one implemented in the CORO. Year 2017 also avoids uncertainties in prices characteristic of the last few years, due to the COVID-19 pandemic before and the present political instabilities now.

Once the bare module cost of each piece of equipment is evaluated, to estimate the total capital expenditure, other costs must be considered other than the direct and indirect costs. These additional costs can be divided into two groups:

- contingency and fee costs: the contingency cost depend on the reliability of the cost data and the completeness of the available process flowsheet. This factor is included in the cost evaluation as a protection against oversights and faulty information. Values of 15% and 3% of the bare module cost are assumed for contingency costs and fees, respectively, unless otherwise stated. These are appropriate values for well understood systems. Adding these costs to the bare module cost provides the total module cost C_{TM} as reported in Equation (2.13);
- auxiliary facilities costs: these include the cost for site development, auxiliary buildings, off-sites and utilities. These terms are generally independent from the materials of construction and the operating pressure of the process. A review of costs for these auxiliary facilities results in a range of approximately 20% to more than 100% of the bare module cost. Unless otherwise stated, these costs are assumed to be equal to 50% of the bare module costs for the base case conditions $C^0_{BM,i}$. Adding these costs to the total module cost provides the grassroots cost C_{GR} as stated in Equation (2.14)(2.13).

$$C_{TM} = \sum_{i=1}^{n} C_{TM,i} = 1.18 \sum_{i=1}^{n} C_{BM,i} \tag{2.13}$$

$$C_{GR} = C_{TM} + 0.5 \sum_{i=1}^{n} C^0_{BM,i} \qquad (2.14)(2.13)$$

The term grassroots (or green field) refers to a completely new facility in which the construction is started on essentially undeveloped land, a grass field. The term total module cost refers to the cost of making small to moderate expansions or alterations to an existing facility. Depending on the project, the fixed capital investment FCI may consist of either the total module cost or the grass-roots cost.

The last element required to calculate the total capital investment TCI as in Equation (2.16) is the working capital cost W_{CAP}, which accounts for all the labor required to get the facility operational. The W_{CAP} is commonly considered as from 15 to 20% of the FCI; in this study the value reported in Equation (2.14) is used.

$$W_{CAP} = 0.175\, C_{GR} \tag{2.14}$$

$$TCI = C_{GR} + W_{CAP} \tag{2.16}$$

2.5.2. OPEX

Cost of manufacture (COM) or OPEX is computed as the sum of these three categories.

Operating costs are influenced by many elements; the most important contributions are the cost of utilities (steam, cooling water, electric power, fuel gas, oil, etc.) and of raw materials, but OPEX considers many other terms. Table 2.7 subdivides the OPEX contributions into:

- Direct Manufacturing Costs (DMC): expenses that vary with the rate of production;
- Fixed Manufacturing Costs (FMC): costs not affected by the level of production;
- General Expenses (GE): costs associated with management-level and administrative activities not directly related to the manufacturing process.

Cost of manufacture (COM) or OPEX is computed as the sum of these three categories as stated in equation (2.16):

$$COM = DMC + FMC + GE \tag{2.16}$$

The cost of manufacturing, COM can be determined throughout Equations (2.17), (2.18) and (2.19) when the following costs are known or can be estimated:

- Fixed capital investment (FCI): (C_{TM} or C_{GR});
- Cost of operating labor (C_{OL});
- Cost of utilities (C_{UT});
- Cost of waste treatment (C_{WT});
- Cost of raw materials (C_{RM}).

$$DMC = C_{RM} + C_{WT} + C_{UT} + 1.33C_{OL} + 0.069FCI + 0.03COM \tag{2.17}$$

$$FMC = 0.708C_{OL} + 0.068FCI + depreciation \tag{2.18}$$

$$GE = 0.177C_{OL} + 0.009FCI + 0.16COM \tag{2.19}$$

From the equations reported above the total manufacturing cost can be obtained by summing the three cost categories together, leading to Equation (2.20), in which the cost of manufacture is evaluated without depreciation.

$$COM = 0.18FCI + 2.73C_{OL} + 1.23(C_{RM} + C_{WT} + C_{UT}) \tag{2.20}$$

To evaluate the direct costs, two types of information are required: utility prices and annual usage derived from Aspen HYSYS simulations. The number of operating hours in a year is set to be equal to 8760.

Table 2.7: Factors Affecting the Cost of Manufacturing (COM) for a Chemical Product [47].

Direct costs DMC	
Raw materials	C_{RM}
Waste treatment	C_{WT}
Utilities	C_{UT}
Operating labor	C_{OL}
Direct supervisory and clerical labor	
Maintenance and repairs	
Operating supplies	
Laboratory charges	
Patents and royalties	
Fixed costs FMC	
Depreciation	
Local taxes and insurance	
Plant overhead costs	
Contingency and fee	
Contingency	C_{Cont}
Contractor fee	C_{Fee}
General expenses GE	
Administration costs	
Distribution and selling costs	
Research and development	

Operating labor

The process plants presented in this work are small scale plants. The number of operators needed to operate projects of this size is overestimated in correlations like the one presented in in the Turton handbook [47]. Unit operations like the ones present in the two process plants do not need the constant supervision of a specialized operator. Plants like those in this study can virtually work automatically, with all the important operative parameters measured and controlled by the instrumentation. Therefore, the decision to not follow the directions reported in the [47] about the evaluation of the cost of the operating labor has been made.

Neglecting the operating labor cost is not an uncommon choice in the feasibility analysis with this level of detail performed in the Chemical engineering field.

Raw materials

Both plants have the same amount of syngas as raw material. However, the syngas used is not produced starting from a fossil source, but from biogas. While the cost of biogas is not hard to determine [11], the cost of syngas produced from biogas is difficult to evaluate. This is since usually syngas is not sold as a product by companies, but it is used right after being produced to convert it into more valuable chemicals, such as methanol or dimethyl-ether. An attempt to determine a trustable and realistic price for syngas from this specific renewable source was done, but the extrapolation of information from different publications as [48] and [49] without exactly knowing which assumptions, simplifications, and operating conditions were used lead to unrealistic values. The design of the syngas production plant from biogas is out of the scope of this study, since the aim is to determine if, for a plant of this size, it is more profitable to sell a bulk product (methanol) or process it to produce DME and sell a higher value good. Since the feasibility of the methanol and DME plants are not uncertain, the decision to perform a comparison without the cost of the raw materials was made. Even though raw materials costs are usually an important contributor to operative costs, this simplification is not impacting on the final result of the analysis, but the quantitative value of the plants that are presented in the following chapters will not reflect the actual profit.

Another simplification introduced in the analysis is neglecting capital and operative costs of the hydrogen membrane since economic correlations for this category of equipment are not present in the Turton handbook [47] and the design of the unit cannot be performed by the simulation software. The reason behind the choice to anyway consider this equipment in the design is reported in Section 3.1. The differential economic analysis outcome is not significantly impacted by this simplification since this equipment is identical in the two plant configurations.

The raw materials cost term is, however, not null, since in this category the replacement of the catalyst should also be considered.

The cost of the CZA catalyst used in the Methanol synthesis and the alumina catalyst employed in the DME synthesis are summarized in Table 2.8 along with the expected lifespan.

Table 2.8 cost of the catalysts used in the two reactors.

catalyst	cost	unit of measure	lifespan [years]
CZA	16 [50]	[$/kg]	3-4 [51]
γ-Al_2O_3	3 [50]	[$/kg]	3-4

For the alumina catalyst the same lifespan of the CZA catalyst was considered since the of catalyst are similar to each other.

Utilities

Utility costs are a fundamental term that affects operating costs and plant feasibility.

The external utilities required for the two plants are:

- Electricity: electricity is required to move pumps and compressors.
- Cooling water: a make-up of cooling water is indispensable to compensate for the cooling water lost during evaporation in the cooling tower. Cooling water is used as cooling utility in the condensers. It is available at 20°C and can be heated up to 30°C.
- Process water: necessary to bring superheated low-pressure steam to saturation temperature and to perform the methanol washing from the light ends stream. The cost of process water is considered equal to the one of the cooling water.
- LP steam: saturated steam at 6 bar, used as hot utility in the reboilers.
- HP steam: saturated steam at 42 bar, used to close the vapor cycle and to heat the inlet reactors stream to the desired temperature.

The price of utilities is affected by market oscillations which are directly influenced by the cost of oil. Oil quotations, indeed, directly impact the price of electricity and steam. To be conservative, multiple scenarios should be investigated to forecast the variations in utility costs, which can highly change during the life of the plant. However, it is a very dispendious job, and it requires sophisticated tools.

The cost of all the utilities required to operate the two process plants are taken from the Turton Handbook [47] and are reported in Table 2.9. These costs represent average values throughout United States.

Table 2.9 2017 cost of utilities provided by off-sites for a plant with multiple process units.

utility	**cost**	**Unit of measure**
electricity	0.06	[$/kWh]
cooling water	0.0000148	[$/kg]
low pressure steam	0.0277	[$/kg]
high pressure steam	0.02997	[$/kg]

Waste treatment

Both Methanol and Dimethyl-ether synthesis plants do not produce a significant amount of waste. The only waste, indeed, is wastewater. Wastewater is the outlet bottom stream of a distillation column for the separation of methanol, and it should require a treatment before releasing into the environment since traces of methanol are present in it. A cost is associated to every waste stream in order to consider those treatments. To not uselessly complicate the economic comparison, this type of cost was not considered.

2.5.3. Depreciation

The physical plant, constituted by equipment and buildings, associated with a chemical process plant has a finite life. The value of this physical plant decreases with time. Some of the equipment wears out and must be replaced and even if the equipment is seldom used and is well maintained, it becomes obsolete and of little value over time. Therefore, when the plant is closed, the plant equipment can be salvaged and sold for only a fraction of their original cost. The cash flows associated with the purchase and installation of equipment are expenses that occur before the plant is operational. This results in a negative cash flow on a discrete cash flow diagram. When the plant is closed, equipment is salvaged, and this results in a positive cash flow at that time. The difference between these costs represents capital depreciation. For tax purposes, the government does not allow companies to charge the full costs of the plant as a onetime expense when the plant is built. Instead, it allows only a fraction of the capital depreciation to be charged as an operating expense each year until the total capital depreciation has been charged [47]. Depreciation is introduced for the benefit of the plant owner since it reduces the taxable income and decreases taxes to be paid, especially at the initial running period when profit is lower and typically a huge investment was made to build the plant.

First, the terms that are used to evaluate depreciation are introduced and defined.

- Fixed Capital Investment FCI_L represents the depreciable capital investment. It is the fixed capital investment necessary to build the plant minus the cost of land. Working capital cannot be depreciated.
- Salvage Value, S represents the fixed capital investment of the plant, minus the value of the land, evaluated at the end of the plant life. In this work, this value is set to zero since the economic analysis is performed only with a horizon of 10 years, and not until the actual closure of the plant.
- Life of the Equipment, n does not reflect the actual working life of the equipment but rather the time allowed for equipment depreciation. In this work, the life of all the pieces of equipment was considered equal to 10 years.
- Yearly Depreciation represents the amount of depreciation per year. The amount allowed in the kth year is denoted d_k.
- Book Value BV_k represents the amount of the depreciable capital that has not yet been depreciated and its expression is reported in Equation (2.21).

$$BV_k = FCI_L - \sum_{j=1}^{k} d_j \tag{2.21}$$

There are multiple strategies to consider depreciation. The easiest way is the straight-line depreciation method, SL. According to this method, an equal amount of depreciation is charged each year over the depreciation period allowed. This method is the one chosen to represent depreciation in this study and described through Equation (2.22).

$$d_k^{SL} = \frac{[FCI_L - S]}{n} \tag{2.22}$$

2.5.4. Revenues

To evaluate annual revenues, it is necessary to know the sale prices of the plant's products and multiplying it for the annual productivity of the plants. Even if the first designed plant aims to produce methanol and the second dimethyl ether, methanol and DME are not the only valuable outlet streams. In both plants there are two different types of by-products: vent gases and light ends. The vent gases stream is a purge required to avoid the blanketing due to build up of inert in the hydrogen recycle to the methanol reactor; while light ends consist in the light impurities separated from methanol during methanol purification. These two streams are by-products because thanks to their composition they can be burned to recover energy.

For simplicity this additional source of value is not considered in the economic analysis and therefore methanol and DME represent the only sources of revenues. The product streams, in fact, are designed to respect the specifications required by the market and therefore they can be sold at their market price.

Methanol price, as well as DME price oscillates over time, being bound to oil quotations. For simplicity, the prices for methanol and DME ware considered constant over the years. The average price of the year 2022 for the European market was chosen to evaluate the revenues of the plants. Table 2.10 summarize these prices.

Table 2.10 Methanol and Dimethyl-ether average price in Europe during 2022.

chemical	Cost [$/kg]
Methanol	0.45 [52],[53]
Dimethyl-ether	1.25 [54]

The year 2022 was chosen as a compromise to well describe the forecasted trend of the price of the two chemicals for the next few years.

Even if, for example, in Italy the inter-ministerial decree of March 2nd, 2018 promotes the use of biomethane and other advanced biofuels in the transport sector with the introduction of government incentives for maximum duration of 10 years [30], in this comparison the choice to not consider this type of incentive for the DME plant was made. This is due to the fact that even if the decree considers the DME as an advanced biofuel and therefore eligible to the incentive, it is better for a company to not relate to much on them.

Among the different analyses present in this work, at the end a market analysis will be performed. Some of the indicators will be calculated again, changing the price of the two products according to their value in a market different from the European one. The other geographical locations investigated are United States and China. Table 2.11 contains the average price of the year 2022 of the two chemicals according to the United States market and the Chinese market.

Table 2.11 Methanol and Dimethyl-ether average price in United States and China during 2022 [52] [54].

market	chemical	Cost [$/kg]
United States	Methanol	0.45
	Dimethyl-ether	2.15
China	Methanol	0.33
	Dimethyl-ether	0.75

2.5.5. Project cash flow

To evaluate the feasibility of a project, the cash flow diagram is an important tool that provides a clear view of what could be the profit during the plant's lifetime. At any time, the net cash flow is the difference between the earnings and expenditure.

A cash-flow diagram, such as that shown in Figure 2.2, shows the forecasted cumulative net cash flow over the life of a project.

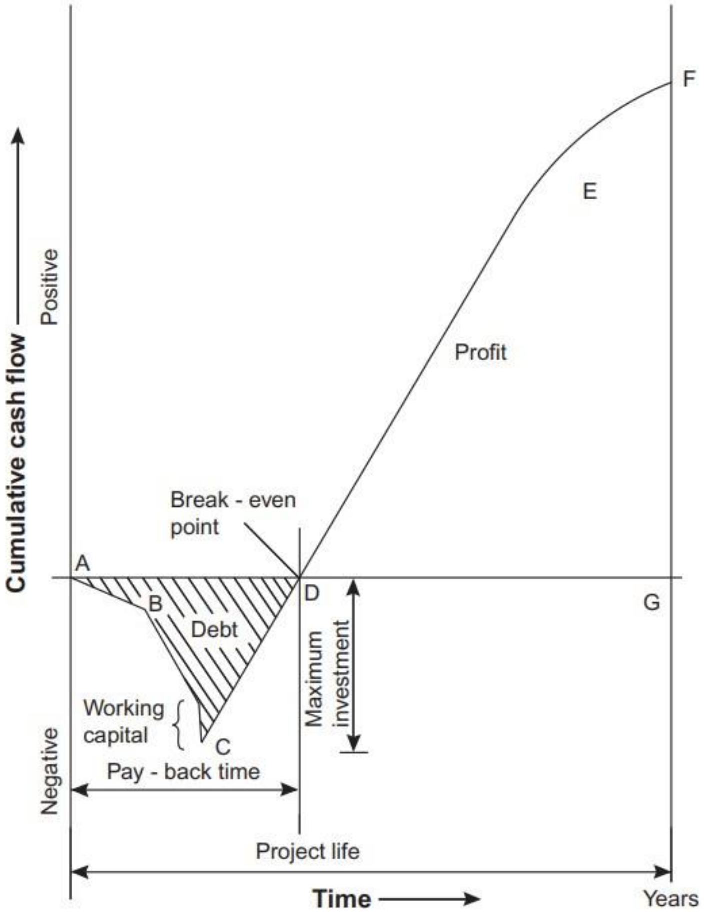


Figure 2.2 Project cash flow diagram [55].

The cash flows are based on the best possible estimates of capital investment, operating costs, sales volumes, and sales prices that can be made for the project. A cash-flow diagram clearly shows the resources needed for the project and the timing of the revenues. The diagram can be divided into the following distinct regions:

- A–B: Investment required to design the plant;
- B–C: Flow of capital required to build the plant and provide funds for start-up, including working capital;
- C–D: Cash-flow curve rises at C, as the process starts up and the sales generate revenues. The net cash flow is now positive, but the cumulative amount will remain negative until the investment is paid off (point D). Point D is known as the break-even point and the time it takes to reach the break-even point is called the pay-back time;
- D–E: Cumulative cash flow is positive. The project gives a return on the investment;
- E–F: Toward the end of project life, the slope of the curve changes as the rate of cash flow tend to decline due to higher operating costs and lower sales volumes

and prices due to equipment obsolescence. Point F represents the final cumulative net cash flow at the end of the project life.

To have a clear overview of the economic outcomes of the two alternatives a typical strategy is to calculate and then compare some economic indicators. The indicators chosen in this study are reported and described in the following sections.

2.5.5.1. Payback time

Payback time (PBT) is the simplest of the indicators used in the analysis. Payback time is easily estimated by dividing the total initial capital investment (fixed and working capital) by the average annual cash flow as in (2.23).

$$PBT = \frac{Total\ Investment}{Annual\ Cash\ Flow} \tag{2.23}$$

This is different from the pay-back time introduced in the cash-flow diagram presented in Figure 2.2, as it assumes that all the investment is made in year zero and revenues begin immediately. For most chemical plant projects, this is not realistic as investments are typically spread over one to three years and revenues may not reach 100% of the design basis until the second year of operation. The simple pay-back time also neglects taxes and depreciation.

Therefore, PBT alone is not sufficient to provide a complete economic vision of the process and other indicators were analyzed.

2.5.5.2. Net Present Value

The net present value (NPV) of a project is the sum of the present values of the future cash flows CF_n. It is evaluated with Equation (2.24) thanks to the standard procedure available in manuals as [47] and [55].

$$NPV = \sum_{n=1}^{t} \frac{CF_n}{(1+i)^n} \tag{2.24}$$

Some assumptions considered in the evaluation are stated below:

- A discount rate i was selected equal to 12%;
- Taxes rate T is set equal to the 35% of the taxable income;
- The salvage value of the plant is null;
- The life of the plant is 10 years (t = 10), and it always works at 100% capacity;
- Depreciation d is determined using the straight-line method for 10 years;
- At the end of the project working capital is recovered after taxation and discounting.

Taxes are included in the analysis because the profits generated by most chemical plants are subject to taxation and can have a significant impact on the cash flow of a project. The amount of taxes that must be paid each year is calculated by multiplying the taxable income by the taxation rate. The taxable income is calculated with Equation (2.25).

$$Taxable\ income = Annual\ revenues - Annual\ OPEX - depreciation \tag{2.25}$$

And the non-discounted cash flow CF_n is given by Equation (2.26).

$$CF_n = Annual\ revenues - Annual\ OPEX - taxes \tag{2.26}$$

Another advantage about the Net present value is that it is a more useful economic measure than simple pay-back time since it allows for the time value of money and also for annual variation in expenses and revenues. It has to be reminded that the net present value is always less than the total future worth of the project because of the discounting of future cash flows. NPV indeed answers the statement that money in the future is less valuable with respect to money now.

2.5.5.3. IRR

By calculating the NPV at various interest rates, it is possible to find the interest rate that results in zero cumulative net present value at the end of the project, as shown in (2.27)(2.27). This rate, known as "discounted cash-flow rate of return" (DCFROR) or IRR, is a measure of the maximum interest rate a project could pay and still break even by the end of the project life.

$$\sum_{n=1}^{t} \frac{CF_n}{(1+i')^n} = 0 \tag{2.27}$$

This indicator provides a convenient way to compare the performance of capital for different projects, regardless of the amount of capital used, the life of the plant, or the current interest rates at any given time. A more profitable project may pay a higher IRR.

IRR is a more useful method than NPV when comparing projects of very different sizes. Larger projects usually have a higher net present value than smaller projects, but also a much higher investment.

2.5.6. Size sensitivity

A size sensitivity analysis is performed to have a more comprehensive view of the two investment alternatives. The size sensitivity analysis is performed by studying the same economic indicators explained in the previous sections at different plant capacities. The costs and revenues were calculated with a shortcut method and not from new simulations in Aspen HYSYS. The capital costs are evaluated by correcting the results for the base case studies with the already introduced Equation (2.1) while all the operative costs and revenues were updated using proportions between the production volumes.

2.5.7. Sensitivity analysis

The economic analysis of a project can only be based on the best estimates that can be made of the required investment and the cash flow. The actual cash flow generated in a year will is subject to cost changes and is highly dependent on the sales volume and price. In this study, a sensitivity analysis is performed to examine the impact of prediction uncertainties on plant selection. To perform the analysis, investments and cash flows are first calculated using what are considered the most probable values of various factors, thereby establishing the base case for the analysis. Various parameters of the cost model are then adjusted, assuming a range of errors for each factor. This shows how sensitive the cash flow and economic criteria are to errors and gives an idea of the degree of risk involved in the project [55].

The parameters investigated and the range of variation that is assumed are given in Table 2.12.

Table 2.12 Sensitivity analysis parameters [55].

parameter	Range of variation
Sales price	±20% of base
Production rate	±20% of base
Fixed cost	-20% to + 100% of base
Capital cost	-20% to +50% of base

By varying the rate of production (at constant capital investment and fixed costs) investigates the impact of unexpectedly long down time due to maintenance or operations issues, as well as unexpected difficulties in selling the full volume of product that may be produced. It may also be possible to increase the production rate beyond the design capacity if the plant design margins allow for some extra capacity, or if yields can be improved by using a better catalyst, etc.

3 Simulation design

Through Aspen HYSYS a conceptual design of a Methanol and a Dimethyl-ether production plants starting from syngas made from biogas has been designed. To set up an economic comparison between the two investment alternatives, two different simulations were carried out. Here it is decided to test:

- Production of Methanol: purity 99.85% wt [33] (Methanol Grade A);
- Production of Dimethyl-ether: the methanol produced is converted into DME with a purity of 99% wt. It was chosen to reach a DME purity higher than 98.5% reported by literature [56] due to simplifications in stream composition and reaction set. Indeed, higher alcohols and other low quantity by-products were not considered.

The results of the analysis are reported in Chapter 5.

The methanol plant can be divided into three main sections:

- Methanol synthesis;
- Methanol separation;
- Utilities.

The DME plant configuration is designed starting from the methanol one and then adding the operations required for the DME production. The plant can be divided in four main sections:

- Methanol synthesis;
- Methanol separation;
- DME synthesis and separation;
- Utilities.

Regarding the syngas feedstock composition, it is chosen to consider methane as the only impurity present.

The kinetic scheme chosen to describe the methanol production do not consider side reactions, such as methanol dehydration to DME or hydrocarbon formations. Therefore, even if by-products are experimentally present in traces, they are neglected in these simulations.

In Table 3.1 the component list used in the simulation of the dimethyl ether plant is reported.

Table 3.1 Component list from Aspen HYSYS for the DME plant

component ID	component name	alias	CAS number
CO	Carbon-monoxide	CO	630-08-0
H_2	Hydrogen	H_2	1333-74-0
MeOH	Methanol	CH_4O	67-56-1
CO_2	Carbon-dioxide	CO_2	124-38-9
H_2O	Water	H_2O	7732-18-5
CH_4	Methane	CH_4	74-82-8
N_2	Nitrogen	N_2	7727-37-9
Ar	Argon	Ar	7440-37-1
O_2	Oxygen	O_2	7782-44-7
DME	Dimethyl-ether	C_2H_6O	115-10-6

The CAS number is a unique accession number assigned by the Chemical Abstracts Service (CAS), a division of the American Chemical Society.

The methanol plant's component list is obviously the same except for the absence of DME.

Figure 2.2 and Figure 3.2 depict block flow diagrams of the proposed processes for the two plants studied, excluding the utilities part of the plant, whereas

Figure 3.3 and Figure 3.4 show the global plants in Aspen HYSYS.

The design procedure to arrive at these configurations is explained later in this chapter.

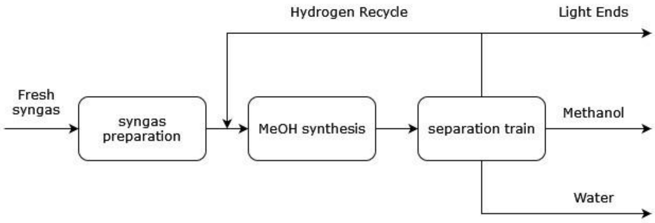


Figure 3.1 Block Flow Diagram of the Process for Methanol synthesis

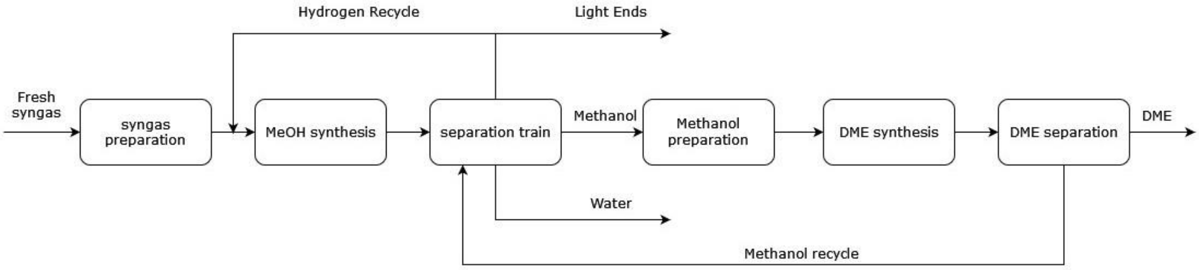


Figure 3.2 Block Flow Diagram of the Process for Dimethyl-ether synthesis

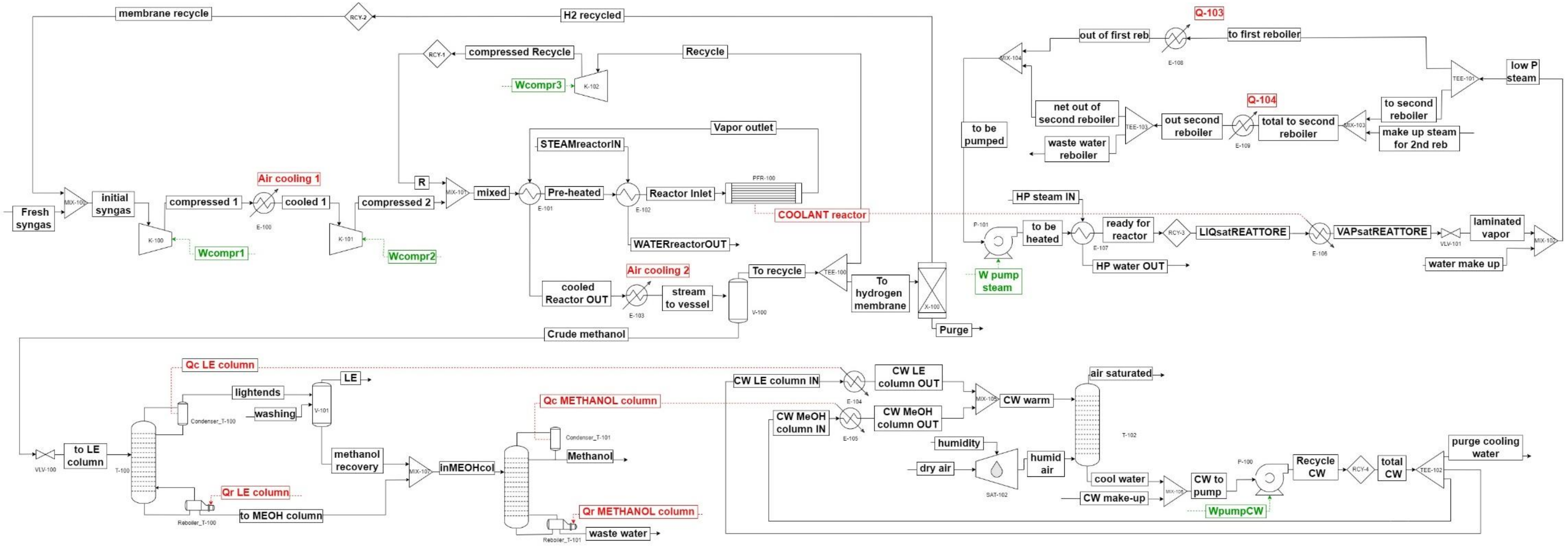


Figure 3.3 Aspen HYSYS scheme for the Methanol plant

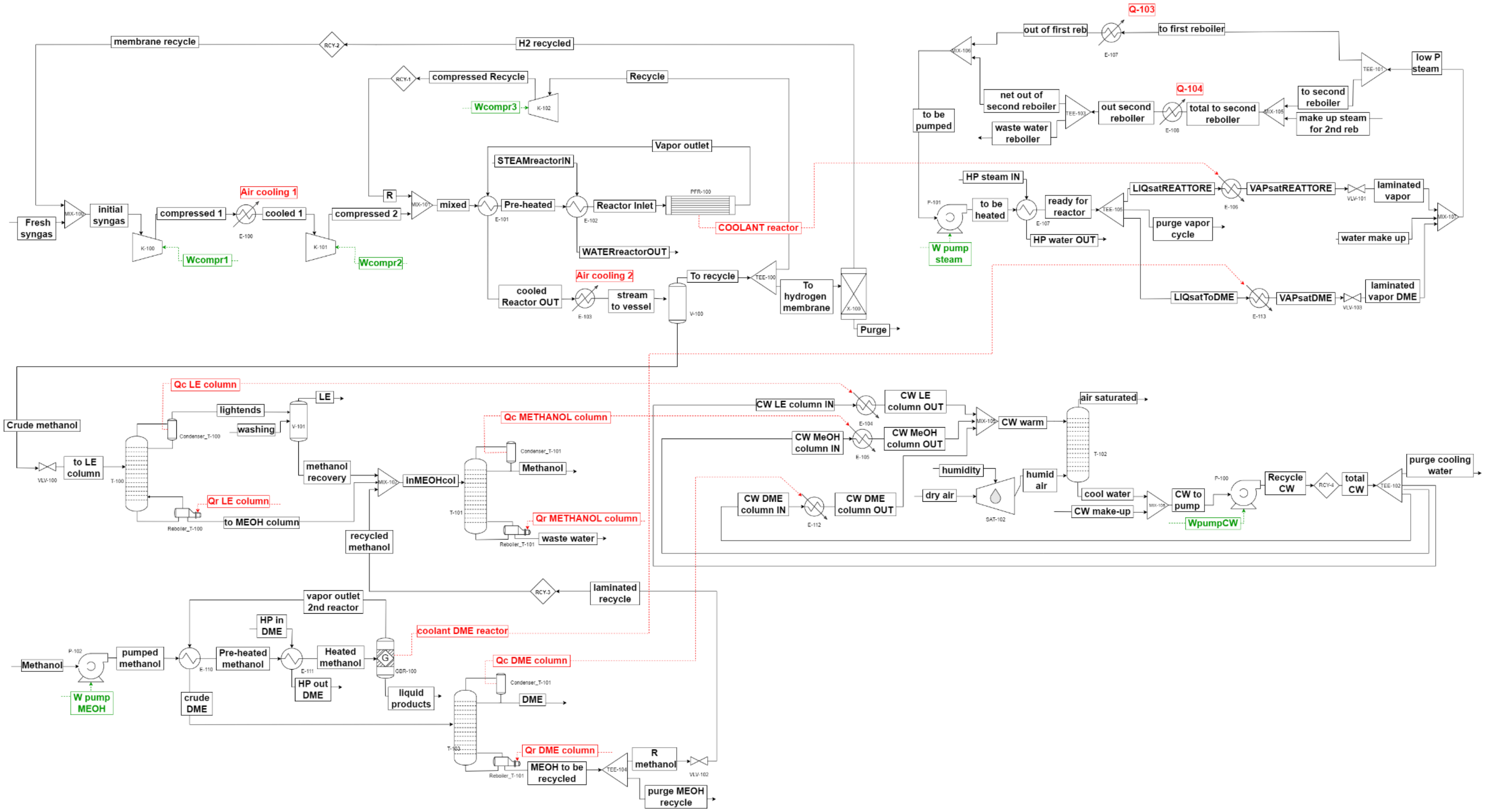


Figure 3.4 Aspen HYSYS scheme for the Dimethyl-ether plant

3.1. Methanol synthesis

Both processes aim to produce methanol, either to sell it or to use it to produce DME.

The starting raw material is syngas produced from biogas. The production of syngas is out of the scope of the thesis and therefore the Aspen HYSYS simulation for syngas production was not implemented.

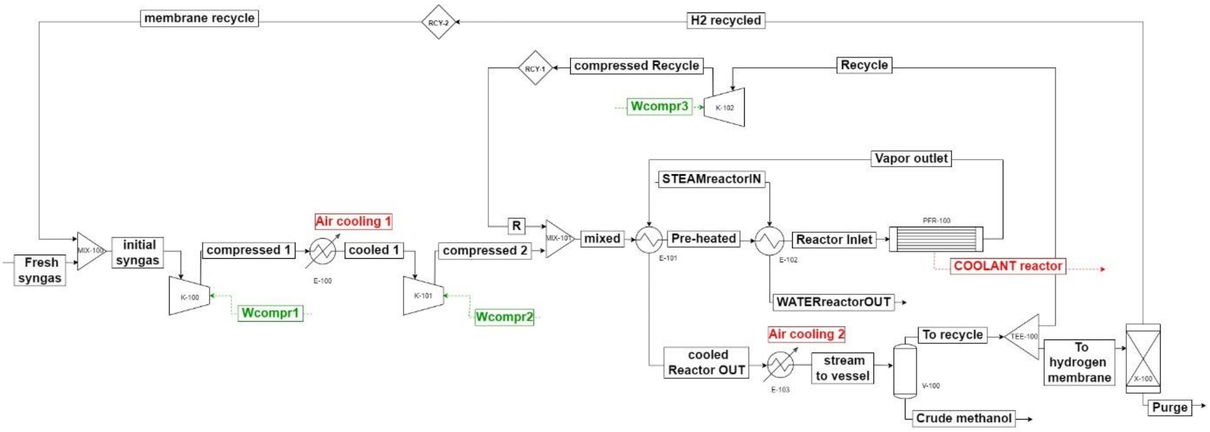


Figure 3.5 Syngas to Methanol plant section on Aspen HYSYS.

In this first plant section, syngas is transformed into methanol. This part is identical for both the configurations.

A stream of 200 kmol/h of syngas at 40 °C and 15 bar, whose component is reported in Table 3.2, represents the raw material of both plants.

Table 3.2 Mass and molar fraction of inlet syngas

component	Molar fraction	Mass fraction
CO	0.2031	0.4706
H_2	0.6628	0.1105
CO_2	0.1041	0.3791
CH_4	0.0300	0.0398

The fresh syngas composition is chosen in order to have the optimal composition at the inlet of the reactor. The parameter used to evaluate the fresh syngas composition will be presented later in this section.

Fresh syngas along with the recycle streams are sent to the reactor for methanol production. As seen in State of the art section , methanol synthesis from syngas is operated with pressure between 50-100 bar and temperature around 200-300°C. An inlet reactor temperature between 235 and 250°C should be selected to respect the range of activity of the catalyst. In this study the methanol reactor is assumed to work at 235°C and 59.80 bar. Thus, syngas feed needs to be compressed and heated.

Since the pressure must be increased up to 60 bar, the compression operation is split and managed by a multi-stage compressors with two stages (K-100 and K-101), in order to not have a temperature too high in the unit thanks to the intermediate cooling. In fact, the compressor cannot operate at temperatures higher than 130-140 °, due to material mechanical limitations. The temperature is lowered up to 50°C with an air cooler in the intermediate cooling stage (E-100). The optimal couple of compressing ratios is defined using the optimization tool present in HYSYS.

Table 3.3 shows pressure and temperature for each stream in the compression stage.

Table 3.3 Temperature and pressure in the multi-stage compression section

stream	Temperature [°C]	Pressure [bar]
Initial syngas	43.70	15
Compressed 1	135.6	30.62
Cooled 1	50	30.52
Compressed 2	138.3	60

The compression stage heats the reactants to 138.3°C, therefore a heat exchanger is required in order to raise the temperature up to the reactor inlet temperature. To lower the energy costs is it profitable to energy integrate the process by using the outlet of the reactor, that needs to be cooled down, as the hot fluid in a process-process heat exchanger (E-101). Since the reactor is designed as almost isothermal the outlet temperature (245 °C) is only slightly higher with respect to the inlet temperature, and therefore the final temperature is reached in a second heat exchanger (E-102) that uses saturated vapor at 42 bar (255.4°C) as external utility. This second heat exchanger is essential to heat up the reactants during the start-up of the plant.

The process-process heat exchanger used in is a 2-2 shell and tube heat exchanger (shell type F [57]).

As already mentioned, the composition of the fresh syngas is adjusted to reach the optimal ratio H/C for the production of methanol. The composition of the inlet of the reactor is different from the one in the fresh syngas due to the presence of the recycles. According to [31], the optimal composition is represented by a stoichiometric number SN (Equation (3.1)) between 2.8 and 3. Another parameter to consider is the carbon oxide ratio COR (Equation (3.2)), which defines the amounts of CO and CO_2 in the reacting mixture. In typical processes, COR is usually held below 0.6.

$$SN = \frac{[H_2] - [CO_2]}{[CO] + [CO_2]} \tag{3.1}$$

$$COR = \frac{[CO_2]}{[CO] + [CO_2]} \tag{3.2}$$

In Table 2.1 the reactor feed composition is reported while the values of SN and COR obtained in the simulations are schematized in Table 3.5.

Table 3.4 Reactor feed composition and properties

component	Molar fraction	Mass fraction
CO	0.0781	0.2029
H_2	0.6790	0.1269
CO_2	0.1153	0.4705
MeOH	0.0065	0.0194
H_2O	0.0008	0.0013
CH_4	0.1203	0.1789

Table 3.5 SN and COR value at the inlet reactor

parameter	value
SN	2.911
COR	0.596

As mentioned in Section 2.3.1, methanol synthesis is the ultimate combination of:

$$CO + 2H_2 \leftrightarrow CH_3OH \qquad \Delta H_{298K} = -90.8\, kJ/kmol \tag{3.3}$$

$$CO_2 + H_2 \leftrightarrow CO + H_2O \qquad \Delta H_{298K} = +41.0\, kJ/kmol \tag{2.13}$$

$$CO_2 + 3H_2 \leftrightarrow CH_3OH + H_2O \qquad \Delta H_{298K} = -49.6\, kJ/kmol \tag{3.4}$$

The methanol reactor (PFR-100) is modelled as a plug-flow reactor, multi-tubular shell-and-tube reactor, with the catalyst inside the tubes. The reaction is exothermic, so this means that is favorite at low temperatures. To limit the temperature increase, the PFR is cooled down, so that the outlet temperature is 245°C. The cooling medium is boiling water at 20 bar (213.4°C) that becomes saturated vapor that is used as hot utility in other parts of the plant as will be explained in Section 3.4.2. The results of the reactor's performance are reported in chapter 5.

The procedure adopted to determinate the volume of the reactor will be explained in Section 0 and the description of the catalyst used will be presented in Section 4.8.

At the outlet of the process-process heat exchanger (E-102), the vapor outlet stream reaches a temperature of 110.2°C. In order to favor the separation between the methanol produced from the unreacted species, the temperature of the stream is lowered to 60°C in an air cooler (E-103). Changes in pressure and temperature between the outlet of the reactor and the outlet of the air cooler are reported in

Table 3.6.

Table 3.6 Pressure and temperature changes after the reactor (PFR-100)

stream	Pressure [bar]	Temperature [°C]
Vapor outlet	57.80	245
Cooled reactor OUT	57.70	110.2
Stream to vessel	57.35	60

Before entering the methanol separation section, which is operated at low pressure, a first flash separation is performed in a high-pressure vessel (V-100). In the process vessel, most non-reacted species are recovered in the gas phase, while the outlet liquid stream contains mainly methanol and water with some of the light species dissolved in the liquid. Table 3.7 reports the molar composition of the streams exiting the process vessel (To recycle and Crude methanol).

Table 3.7 Molar fraction in the outlet streams of vessel V-100

component	To recycle	Crude methanol
CO	0.0428	0.0003
H_2	0.6767	0.0015
CO_2	0.1193	0.0321
MeOH	0.0088	0.7455
H_2O	0.0010	0.2174
CH_4	0.1514	0.0032

The liquid outlet enters the separation section in order to purify methanol to respect market specifications.

As can be seen in Table 3.7, the gaseous outlet contains a lot of hydrogen and other non-reacted species that would be lost if no recycle is implemented. Before mixing the recycle stream with the fresh syngas, a compressor is required to recover the initial value of pressure, lost due to the pressure drops accumulated along all unit operations.

Other than the design of the recycle, a purge stream is needed in order to avoid the build-up of inert methane.

Being the composition of the purge equal to the one of the recycle stream, a non-negligible amount of hydrogen is present. With the objective of recovering the highest amount possible of hydrogen, the economic feasibility of a membrane for hydrogen separation and recovery is analyzed.

In the simulation environment, the membrane is designed as a component splitter (X-100) in which the split factors for each component are fixed. All the split factors relative to the filtered stream (H2 recycle) are reported in

Table 3.8.

Table 3.8 Split factors of the membrane for the filtered stream.

component	H2 recycled
CO	0.15
H_2	0.77
CO_2	0.50
MeOH	0
H_2O	0.82
CH_4	0.12

Hydrogen molar flow recovered thanks to the membrane is equal to 22.58 kmol/h, that gives an annual recovery of 398829.7 kg/y. Even though this hydrogen stream is produced from a renewable source, in order to be conservative its value is evaluated as if it is produced from a fossil source (1.8 $/kg) thus resulting in 756516.1 $/y. Given the high value of this stream the implementation of the membrane is beneficial.

In this study, the conversion between euros and USD is always performed using the average conversion of 2022 [58].

The Purge stream outcome is not investigated in the analysis but in principle it can be sent to a flare to recover its energy content.

The pressure drops across the membrane are significative and the pressure at the outlet of the component splitter is set equal to 15 bar. Since this stream also needs to be compressed it is mixed with the syngas stream before the compression section.

The flow ratio of splitter TEE-100 is calculated to obtain that the amount of purged methane in stream Purge and the amount of methane in stream Crude methanol are sufficient to avoid the build-up of methane in this part of the plant. Therefore, the flow ratio of the stream directed to the membrane is set equal to 6.19%.

3.2. Methanol separation

From this section onwards, specifications will be reported for both the plant alternatives. This section is dedicated to the separation of methanol from all the other species present in the crude methanol, whose molar composition and was already reported in Table 3.7. In Figure 3.6, a detailed Aspen HYSYS scheme is reported for the methanol plant.

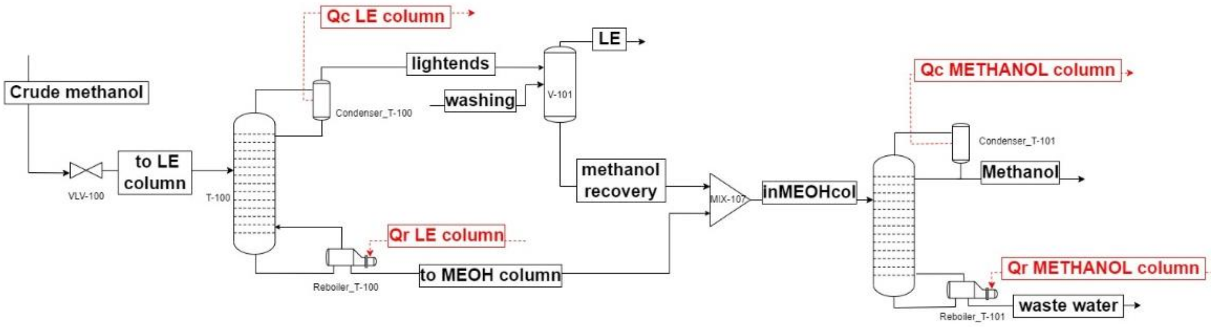


Figure 3.6 Methanol separation section in Aspen HYSYS

The description of the methanol separation section for the Dimethyl-ether plant will be treated after the one for the methanol plant.

The liquid outlet stream from the process vessel enters the separation section, which is composed of a train of distillation columns. The first distillation column manages the separation of the methanol from the more volatile components. The second column, instead, is responsible for the separation of methanol from the less volatile components, in this case only water.

Since the gas removal from methanol is favored by low pressure, before entering the first column (T-100) the stream is laminated to 2.15 bar. The light ends to be separated are composed of CO, CH_4, H_2 and mainly CO_2 due to its high solubility in water.

The distillation column, as well as all the other distillation columns present in this study are designed from the short-cut method present in Aspen HYSYS. Results of this separation column can be seen in Table 3.9 through a comparison between the composition of stream entering and exiting the column.

Table 3.9 Comparison between the molar composition of streams to LE column, lightends and to MEOH column

component	To LE column	lightends	To MEOH column
CO	0.0003	0.0076	0
H_2	0.0015	0.0347	0
CO_2	0.0321	0.7304	0
MeOH	0.7455	0.1507	0.7728
H_2O	0.2174	0.0044	0.2272
CH_4	0.0032	0.0723	0

As can be seen in Table 3.9, there is some methanol in the light-ends stream. This stream is not further investigated, and it would have been considered a waste even if contained 25.89 kg/h of methanol. A cost-benefit analysis on the implementation of a water washing was performed with the aim to determinate if the value of the methanol recovered can overcome the cost of water fed and higher duty in the reboiler of the second distillation column. The results of this analysis are reported in Table 3.10.

Table 3.10 Cost-benefit analysis for methanol washing with water.

Washing [kg/h]	Methanol lost [kg/h]	Additional LP steam [kg/h]	Cost [$/h]
0	15.50	0	6.98
5	11.00	29.0	5.75
10	9.47	46.0	5.54
11	9.27	49.0	5.53
12	**9.07**	**52.0**	**5.52**
14	8.73	59.0	5.57
15	8.58	62.0	5.58

The cost of water and LP steam has already been stated in Table 2.9.

The optimal value of the mass flow of water is 12kg/h.

A saving of 1.46 $/h sums up to 12789.60 $ in a year. As it can be seen in Appendix A, this means that in about two years the cost of the vessel necessary to perform the washing is covered.

The methanol recovery stream is mixed with the bottom stream of the first column and fed to the second distillation column, designed for the separation of methanol and water. The distillate stream is the methanol stream of 1740 kg/h with purity adjusted to respect the market specification (99.85% wt).

The bottom stream is wastewater to be treated before discharging since it contains traces of methanol.

The methanol separation section in the Dimethyl-ether simulation is almost the same as the one already described for the Methanol plant simulation. Remarkable attention is paid to check if a sufficient purification from CO_2 is obtained; since it is difficult to remove from DME, CO_2 content has to be decreased as much as possible before the DME reactor. The only difference is the feed of the second distillation column. As can be seen in Figure 3.7, the column feed also contains the methanol recycled from the bottom of the DME distillation column, mainly composed of methanol and water. A more detailed description of this recycled stream will be delivered in the following section.

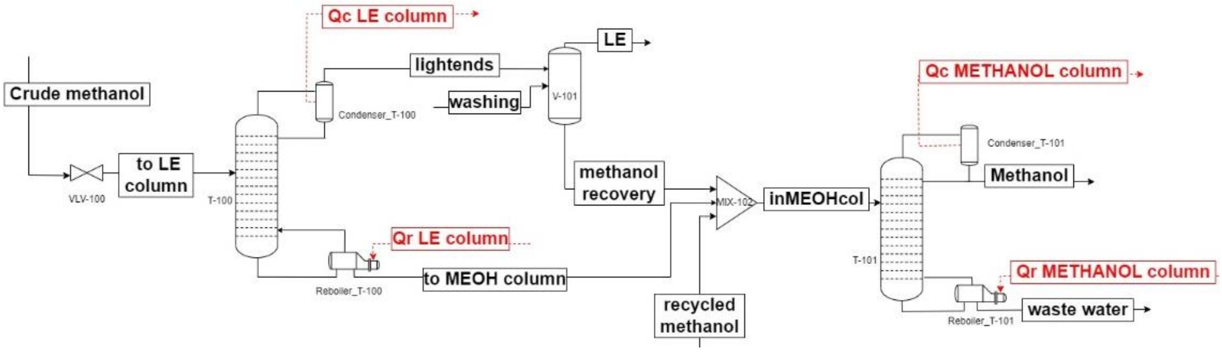


Figure 3.7 Methanol distillation column in the Dimethyl-ether simulation

The parameters assigned for design of the distillation column, however, do not change. Nevertheless, the duty of condenser and reboiler will be bigger, as well as the flowrate of the streams exiting the column. The specification of purity for methanol is considered stringent also in this case since methanol is required to be as pure as possible for the DME synthesis. Water is separated from methanol before the dehydration reactor since it is a product of the DME synthesis reaction and its presence in the feed stream inhibits the reaction; so, the removal of water enhances the conversion. Molar composition of the methanol stream that is entering the DME synthesis and separation section is reported in Table 3.11.

Table 3.11 Molar composition of the methanol stream

component	Methanol
CO	0
H_2	0
CO_2	0
MeOH	0.9976
H_2O	0.0022
CH_4	0
DME	0.0002

3.3. Dimethyl-ether synthesis and separation

The liquid methanol stream enters the DME synthesis section and is pumped to 12.70 bar. Pressure, as seen in section 1.3, does not affect the thermodynamic equilibrium of the dehydration reaction. This value of pressure is selected to operate the following distillation column at 10.15 bar resulting in a distillate temperature of 40.29°C allowing the use of cooling water as cooling medium in the total condenser. Indeed, cooling water cannot be heated over 30°C. Thus, a ΔT of a minimum of 10°C is guaranteed.

Methanol feed is preheated with the reactor outlet stream (E-110) and then it is heated to 230°C by an external utility (E-111). The DME reactor is simulated as a Gibbs reactor (GBR-100) working at 230°C where only reaction (2.4) occurs.

In Figure 3.8 the simulation of the DME synthesis and separation section is shown.

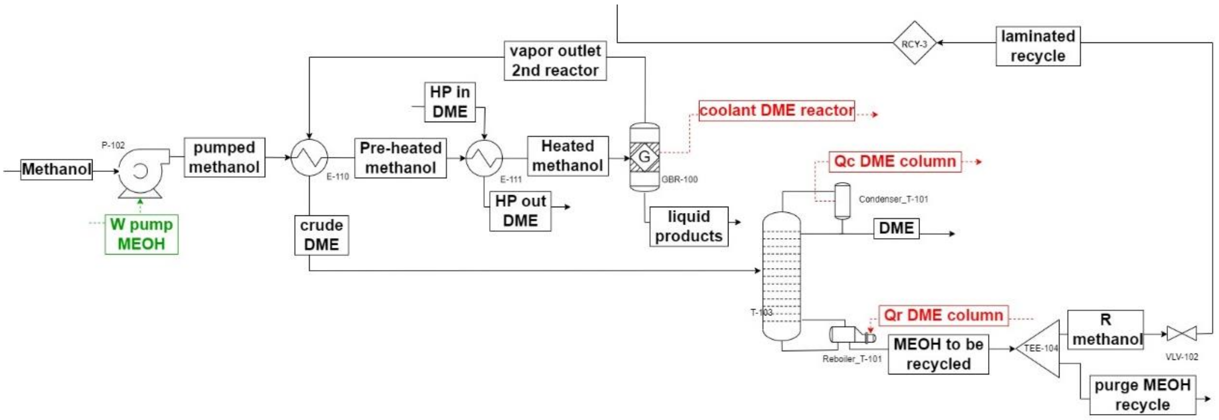


Figure 3.8 DME synthesis and separation section.

The reactor outlet exits from heat exchanger E-110 at 81°C and goes to distillation column T-103. Distillate DME is the product of interest of the entire process and consists in a stream of 1255 kg/h of high purity DME, while the bottom stream is recycled back to column T-101 after being laminated to the column pressure.

3.4. Utilities

To better analyze and comprehend the possible strategies for energy integration and to have a clearer view of the cost of utility production and management, a section of the plant is designed to deal with the utilities.

The cold utility used in the condensers is cooling water. Its management has been deepened by designing the cooling tower necessary to close the cooling water cycle. This part of the plant is described in the following section.

While the high-pressure steam is entirely considered as an external utility, paid accordingly to what already stated in Section 2.5.2; part of the low-pressure steam, used as hot utility in the reboilers, is produced in loco exploiting the heat released by the reactions. The vapor cycle is explained in the last section of this chapter.

3.4.1. Cooling water cycle

The cooling of the water occurs in a cooling tower where some of the water is evaporated during the process. To make up for this loss, makeup water is added to the circulating cooling water stream. The general structure of a cooling water cycle is schematized in Figure 3.9.

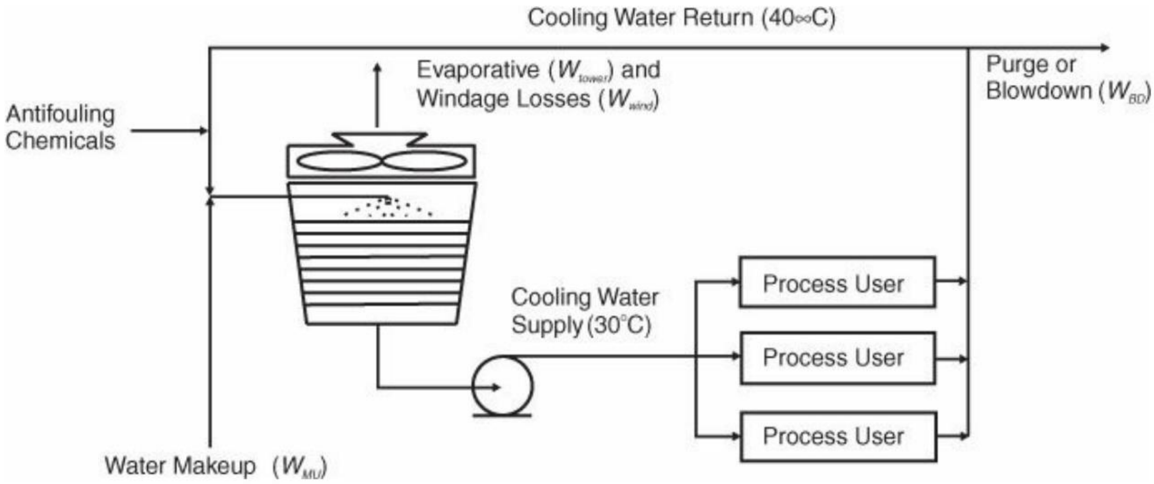


Figure 3.9 Schematic diagram of cooling water loop [47].

In order to make explicit the energy integration, each condenser present in the simulations is modelled as a shell and tube heat exchanger that heats cooling water up to 30°C. The molar flow of each stream of cooling water is set to have the duty of the exchangers equal to the ones of the column condensers calculated by Aspen HYSYS. The cooling tower is designed as an absorption column, whose detailed explanation is reported in Section 0. Figure 3.10 shows the cooling water loop for the methanol plant.

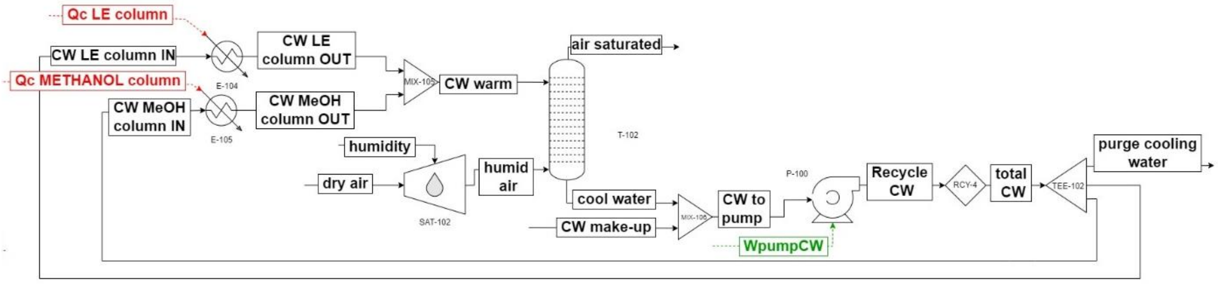


Figure 3.10 Cooling water loop for the methanol plant

As can be seen in Figure 3.11, the cooling water cycle of the Dimethyl-ether plant is designed as the one of the methanol plant, the only difference is the amount of cooling water in the cycle, and therefore all the quantities related to the dimension of the loop. This difference is due to the presence of a third column, so a third condenser (E-112) that requires cooling water as cooling utility.

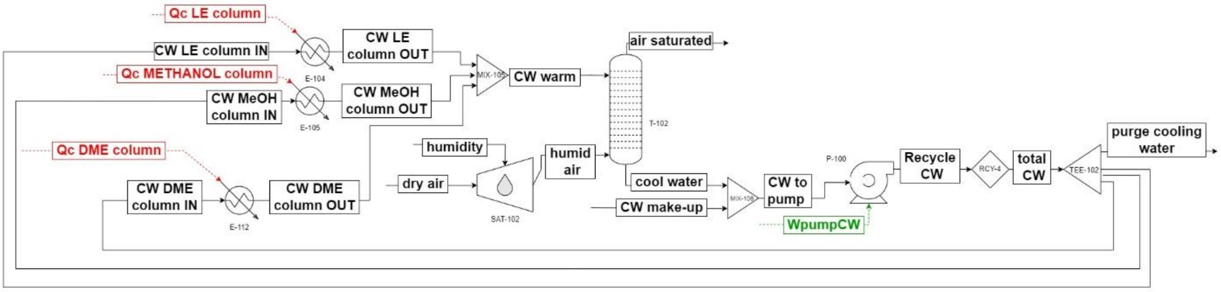


Figure 3.11 Cooling water loop for the DME plant

3.4.2. Vapor cycle

To control the temperature in the reactors and maintain the reactor iso-thermal, boiling water at 20 bar is used. By exploiting the phase transition to gaseous phase, a low mass flow of water is required, and at the same time medium pressure steam, a valuable utility, is produced.

The generated saturated steam is then laminated to 6 bar, since in the plant low-pressure steam is required as utility in the reboilers. The lamination process moves the steam from the saturation condition to super-heated steam. To increase the mass flow of steam a water injection is added. Its mass flow is controlled in order to have steam at saturated conditions after this injection. The LP vapor stream is then split towards the reboilers. Figure 3.12 shows the vapor cycle loop for the methanol plant. It can be seen that the amount of steam produced totally covers the duty requested by the reboiler of the first distillation column (T-100). For what concern the second distillation column a make-up of LP steam is needed to fulfill the duty. This steam is considered coming from an external supplier and its cost has already been stated in Section 382.5.2.

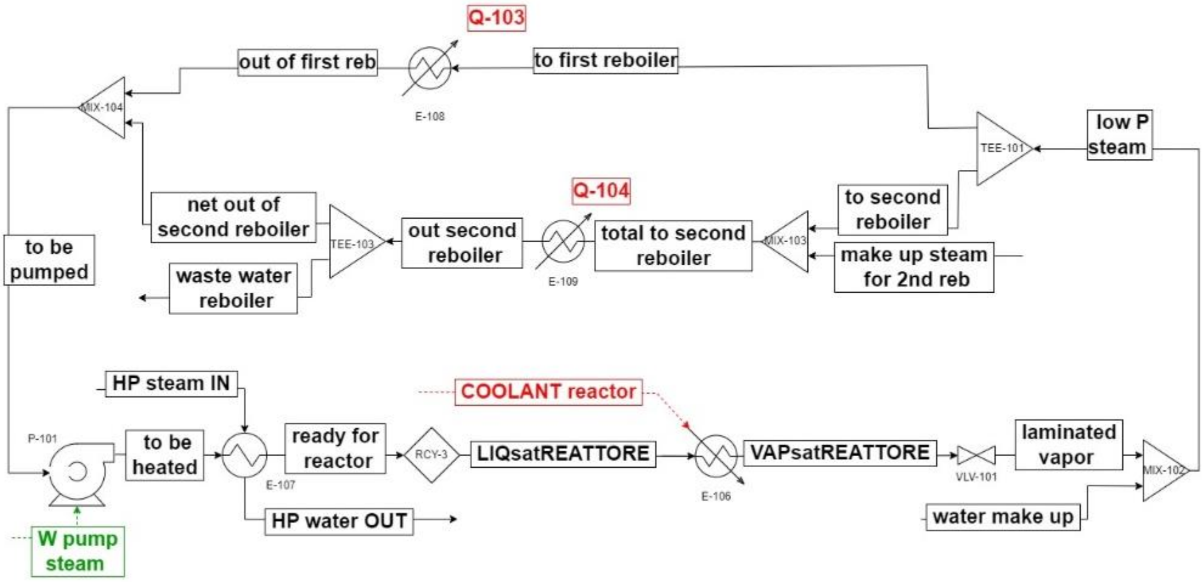


Figure 3.12 Vapor cycle for the methanol plant

The structure of the vapor cycle loop is the same between the two plant alternatives. The loop for the Dimethyl-ether plant is more complex, though, since there are two reactors that use boiling water to produce MP steam and then there are three reboilers that require LP steam. The heat of reaction released in the DME reactor is significantly lower than the ones produced in the methanol reactor. The steam produced, in fact, is not enough to saturate the needing of T-101 reboiler, resulting in T-103 reboiler fully relying on external LP steam.

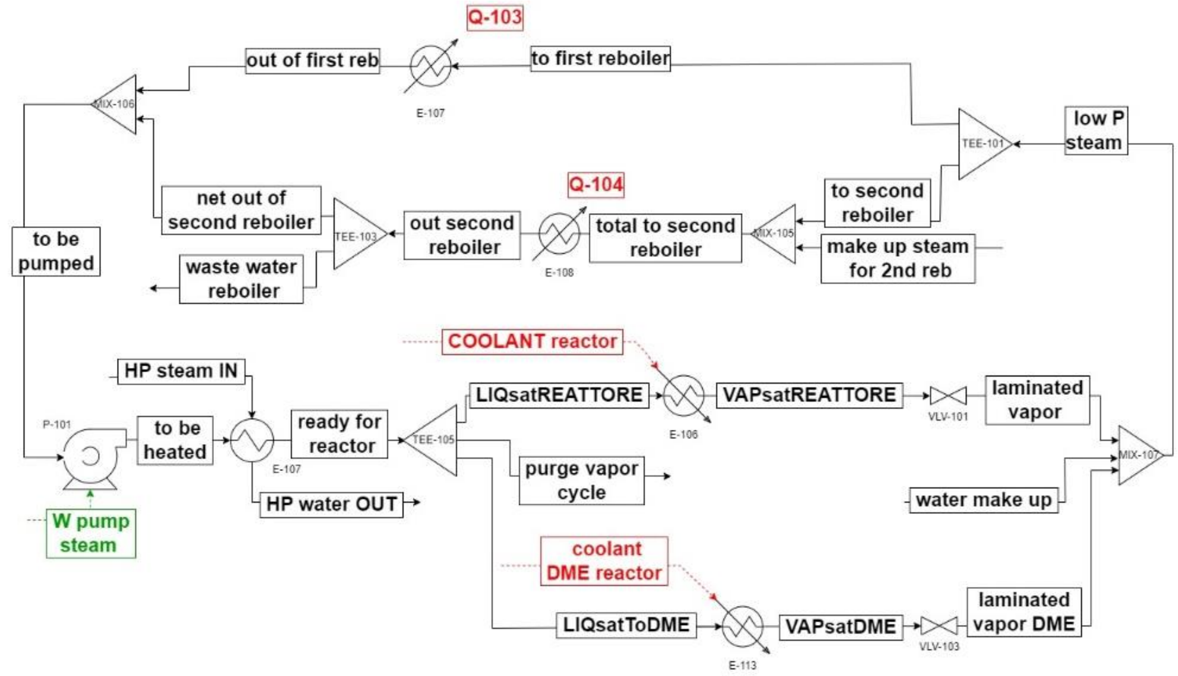


Figure 3.13 Vapor cycle for the DME plant

4 Unit operations sizing

In this chapter the detailed design of the unit operations is reported, and the characteristic size parameter for each equipment, necessary for CAPEX calculation, will be evaluated. The chapter is divided into sections, one for each type of unit, and the characteristic size of each equipment are summarized at the end of the corresponding section. In the two Aspen HYSYS simulations, some equipment are designed using more than one unit operation to explain the occurring phenomena. Therefore, the absence in this chapter of some equipment displayed in the figures in the previous chapter is due to the fact that those units do not actually exist.

4.1. Heat exchangers sizing

There are three types of heat exchangers employed in the two plant alternatives: fixed tube heat exchangers, air coolers and kettle reboilers. The heat exchange area is the size parameter that must be evaluated in order to calculate the cost of each of these heat exchangers. Aspen HYSYS does not give the area of the exchanger, but it returns only thermal information. The sizing of heat exchangers is performed by CORO using Equations (4.1)(4.1) and (4.2) and knowing the temperature drop, the heat exchanged, and fixing the global heat transfer coefficient U according to some known values dependent on the type of fluids that interact in the heat exchangers.

$$A = \frac{Q}{U \Delta T_{ml}} \tag{4.1}$$

$$\Delta T_{ml} = \frac{\Delta T_1 - \Delta T_2}{\ln\left(\frac{\Delta T_1}{\Delta T_2}\right)} \tag{2.13}$$

1 and 2 represent the inlet and outlet of the heat exchanger.

Some values for U are reported in Table 4.1.

Table 4.1 Global heat transfer coefficient U range for different fluids interaction (values on the right have to be considered as the maximum value for the category on the left)

$U\ [kW/m^2K]$	
0.2	Gas/Gas
0.5	Gas/Liquid
0.8	Liquid/ Liquid
1.1	Liquid/Phase transition

Table 4.2 collect the area of every heat exchanger present in the two Aspen HYSYS simulations. Little differences in the resulting sizing for units that in principle are the same are caused by the recycle management, that is operated numerically, leading to these small inconsistencies.

Table 4.2 Heat exchangers exchange area for both plants.

Methanol plant			**DME plant**		
Heat Exchanger	**Type**	**A Area [m²]**	**Heat Exchanger**	**Type**	**A Area [m²]**
E-100	Air cooler	3.80	E-100	Air cooler	3.82
E-101	Fixed tube	30.38	E-101	Fixed tube	30.40
E-102	Fixed tube	10.94	E-102	Fixed tube	10.96
E-103	Air cooler	22.31	E-103	Air cooler	22.31
E-104	Fixed tube	3.08	E-104	Fixed tube	3.08
E-105	Fixed tube	97.11	E-105	Fixed tube	119.35
E-107	Fixed tube	4.97	E-109	Fixed tube	5.70
Reboiler T-100	Kettle	6.40	E-110	Fixed tube	11.60
Reboiler T-101	Kettle	121.21	E-111	Fixed tube	15.44
			E-112	Fixed tube	19.07
			Reboiler T-100	Kettle	6.41
			Reboiler T-101	Kettle	150.00
			Reboiler T-103	Kettle	25.52

4.2. Reactor sizing

Methanol and DME synthesis reactors are PFR cooled down by an external utility. In order to be modeled using the correlations presented in [47] they are considered as fixed tube heat exchangers in which the tubes filled with the catalyst represent the reaction volume while the shell side is filled with the cooling utility. Being considered as a heat exchanger, it is necessary to evaluate the surface area of the two reactors.

The volume of the reactors is determined considering that the gas hourly space velocity GHSV, which is used to relate the volumetric flowrate to the catalyst volume as shown in equation (4.2), should be in a range between 2000 and 15000 h^{-1}.

$$GHSV = \frac{volumetric\ flow\ [standard\ m^3/h]}{V(1-\xi)\ [m^3]} \tag{4.2}$$

The void fraction ξ is equal to 0.4 for both reactors, giving that the volume occupied by the catalyst is $0.6V$.

For what concern the methanol reactor, in order to minimize the volume of the reactor, a high value of GHSV is needed. At the same, to avoid too high velocities the value of 10000 $Sm^3/h/m^3_{cat}$ has been chosen. Once the value of the GHSV has been set, it is possible to determine the volume of the PFR.

Considering that the dimensions of the reactor should be harmonic, the number of tubes is set so that the tubes diameter is equal to 0.03 m and the reactor length is between 6 and 7 meters. Table 4.3 summarize the reactor size parameters.

Table 4.3 Methanol reactor detailed design.

Methanol reactor	
T_{in}	235 °C
T_{out}	245 °C
P	59.80 bar
Void fraction	0.4
GHSV	10060 $Sm^3/h/m^3_{cat}$
Reactor volume	3.487 m^3
Tube diameter	0.03 m
Number of tubes	700
Length	7.047 m
Heat exchange area	**464.91 m^2**

Even though the DME reactor is designed as an equilibrium reactor, the sizing procedure is performed in the same way, with the only exception being the selected value for the GHSV, that in this case is equal to 3000 $Sm^3/h/m^3_{cat}$. Table 4.4 collect the detailed size parameter for the DME reactor.

Table 4.4 Dimethyl-ether reactor detailed design.

Dimethyl- ether reactor	
T_{in}	230°C
T_{out}	230°C
P	12.50 bar
Void fraction	0.4
GHSV	3000 $Sm^3/h/m^3_{cat}$
Reactor volume	0.80 m^3
Tube diameter	0.03 m
Number of tubes	175
Length	6.48 m
Heat exchange area	**106.89 m^2**

4.3. Distillation columns sizing

To estimate the distillation column costs, volume is required. To compute the column volume the estimation of the height is necessary. Once the height is found, the CORO can easily compute the volume using column diameter and height calculated by Aspen HYSYS.

This procedure considers only costs related to column vessel, to estimate total column costs it is necessary to evaluate tray or packing costs. Trays are considered sieve trays and Turton handbook [47] allows them to estimate their costs by relying on their area and number. Trays are considered sieve trays and Turton handbook [47] allows them to estimate their costs by relying on their area and number. For what concerns column packing, their cost is evaluated using column volume only.

Specifications, along with design decisions made for each column, are listed in this section.

T-100

The light ends column is designed to separate components lighter than methanol from the crude methanol stream. This column is simulated in the same way in the two simulations, little differences are present due to slightly different numerical solutions in the first part of the plant. The condenser of this column is a full reflux condenser since the highest amount of methanol must be recovered from the distillate stream. The reboiler is a kettle reboiler. The column is a packed column. The first specification given is the condenser temperature equal to 40°C, in order to avoid cryogenic separation and to use cooling water as cold utility in the condenser. The second degree of freedom is saturated imposing a reflux ratio to 1.5. Table 4.5 summarize the column design and all information necessary to evaluate the volume.

Table 4.5 T-100 detailed sizing.

T-100	Methanol plant	DME plant
N of stages	5	5
Stage efficiency	0.85	0.85
Condenser pressure drops	10 kPa	10 kPa
Reboiler pressure drops	10 kPa	10 kPa
Condenser duty	56.66 kW	56.66 kW
Reboiler duty	154.90 kW	155.10 kW
Inlet stage	2	2
Reflux ratio	1.5	1.5
Internal type	Packed	Packed
Packed height per stage	0.30 m	0.30 m
Section packed height	1.50 m	1.50 m
Diameter	0.27 m	0.27 m
Volume	0.09 m^3	0.09 m^3

T-101

The methanol column is designed to separate methanol and water, recovering in the distillate a methanol stream that respect market specification. The column is a tray column. The first specification given is methanol mass fraction equal to 99.85% in the distillate and the second degree of freedom is saturated imposing molar methanol recovery in the distillate equal to 99.95%. This column manage different flower rates in the two cases. The number of trays is not the same in order to avoid a too high value of the reflux ratio and too high duties in the condenser and reboilers. The condenser of this column is a total condenser. The reboiler is a kettle reboiler.

Table 4.6 summarize the column design and all information necessary to evaluate volume and tray area.

Table 4.6 T-101 detailed sizing

T-101	Methanol plant	DME plant
N of stages	35	39
Stage efficiency	0.85	0.85
Condenser pressure drops	10 kPa	10 kPa
Reboiler pressure drops	10 kPa	10 kPa
Condenser duty	1785 kW	2194 kW
Reboiler duty	1752 kW	2120 kW
Inlet stage	11	13
Reflux ratio	2.16	2.46
Internal type	Sieve Tray	Sieve Tray
Tray spacing	0.61 m	0.61 m
Tray area	0.50 m	0.62 m
Diameter	0.80 m	0.89 m
Volume	11.30 m^3	15.54 m^3

T-103

The Dimethyl-ether column is designed to separate dimethyl-ether as distillate from the mixture of methanol and water. The condenser of this column is a total condenser. The reboiler is a kettle reboiler. The column is a packed column. The first specification given is DME mass fraction equal to 99% in the distillate, in order to meet market specifications. The second degree of freedom is saturated imposing the reflux ratio equal to 1.5.

Table 4.7 summarize the column design and all information necessary to evaluate the volume.

Table 4.7 T-103 detailed sizing

T-103	
N of stages	5
Stage efficiency	0.85
Condenser pressure drops	10 kPa
Reboiler pressure drops	10 kPa
Condenser duty	350.5 kW
Reboiler duty	228.6 kW
Inlet stage	5
Reflux ratio	1.5
Internal type	Packed
Packed height per stage	0.30 m
Section packed height	1.50 m
Diameter	0.38 m

Volume	0.17 m^3

4.4. Cooling tower sizing

As with the other towers, the characteristic dimension of the cooling tower necessary for CAPEX evaluation is the volume. To estimate the total column costs is necessary to also evaluate the packing cost. Volume is again the size parameter requested by the methodology.

Cooling tower is modelled as an absorption column with ambient air entering from the bottom and the water that needs to be cooled down from the top. The ambient air composition is obtained using a stream saturator set to produce a stream of air with 75% relative humidity from dry air at 20°C. The absorber has 10 stages and works at 1 bar. Pressure drop along the column are neglected. In fact, pressure drops along the cooling water loop are considered condensed in the exchangers. The column is a packing column.

Table 4.8 summarize the column design and all information necessary to evaluate the volume.

Table 4.8 T-102 detailed sizing

T-102	Methanol plant	DME plant
N of stages	10	10
Stage efficiency	1	1
Internal type	Packed	Packed
Packed height per stage	0.15 m	0.15 m
Section packed height	1.50 m	1.50 m
Diameter	6.73 m	6.76 m

Volume	56.03 m^3	56.50 m^3

4.5. Process vessels sizing

The characteristic dimension necessary to evaluate the cost of process vessels is volume. The volume of the flash units designed in the two simulations can be calculated by the software itself. All process vessels are considered vertical units. No differences are present in the units in the two simulations. Table 4.9 summarize sizing of all vessels.

Table 4.9 V-100 and V-101 detailed sizing

	V-100	V-101
Height	3.35 m	2.51 m
Diameter	0.61 m	0.46 m
Volume	0.98 m^3	0.41 m^3

4.6. Pumps and compressors

The size parameter for pumps and compressors is the shaft power. The shaft power of each unit is calculated by the Aspen HYSYS. Shaft power is also the quantity necessary to calculate the electricity contribution in the OPEX evaluation. Table 4.10 and

Table 4.11 summarize the power of each unit for both plant alternatives.

Table 4.10 Methanol plant power demand of pumps and compressors

Pumps duty [kW]	
P-100	8.58
P-101	1.63
Compressors duty [kW]	
K-100	176.34
K-101	171.32

K-102	36.04

Table 4.11 Dimethyl-ether plant power demand of pumps and compressors

Pumps duty [kW]	
P-100	12.10
P-101	1.84
P-102	1.12
Compressors duty [kW]	
K-100	178.12
K-101	169.62
K-102	36.10

4.7. Equipment materials

The criterium used for the selection of equipment material is to use stainless steel for the units or for the part of the units in direct contact with process streams, and carbon steel for utilities management units, contacting just water.

Stainless steel is used because in process streams hydrogen is present, which may cause damage if the material is not wisely chosen. Hydrogen embrittlement is a reduction in the ductility of a metal due to absorbed hydrogen. Indeed, hydrogen atoms are small and can permeate solid metals and once absorbed, hydrogen lowers the stress required for cracks in the metal to initiate and propagate, resulting in embrittlement. Hydrogen embrittlement occurs most notably in steels, while stainless steel is less susceptible to this phenomenon, making it the best choice, even if it is a more expensive metal.

For the column packing metal was chosen.

4.8. Catalyst replacement

Methanol reactor

Inside methanol reactor, there is a CZA catalyst described by Bisotti et al. [31]. This type of catalyst is the most widespread catalyst for methanol synthesis; its composition varies according to the producer; general ranges of composition are reported in .

Table 4.12.

Table 4.12 Typical CZA catalyst composition.

Component	Content %

Copper	20-80
Zinc oxide	15-50
Al_2O_3	4-30

Additives and additional promoters, for instance, MgO, are present to decrease sintering resistance and increase the catalyst lifetime. CZA catalysts are active between 220 and 280 °C, and their selectivity to methanol reaches 99%. The catalyst activity decreases due to deactivation by poisoning as well as thermal sintering.

The catalyst density considered in this study is 1300 kg/m^3 [59] and the selected average lifetime is 4 years.

The volume of catalyst inside the reactor is easily evaluated since the void fraction is known, and it is equal to 2.09 m^3. Knowing the volume of the and the density of the catalyst it is easy to compute the mass of catalyst required to fill the reactor, which results in 2719.86 kg. Considering the lifetime, the annual replacement of the catalyst amounts to 680.0 kg.

Dimethyl-ether

Inside dimethyl-ether reactor, there are 3mm γ-Al_2O_3 pellets as described by Bercic et al. [38]. Acidic catalysts are the most widespread catalyst for methanol dehydration.

The reaction takes place on pure γ -alumina and on γ -alumina slightly modified with phosphates or titanates, in a temperature range of 250-400° C.

The catalyst density considered in this study is 1470 kg/m^3 [38] and the selected average lifetime is 3 years.

As for the first reactor, given the void fraction, the volume of catalyst is easily evaluated, and it is equal to 0.48 m^3. Knowing the volume of the and the density of the catalyst it is easy to compute the mass of catalyst required to fill the reactor, which results in 707.05 kg. Considering the lifetime, the annual replacement of the catalyst amounts to 235.68 kg.

5 Results and discussions

This chapter presents the simulation results and their discussion. To perform a proper comparison between the two alternatives, several Key Performance Indicators (KPIs) and a comprehensive economic analysis are presented in the following sections. It is relevant to indicate that all material streams used in the calculation are listed in Appendix C.

5.1. Technical key performance indicators

In this section a series of technical KPIs from the are evaluated. In particular, it is interesting to address conversion, yield, productivity, purity. Parallel reactions are not considered in the kinetic models; therefore, the calculation of selectivity is meaningless. Equation (5.1) is used to evaluate the conversion per pass of component j-th across a reactor.

$$\chi_j = 1 - \frac{\dot{n}_{j,out}}{\dot{n}_{j,in}} \tag{5.1}$$

Also, total conversion across the recycle loops are evaluated.

Equilibrium conversions for the methanol synthesis are reported in Table 5.1. The conversion is equal in both plant since the first part of the plant is the same.

Table 5.1 H2, CO, COx global and per pass conversion in methanol synthesis.

H2 conversion per pass	20.80%
CO conversion per pass	55.91%
COx conversion per pass	31.85%
H2 global conversion	94.78%
CO global conversion	95.96%
COx global conversion	89.27%

Hydrogen conversion is lower since the reactor works more than hydrogen.

Table 5.2 reports the equilibrium conversion of methanol in the Dimethyl-ether plant.

Table 5.2 Methanol global and per pass conversion in dimethyl-ether synthesis.

MeOH conversion per pass	88.76%
MeOH global conversion	99.48%

Equation (5.2) is used to evaluate the yield of component j-th in the plant.

$$Y_j = \frac{n(\dot{n}_{j,out} - \dot{n}_{j,in})}{\dot{n}_{COx,in} - \dot{n}_{COx,out}} \tag{5.2}$$

Where n is the number of carbon atom of j-th molecule considered.

In Table 5.3, the yield of methanol and dimethyl-ether with respect to COx is presented.

Table 5.3 Yield of methanol and DME in the respective plants.

MeOH yield	98.74%
DME yield	98.36%

For Methanol plant, methanol productivity is 1738 kg/h, which for 8760 h/y of operations is 15226 tons/y. For Dimethyl-ether, DME productivity is 1255 kg/h, or 10993 tons/y.

5.2. Capital and operative expenditure

As stated in Chapter 2.5, to perform the cash flow analysis is necessary to estimate CAPEX, OPEX and annual revenues.

According to the method explained in Chapter 2.5.1, all process equipment cost is evaluated. Detailed calculations for each piece of equipment, dived per category, are reported in Appendix A.

In Table 5.4, a significative summary of CAPEX evaluation is reported.

Table 5.4 Summary of CAPEX evaluation for Methanol and Dimethyl-ether plants.

	MeOH plant	**DME plant**
Total module cost	6835 k$	8409 k$
Grass root cost	8277 k$	10239 k$

Working capital	1448 k$	1792 k$
Total capital investment	9725 k$	12031 k$

The corresponding CAPEX of Dimethyl-ether plant are higher. This calculation, however, is necessary to quantify the difference. The DME plant costs about 25% more than the methanol plant. As can be seen in Chapter 3 the additional unit operations are a reactor, a pump, a distillation column with its condenser and reboiler and two heat exchangers.

How the costs are distributed and what are the major contributions in the capital investment are questions analyzed in the next section.

5.2.1. CAPEX Breakdown

In this section, the different sections are analysed more in detail, identifying how the costs are distributed along the process line and highlighting the differences between the two plants.

Methanol plant

Hereafter, in Figure 5.1, the CAPEX breakdown for Methanol plant is reported.

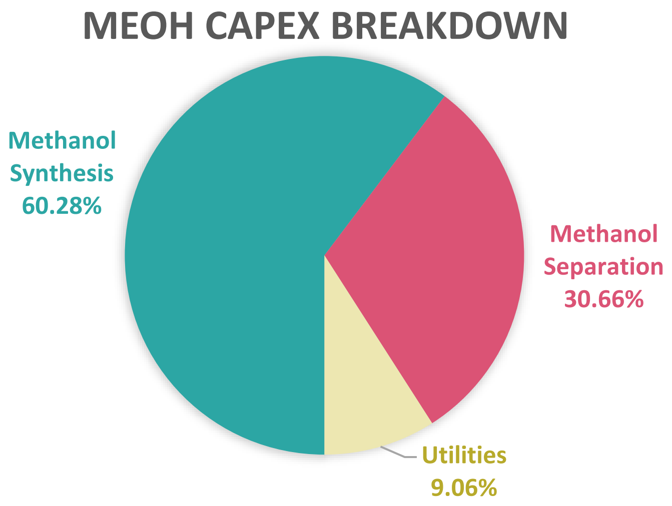


Figure 5.1 Methanol plant CAPEX breakdown

This type of consideration is helpful to understand where an improvement in the units and technologies used in the simulations can bring significative savings. Is it clear that with these results, a change in the design of the utilities section will probably bring less benefit with respect to an improvement of the methanol synthesis section.

In order to easily understand what equipment weight more in each section Figure 5.2, Figure 5.3 and Figure 5.4 are reported.

Figure 5.2 shows the contribution of each class of equipment within the methanol synthesis section.

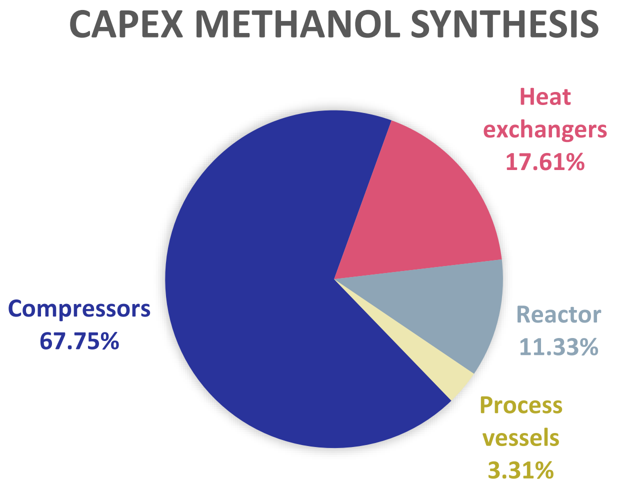


Figure 5.2 CAPEX contributions of methanol synthesis section in the Methanol plant.

As can be seen in Figure 5.3 compressors are the most expensive type of equipment. The three compressors cost up to 2.365 M$.

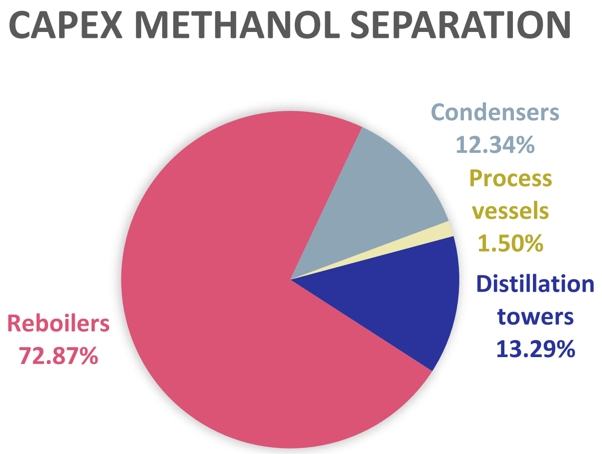


Figure 5.3 CAPEX contributions of methanol separation section in the Methanol plant.

Figure 5.3 shows how reboilers are the most expensive equipment in the distillation operation, especially the reboiler of column T-101 which is a big unit that, alone, costs 1.139 M$.

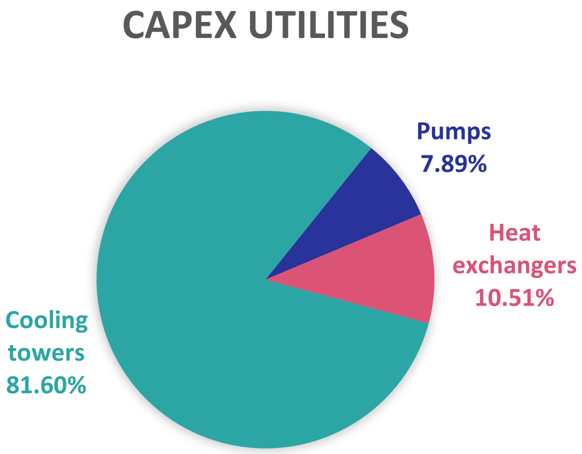


Figure 5.4 CAPEX contributions of utilities section in the Methanol plant.

The majority of the equipment cost of the utility section is represented by the absorption column in the cooling water cycle, but its cost is low with respect to the other units highlighted in this section, since it amounts to 428 k$.

Globally the most expensive category of equipment is compressor with 2.365 M$, followed by heat exchangers network (2.183 M$).

Dimethyl-ether plant

As done for the methanol plant, hereafter the CAPEX breakdown for Methanol plant is reported in Figure 5.5.

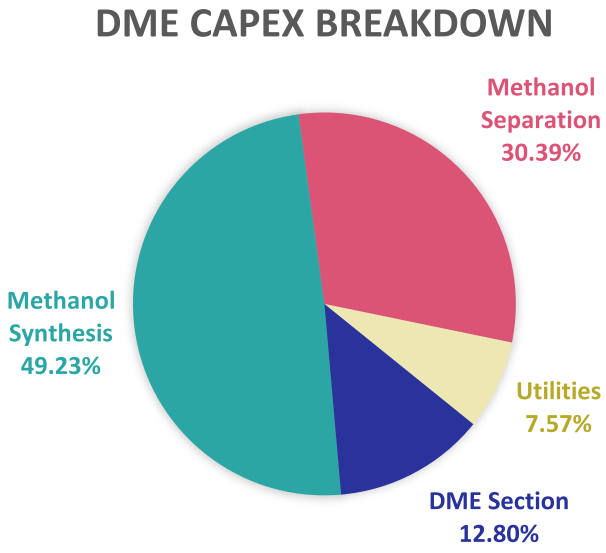


Figure 5.5 Dimethyl-ether plant CAPEX breakdown

From Figure 5.5 it can be seen that methanol synthesis section remains the most expensive part of the plant, still followed by methanol separation section. As already mentioned, the methanol separation section is virtually identical between the plants, in fact the cost is almost the same. The separation section of the DME plant has some differences in the design of the second distillation column, resulting in an additional 380k$. In the utilities section only minor differences are present and the additional costs amount to 12k$. Obviously, the major contribution to the difference between the CAPEX of the two alternatives lies in the dimethyl-ether synthesis and separation section, that cost 907 938 $.

Again, to understand what equipment weight more in each section, Figure 5.6, Figure 5.7 and Figure 5.8Figure 5.4 are reported.

The chart of methanol synthesis section of the dimethyl-ether plant is not reported since shows the same information of Figure 5.2 and therefore, the same consideration are valid.

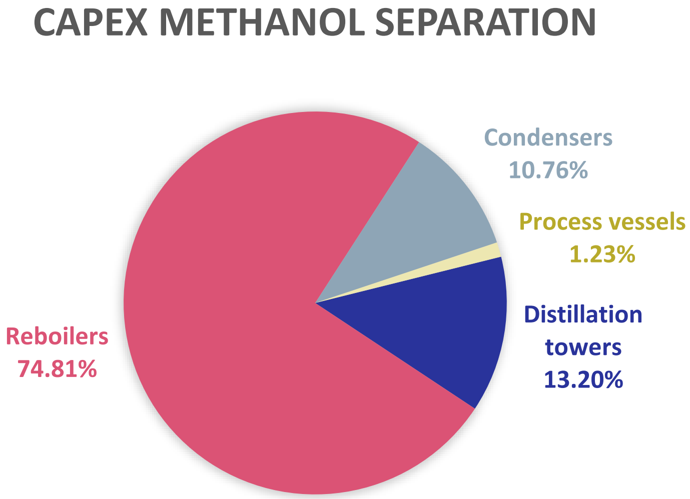


Figure 5.6 CAPEX contributions of methanol separation section in the Dimethyl-ether plant.

Figure 5.6 highlights again how reboilers are the most expensive equipment in the distillation operation, especially the reboiler of column T-101 which, in this case, is even bigger than in the other simulation, resulting in a costs of 1.457 M$.

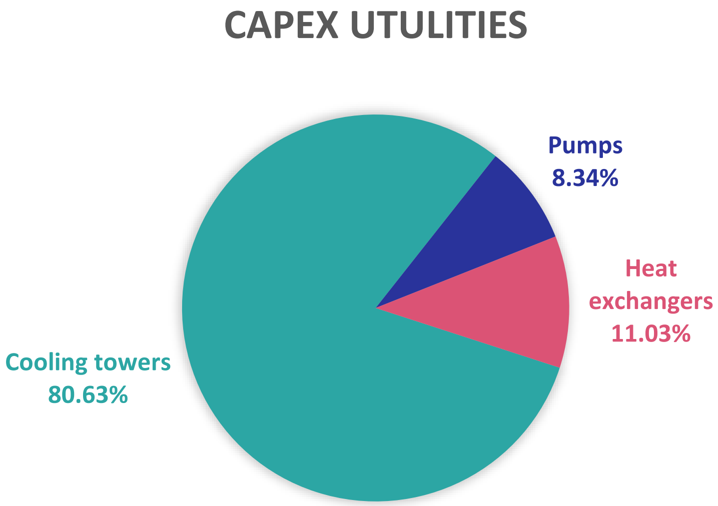


Figure 5.7 CAPEX contributions of utilities section in the Dimethyl-ether plant.

The majority of the equipment cost of the utility section is represented also in this case by the absorption column in the cooling water cycle. This unit is bigger in this simulation since a higher flowrate of cooling water is required in the condensers. The difference is however small, the cooling tower of the DME plant costs 433 071 k$.

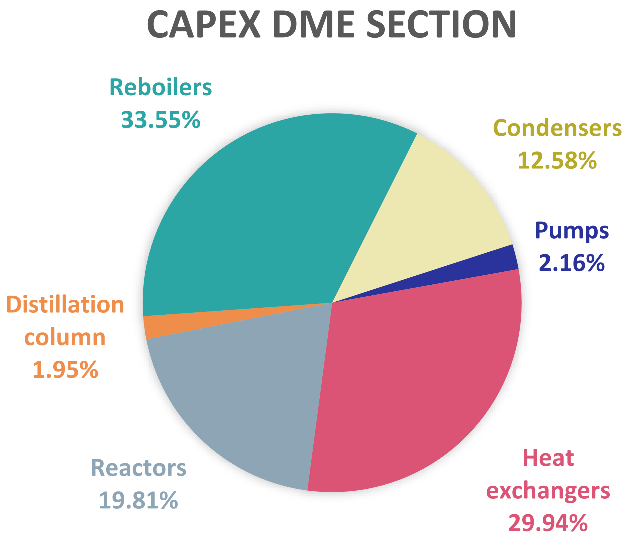


Figure 5.8 CAPEX contributions of utilities section in the Dimethyl-ether plant

The main contributors to the cost of this section are the heat exchangers, in which the reboiler cost 304651 $ and the other heat exchangers and the condenser amount to 386096 $. All the exchanger units together cover up 76.08% of the entire cost of the dimethyl-ether synthesis and separation section of the DME plant.

Globally the most expensive category of equipment is the heat exchangers network (3.209 M$), followed by compressors with 2.365 M$.

5.2.2. OPEX Breakdown

Operative Expenditure are evaluated according to what stated in Chapter 2.5.2.

In Table 5.5 the OPEX for both plants are reported.

Table 5.5 OPEX for Methanol and Dimethyl-ether plants.

	MeOH plant	**DME plant**
Sum of expenses	563 k$/y	1080 k$/y
COMd	2183 k$/y	3165 k$/y

It is reminded again that the cost of raw materials has been neglected. Values in Table 5.5, therefore, do not reflect the actual OPEX of a plant. Raw material cost, in fact, usually represents the most important contribution in a chemical plant.

Table 5.6 general overview of number of utilities and materials required for both configurations is reported.

Table 5.6 Summary of OPEX evaluation for Methanol and Dimethyl-ether plants.

	MeOH plant	**DME plant**
LP steam	664 kg/h	2110 kg/h
HP steam	701 kg/h	1320 kg/h
Water	2535 kg/h	3797 kg/h
Electricity	394 kWh	399 kWh
Catalyst	680 kg/y	680+236 kg/y

LP steam only represents the low-pressure steam that cannot be covered by the lamination process of the generated medium-pressure steam in the vapor cycle loop. Within "water" both cooling water and process water are included since their cost is assumed to be equal. Electricity is mostly required to run compressors and pumps. For what concern catalyst replacement, in the DME plant 680 kg/y of CZA are required to maintain active the methanol synthesis reactor, while 236 kg/y of γ-alumina are needed in the dimethyl-ether synthesis reactor.

Finally, direct manufacturing costs, fixed manufacturing costs, and general expenses can be evaluated to perform the estimation of operating costs without depreciation (COMd), whose value was presented at the beginning of the section in Table 5.5.

Methanol plant

Hereafter, in Figure 5.9, the OPEX breakdown for Methanol plant is reported.

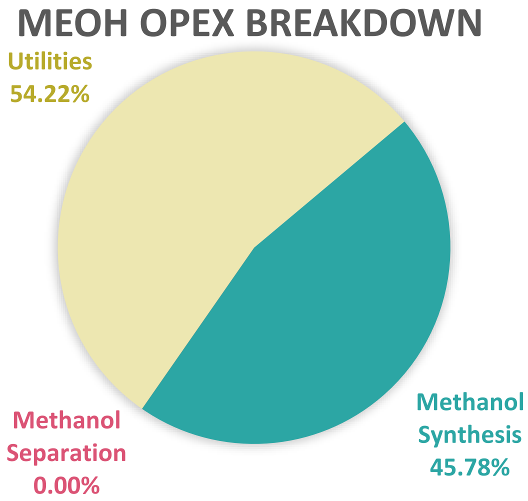


Figure 5.9 Methanol plant OPEX breakdown.

The first thing that it can be seen in Figure 5.9 is that methanol separation section does not have operative costs. This is because the utilities side of condensers and reboilers are accounted in the utilities section. OPEX costs are almost equally divided between the other two parts, but the nature of these cost is not the same and it will be investigated thanks to Figure 5.10 and Figure 5.11.

Figure 5.10 shows the contribution of each category within the methanol synthesis section.

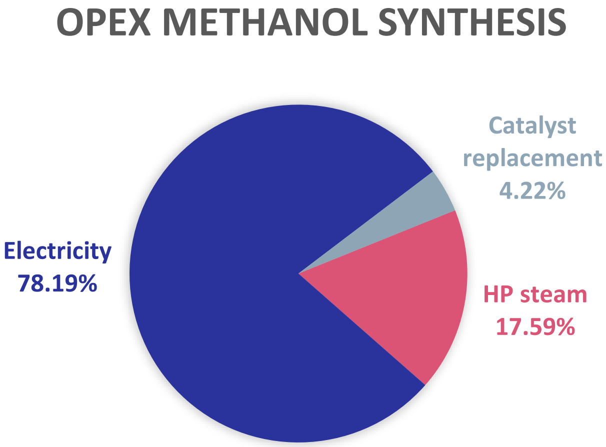


Figure 5.10 OPEX contributions of methanol synthesis section in the Methanol plant.

The main contribution in the first section of the plant is electricity, that is needed to operate the three compressors present in this section. Compression operation proves to be one of the most expensive operations also from the point of view of operative expenses, with a cost of 2.365 M$/y.

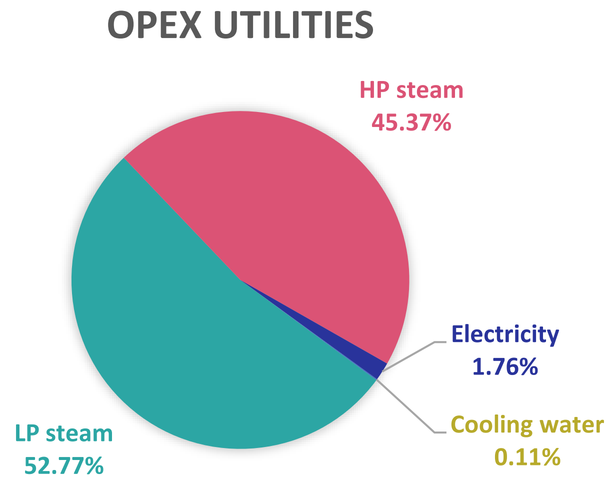


Figure 5.11 OPEX contributions of utilities section in the Methanol plant.

As can be seen in Figure 5.11, for this section almost all costs are attributed to vapor: low pressure steam requirement costs 161 k$/y, while high-pressure steam cost sums up to 139 k$/y.

Electricity is the most expensive invoice in the OPEX evaluation of the Methanol plant with 207 k$/y followed by high and low-pressure steam with 184 k$/y and 161 k$/y, respectively.

Dimethyl-ether plant

Figure 5.12 shows the OPEX breakdown for Dimethyl-ether plant.

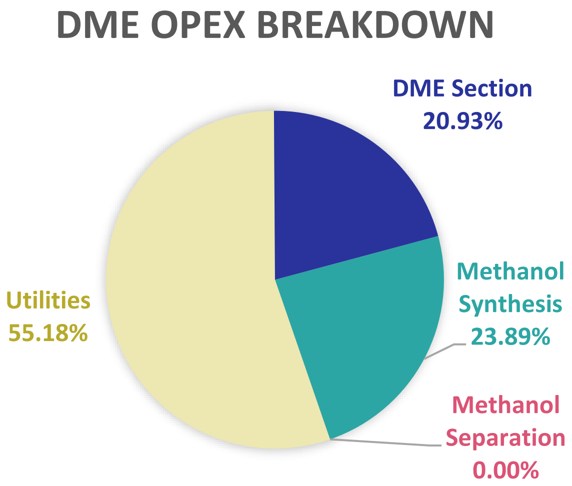


Figure 5.12 Dimethyl-ether plant OPEX breakdown.

Methanol separation section does not have operative costs also in the DME plant, for the same reason stated for the other plant. The methanol synthesis section is identical in the two simulations, and it will not be further investigated. The most important contributor is the utilities section, that it is also more expensive than the utilities section of the methanol plant, now costing 596206 \$/y. The most important category of costs of the utilities section and of the dimethyl-ether synthesis and separation are analyzed in Figure 5.13 and Figure 5.14, respectively.

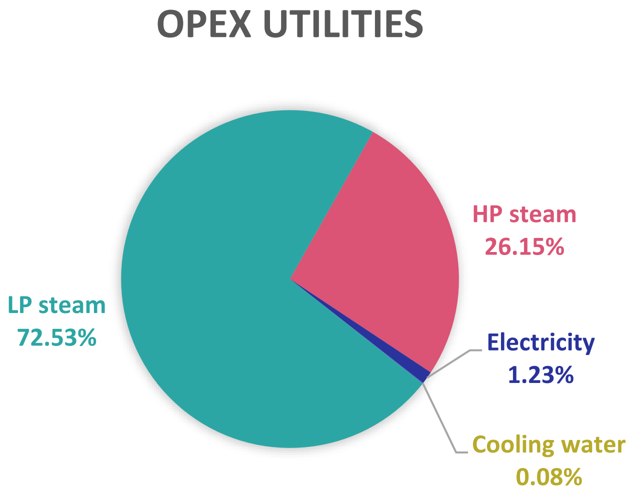


Figure 5.13 OPEX contributions of utilities section in the Dimethyl-ether plant.

Figure 5.13 shows that low pressure steam covers the main part of the operative cost of the plant section. Low pressure steam costs 432 k\$/y, the 271 k\$/y difference with respect to the cost of low-pressure steam in the utilities section in the dimethyl-ether plant lies in the higher duty required by the reboiler of the second distillation column, that is not entirely covered by the vapor cycle and requires external vapor. The cost of high-pressure steam is slightly higher (156 k\$/y) since the flow in the vapor cycle loop is bigger in this plant due to the presence of the vapor generated with the cooling of the dehydration reactor.

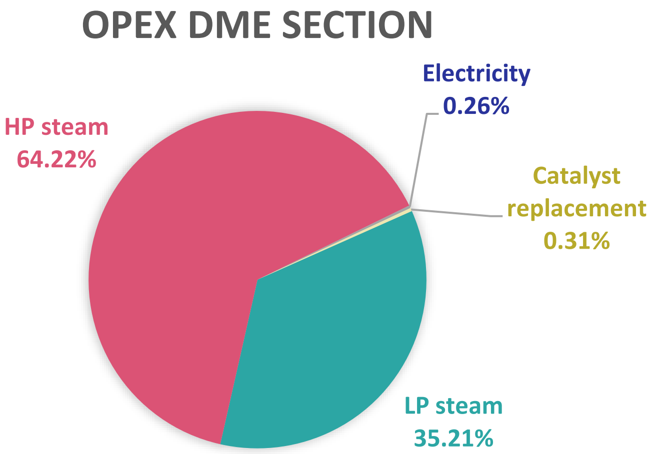


Figure 5.14 OPEX contributions of dimethyl-ether synthesis and separation section in the Dimethyl-ether plant.

The principal category in the operative cost is, again, steam. The high-pressure steam is the hot utility required in the heat exchanger before the reactor, this steam costs 145 k$/y. The low-pressure steam, instead, represent the hot utility of the reboiler of the distillation column present in this section of the plant, with a cost of 80 k$/y.

Low-pressure steam is the most expensive invoice in the OPEX evaluation for the Dimethyl-ether plant with 512 k$/y, followed by high-pressure steam with 346 k$/y and electricity with 210 k$/y.

5.3. Cash flow analysis

CAPEX and OPEX have been evaluated for the two plant alternatives. To perform a cash flow analysis, revenues need to be calculated. Assuming that, every year, all the product produced is sold at the price stated in Section 0, the revenues of the two process plants are reported in Table 5.7.

Table 5.7 Annual revenues for Methanol and Dimethyl-ether plants.

Revenues	
MeOH plant	6.852 M$/y
DME plant	13.741 M$/y

The following sections deal with the calculation of economic indicators to quantify the benefits of each investment.

5.3.1. Payback time

The first indicator to be calculated for both plants is the payback time. The results are reported in Table 5.8

Table 5.8 Simple payback time for Methanol and Dimethyl-ether plants.

PBT	
MeOH plant	2.08 years
DME plant	1.13 years

Of course, the numbers in Table 5.8 do not represent realistic payback time for chemicals plants, but it can already show which option seems to be more promising: the PBT for the DME plant is almost half the one of the methanol plants.

5.3.2. Discounted net present value

With just the few additional information, stated in Section 2.5.5.2, the Net Present Value can be evaluated. Cash Flow diagram for the two plant alternatives are shown in Figure 5.15 and the NPV of each plant after 10 years is reported in Table 5.9. Complete tables for both plants with all the calculations and information are reported in Appendix B.

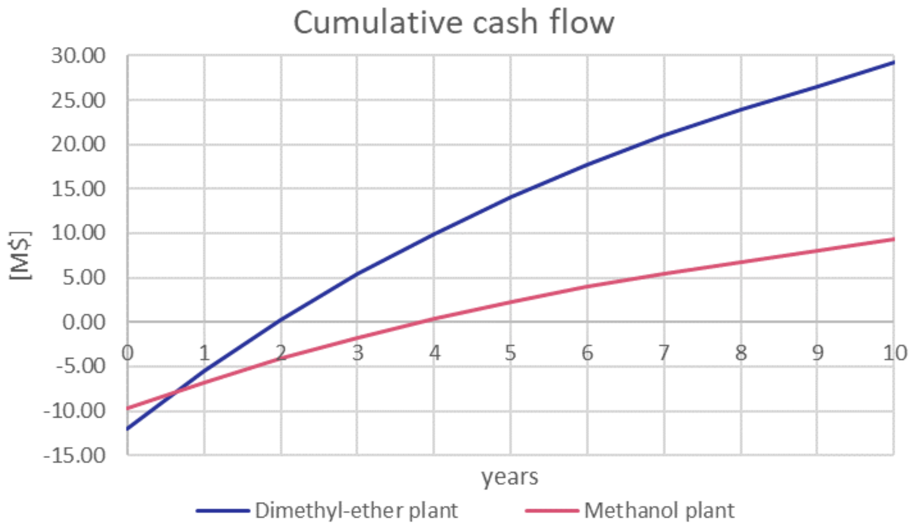


Figure 5.15 Cash Flow diagram for Methanol and Dimethyl-ether plants.

Figure 5.15 shows that the Dimethyl-ether plant is significantly more profitable than the Methanol plant when a huge difference in their sales value is present.

Table 5.9 Net Present Value for Methanol and Dimethyl-ether plants after 10 years.

NPV	
MeOH plant	9363 k$
DME plant	29250 k$

NPV of the Dimethyl-ether plant is more than three times higher than the one of the Methanol plants. This indicates that if huge changes in the price of the two chemicals are not expected, investing in a DME is certainly more profitable, also with this capacity.

5.3.3. Internal rate of return

Net Present Value is a measure of net worth added by an investment, whereas the internal rate of return is an indicator of the profitability, efficiency, quality, or rate of return of an investment. Table 5.10 shows the IRR of the two plant alternatives after the 10 years which represent the considered lifetime for the analysis.

Table 5.10 Internal Rate of Return for Methanol and Dimethyl-ether plants.

IRR	
MeOH plant	32.29%
DME plant	59.84%

IRR behaves accordingly to the other analysis executed, confirming the higher profitability of the Dimethyl-ether plant. It is worth mentioning, though, that the Methanol plant also shows a high value of IRR, which assumingly will still remain positive also in a realistic analysis in which raw materials are considered.

5.3.4. Sensitivity analysis

In this section the results of two different types of sensitivity analysis are reported. The first one focus on understanding how much the capacity of the plant affects the outcomes of the comparison. The latter explores the stability of the results with respect to the accuracy of the information used for the economic appraisal and market oscillations.

5.3.4.1. Size sensitivity

Both simulated plants are fed with the same amount of syngas, equal to 4483 Nm^3/h. To have a better comprehension of the size of the upstream biogas plant for syngas production, it is reported that 5000 Nm^3/h of syngas are produced from 2000 Nm^3/h of biogas, which corresponds to 3.6 MW of biogas [60].

The range of capacity analysed, however, is not centred around the capacity of the base case. This is due to the fact that that capacity is already high considering the typical size of the syngas plant from biogas.

Taking this into consideration, the investigated range of plant capacity is focused on the study of smaller plant with respect to the base case. This decision will also highlight how much the economy of scale negatively impacts on smaller plants.

Figure 5.16 collects the Methanol plant cash flow analysis of the five different plant capacity investigated: the base case and other four.

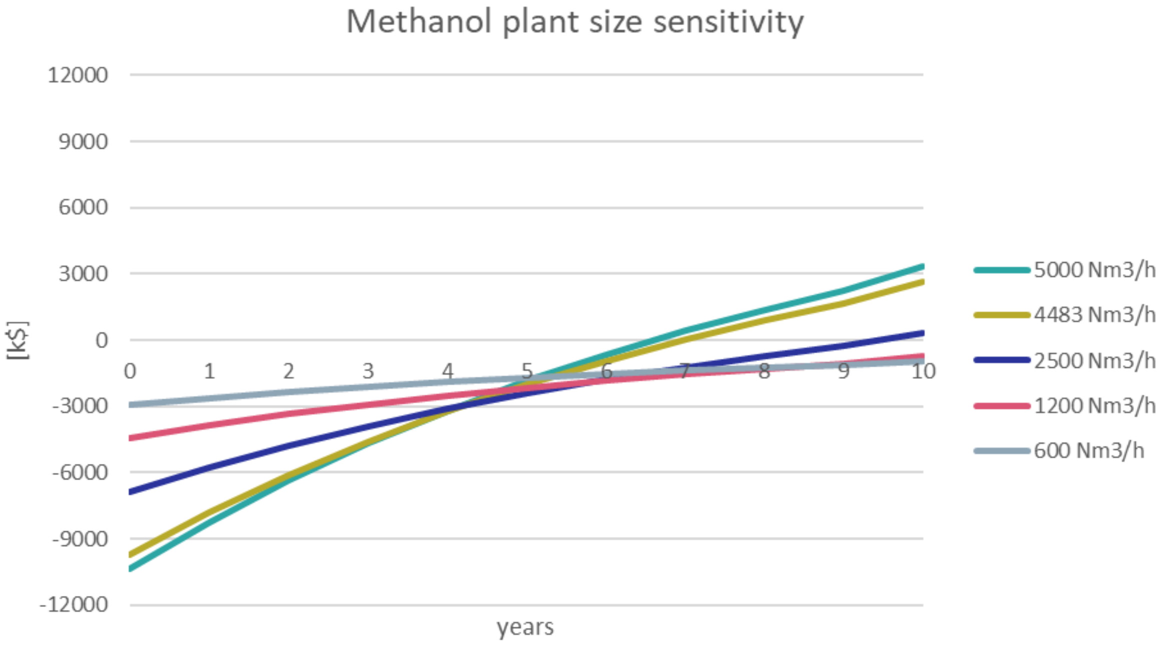


Figure 5.16 Methanol plant cash flow analysis at different plant sizes.

The results showed in Figure 5.16 are in accordance with what the economy of scale principle states. The consideration that can be made from this analysis is that the capacities lower than 2500 Nm^3/h are not going to be profitable enough once raw material cost is considered. Figure 5.17 collects the Dimethyl-ether plant cash flow analysis for the same capacities investigated for the first plant.

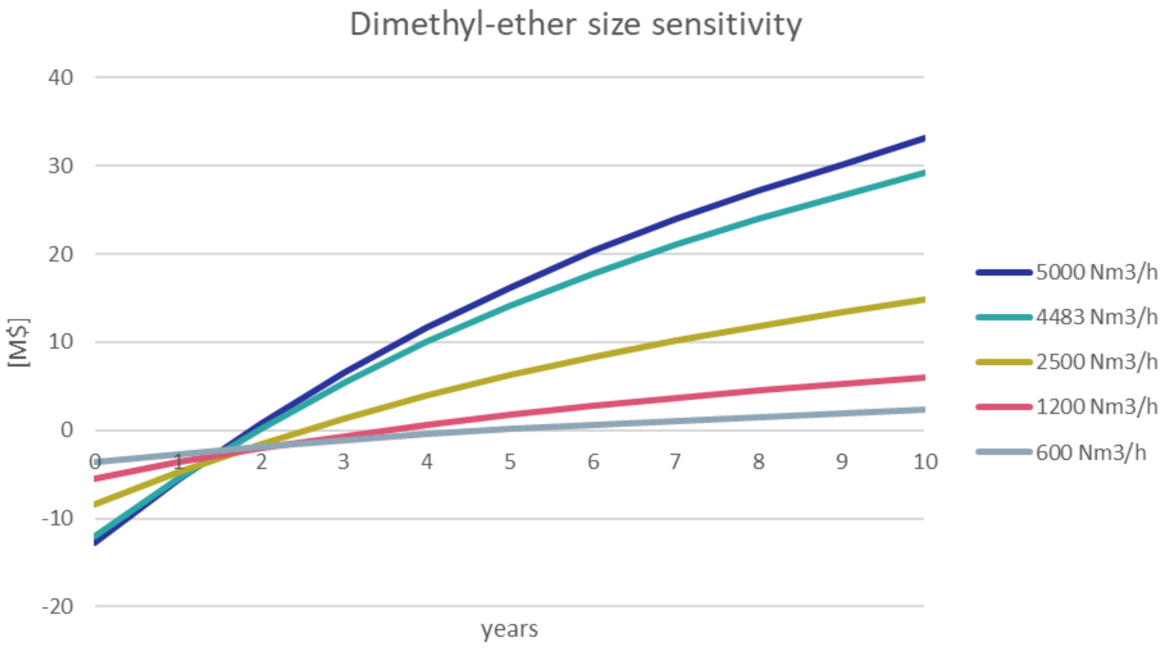


Figure 5.17 Dimethyl-ether plant cash flow analysis at different plant sizes.

Figure 5.17 shows also in this case that the profitability of smaller plants decrease significantly. It can be seen that the DME plant with a capacity of 1200 Nm^3/h has a higher NPV with respect to a Methanol plant with double capacity.

Figure 5.18, Figure 5.19 and Figure 5.20 summarize the trend of payback time, net present value and internal rate of return.

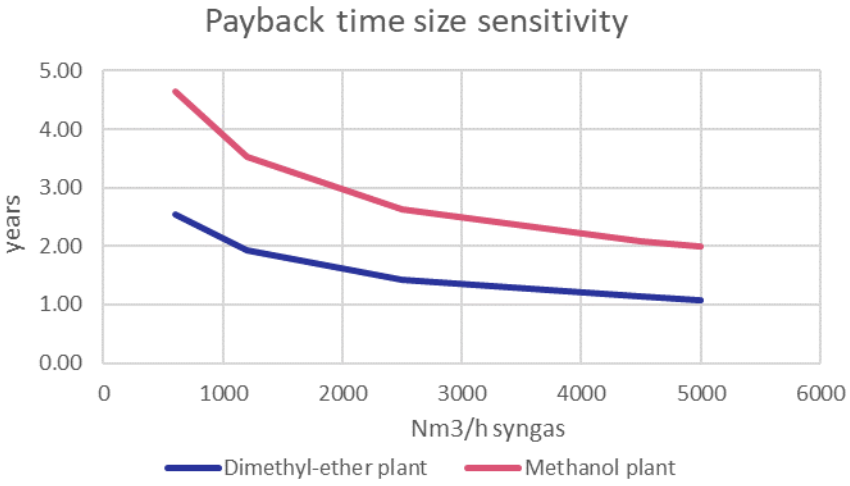


Figure 5.18 Payback time at different plant capacities for Methanol and Dimethyl-ether plants.

Figure 5.18 shows that for each capacity methanol plant has always a payback time more or less double than the corresponding parameter for the DME plant.

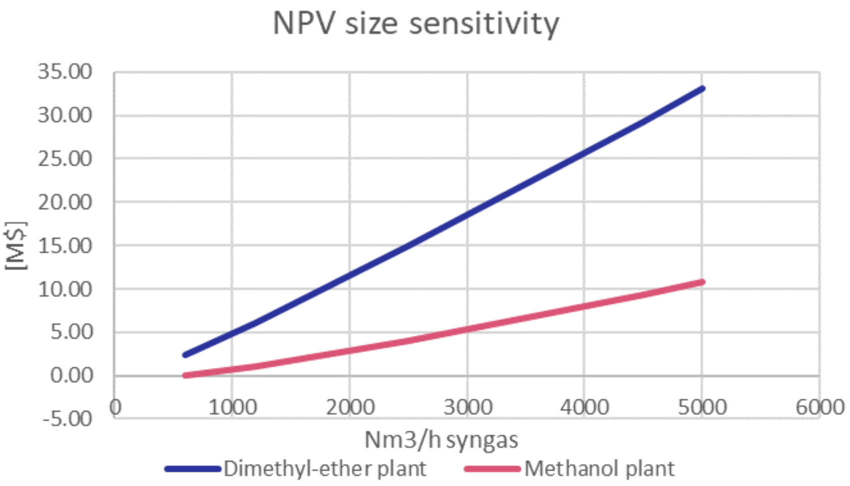


Figure 5.19 Net Present value at different plant capacities for Methanol and Dimethyl-ether plants.

Figure 5.19 shows how the economy of scale effect behave at changing plant capacity, highly increasing the difference in profit between the two alternatives for the bigger plants.

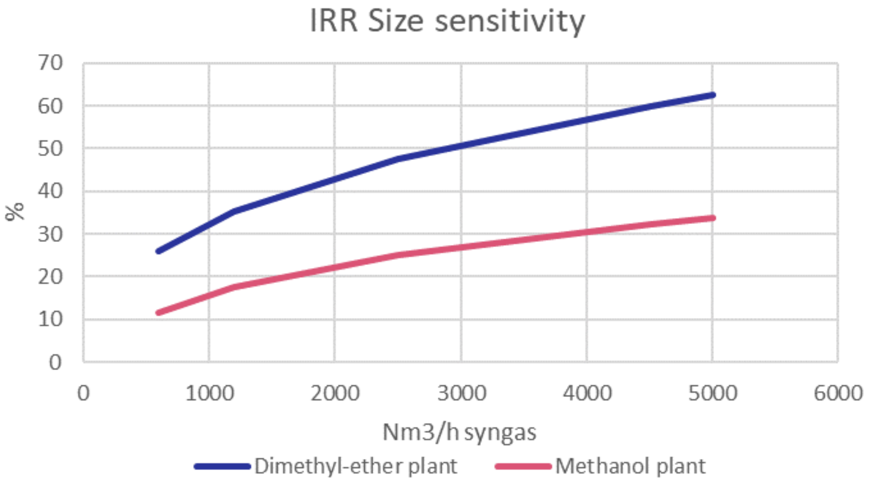


Figure 5.20 Internal rate of return at different plant capacities for Methanol and Dimethyl-ether plants.

IRR values reported in Figure 5.20 shows differences between the two options, while remaining promising values for almost each case study. However, it is reminded that these value are not representative of the actual situation, and the introduction of the raw material cost will inevitably largely worsen the results.

The worst plant alternative, that will probably loose all profit after the elimination of all the assumptions are the methanol plants with low capacity.

5.3.4.2. Project sensitivity

In this section the results of the project sensitivity analysis are reported. The aim of this analysis is to understand how much the uncertainty of the estimation of the project investment and expenses and external factors affect the outcomes. Figure 5.21 express how the net present value changes if the price of the product is not equal to the one assumed for the original calculation. Figure 5.22, instead, focus in understanding how much the reduction of the amount of product produced affects the results, and what are the additional revenues if the production is increased, for example if a more active and selective catalyst is used.

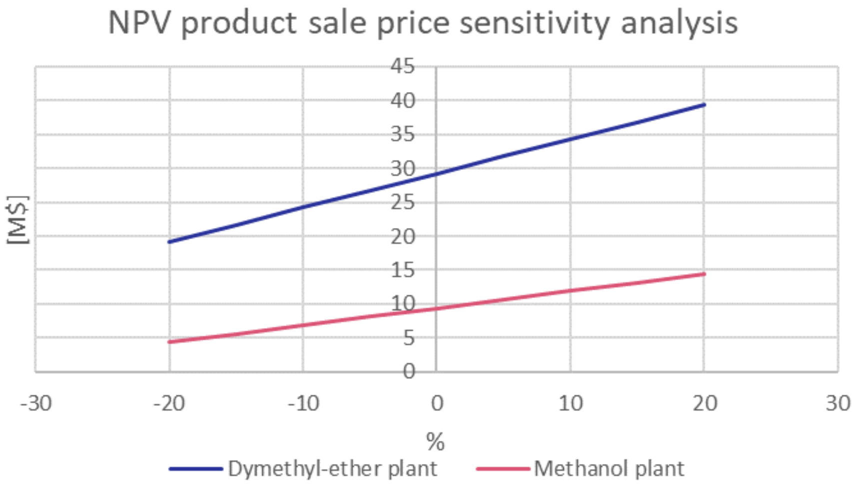


Figure 5.21 Product sale price sensitivity analysis for methanol and dimethyl-ether plants.

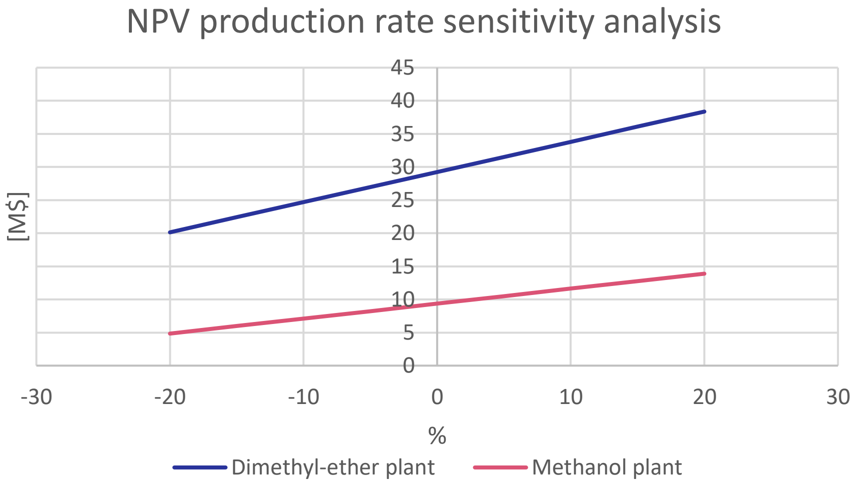


Figure 5.22 Production rate sensitivity analysis for methanol and dimethyl-ether plants.

Both graphs shows that the DME plant shows the biggest variation, while always remaining more profitable than the methanol plant.

Figure 5.23 and Figure 5.24 shows the effects of the variation of the fixed costs and of the grassroot costs, respectively. It can be seen that the variation on this types of costs cause less variation in the net present value trends, and this is symptom of the OPEX being the main discriminant factor for the feasibility of these two plants, especially for the dimethyl-ether plant.

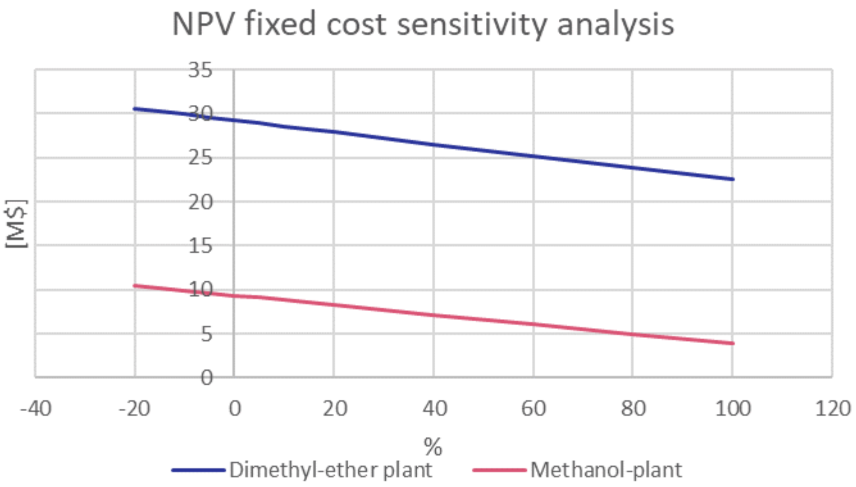


Figure 5.23 Fixed cost sensitivity analysis for methanol and dimethyl-ether plants.

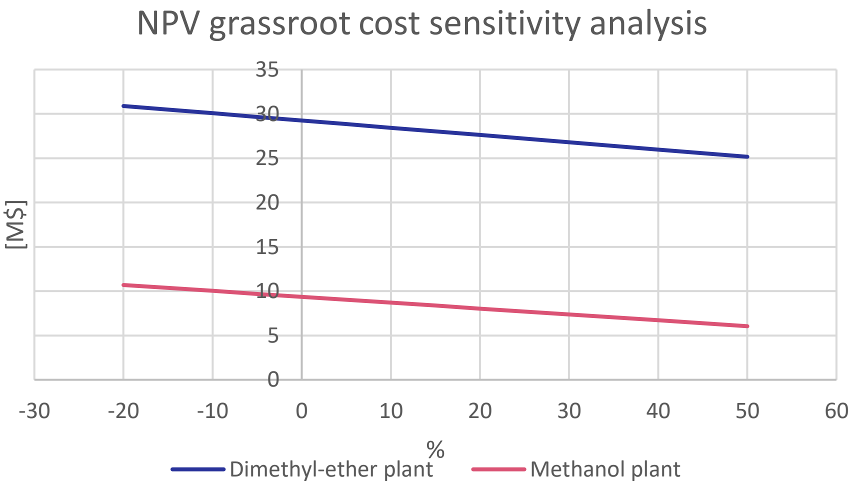


Figure 5.24 Grassroot cost sensitivity analysis for methanol and dimethyl-ether plants.

5.4. Market analysis

Taking into consideration the results of all the previous analysis, an economic appraisal on the United State market is meaningless: while the methanol price is the same as for the European market, the dimethyl-ether has even a higher value. This analysis will arrive at the same conclusion, declaring the more profitability of the dimethyl-ether.

For the Chinese market both prices vary and a conclusion without the calculation of any index cannot be provided. Table 5.11 provide the net present value calculated for both plant alternatives using revenues evaluated using the product prices of the Chinese market.

Table 5.11 Net present value of the methanol and dimethyl-ether plant after 10 years, for the Chinese market.

NPV	
MeOH plant	2652 k$
DME plant	9063 k$

It can be seen that the dimethyl-ether plant is steel more profitable with respect to the alternative, but the profit is considerably diminished.

Another consideration that must be made is that in the year (2022) chosen to determine the product prices there was a pick in the dimethyl-ether price and that in 2023 the price is lower and has returned to follow the trend of the past few years. The predicted average DME price during 2023 in China will be 0.66 $/kg, that will result for the discussed plant in a net present value of 5429 k$. Even if the value is small is still higher than the net present value for the methanol plant.

However, reminding again that these values are not representative of the reality, the important information given by this analysis is that a small plant for DME like the one present in this work will probably not be a smart choice in a market like the Chinese one, where the DME market is well established, and a lot of bigger plants exists and dictate the DME price.

The last consideration provided is that assuming that the methanol price will not significantly vary with respect to the value considered in this work, the dimethyl-ether plant will be preferable if DME is expected not to decrease below 0.76 $/kg.

6 Conclusion and future developments

This thesis work has been conceived to propose the best opportunity to exploit a stream of syngas coming from a renewable source and converting it into valuable products. Biogas can be used as renewable feedstock. The alternatives investigated in this work are the production of methanol from syngas and the production of dimethyl-ether produced from the methanol synthetized from syngas.

The principal limitation for both plant alternatives is represented by their capacity. The size of the plant is established by the size of the upstream syngas production plant from biogas, which is quite small with respect to syngas production from fossil feedstocks. This constraint deprives the plant form the benefit of the economy of scale principle.

The main hypothesis adopted in this work is neglecting the cost of the raw material in the economic appraisal. The reason is the lack of reliable data on the cost of a stream of syngas coming from a renewable source. Indeed, syngas is often produced just as an intermediate, and it is immediately transformed into a more valuable chemical and not sold to someone else. This simplification result in obtaining economic results not representative of the reality of the profit of the investment, but since the raw material cost is the same among the two studied alternatives, the outcomes of the conducted differential analysis do not change according to it.

In this thesis an optimal design for both plant alternatives were derived, as well as an accurate sizing of the principal pieces of equipment, in order to obtain a value for the capital investment of the two plants as trustable as possible. To have reliable results also for the operative expenditure for the utilities the design of the utilities section was also realized in the simulation software used, that is Aspen HYSYS.

The economic analysis resulted in determining that the dimethyl-ether plant is more profitable than the methanol one. It is not surprising since the additional DME module consists mainly just of a reactor and a distillation column, which costs, both capital and operative, can be paid off by the higher value of the DME in the market. An important note on this information is that, thanks to the market analysis conducted and presented in the previous chapter, it can be assessed that a small plant like the one discussed in this study is not suitable in a market like the Chinese one, where the production of dimethyl-ether is very developed and where the price of the DME is lower with respect to the rest of the world.

Potential future developments for this work may be:

1. a more accurate analysis in which the assumptions present in this work are removed, resulting in values which are indicative of the real investment, by including the biogas to syngas plant in the study;
2. the analysis of other design alternatives for the production of dimethyl-ether, like the direct synthesis of DME from syngas, in which the plant layout may have a lower capital investment;
3. It is emerged that the dimethyl-ether profitability heavily depends on its market value, which had a non-predictable trend in the last few years. Given that, another possible economic appraisal may be conducted on a modular plant for the indirect synthesis of dimethyl-ether in which the production of DME can be turned off if DME price decrease below the minimum price for which the plant is gaining value. When this happens the first part of the plant can still work to produce and sell methanol;
4. A sensitivity analysis on the operation condition can be performed, for example on the temperature and pressure in the reactors;
5. A research on the optimal reactor configuration;
6. A systematic energy integration of the process;
7. A Life Cycle Assessment on the whole plant to determine the emissions and the impact on global warming, ozone depletion etc.

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A Appendix A

In this Appendix data in support of economic evaluation are reported. For each plant the parameters to evaluate the cost of each piece of equipment are presented. The correlation to be used are those explained in Section 2.5.1. Every section of this Appendix is devoted to the analysis of a specific class of equipment.

A.1. Methanol plant CAPEX

A.1.1 Heat exchangers

Heat Exchanger	**Type**	**K_1**	**K_2**	**K_3**	**A Area [m^2]**	**c_p^0 (2001) [$]**
E-100	Air cooler	4.0336	0.2341	0.0497	3.80	86440.00
E-101	Fixed tube	4.3247	-0.303	0.1634	30.38	191226.22
E-102	Fixed tube	4.3247	-0.303	0.1634	10.94	126303.14
E-103	Air cooler	4.0336	0.2341	0.0497	22.31	210886.63
E-104	Fixed tube	4.3247	-0.303	0.1634	3.08	53604.911
E-105	Fixed tube	4.3247	-0.303	0.1634	97.11	165435.43
E-107	Fixed tube	4.3247	-0.303	0.1634	4.97	55167.881
Reboiler T-100	Kettle	4.46460	-0.5277	0.3955	6.40	155083.46
Reboiler T-101	Kettle	4.46460	-0.5277	0.3955	121.21	1138909.65

Heat Exchanger	C_1	C_2	C_3	P [barg]	F_P	F_M	B_1	B_2	F_{BM}
E-100	-0.125	0.15361	-0.02861	29.81	1.10	2.94	0.96	1.21	4.85
E-101	0.03881	-0.11272	0.08183	59.00	1.25	2.74	1.63	1.66	7.29
E-102	0.03881	-0.11272	0.08183	58.90	1.25	1.83	1.63	1.66	5.41
E-103	-0.125	0.15361	-0.02861	56.7	1.14	2.94	0.96	1.21	5.01
E-104	0	0	0	2	1	1.83	1.63	1.66	4.67
E-105	0	0	0	2	1	1.83	1.63	1.66	4.67
E-107	0.03881	-0.11272	0.08183	41	1.17	1	1.63	1.66	3.58
Reboiler T-100	0	0	0	1.15	1	2.74	1.63	1.66	6.17
Reboiler T-101	0	0	0	0.88	1	2.74	1.63	1.66	6.17

Heat Exchanger	c_{BM} (2017) [$\$$]	c^0_{BM} (2017) [$\$$]
E-100	86440.00	38610.80
E-101	191226.22	86416.97
E-102	126303.14	77309.43
E-103	210886.63	91383.73
E-104	53604.91	38052.94
E-105	165435.43	117438.79
E-107	55167.88	50704.38
Reboiler T-100	155083.46	82804.47
Reboiler T-101	1138909.65	608106.06

A.1.2 Compressors

Compressors	Type	K_1	K_2	K_3	A Fluid power [kW]	c^0_p (2001) [$\$$]
K-100	Axial	2.2897	1.3604	-0.1027	176.34	85517.31
K-101	Axial	2.2897	1.3604	-0.1027	171.32	84048.61
K-102	Centrifugal	2.2897	1.3604	-0.1027	36.04	32983.79

Compressors	F_{BM}	c_{BM} (2017) [$]	c^0_{BM} (2017) [$]
K-100	8.02	1045441.67	82804.47
K-101	8.02	1027486.88	38052.94
K-102	5.74	292337.36	117438.79

A.1.3 Pumps

Pumps	Type	K_1	K_2	K_3	A Shaft power [kW]	c^0_p (2001) [$]
P-100	Centrifugal	3.3892	0.0536	0.1538	8.58	3742.98
P-101	Centrifugal	3.3892	0.0536	0.1538	1.63	2555.86

Pumps	C_1	C_2	C_3	P [barg]	F_P	F_M	B_1	B_2	F_{BM}
P-100	0	0	0	2.00	1	1.56	1.89	1.35	4.00
P-101	-0.3935	0.3957	-0.00226	19.00	1.28	1.56	1.89	1.35	4.60

Pumps	c_{BM} (2017) [$]	c^0_{BM} (2017) [$]
P-100	23196.86	22888.16
P-101	18241.99	15628.94

A.1.4 Reactors

As already mentioned, the reactors are modelled as heat exchangers.

Reactor	Type	K_1	K_2	K_3	A Area [m²]	c^0_p (2001) [$]
PFR-100	Fixed tube	4.3247	-0.303	0.1634	464.91	47758.90

Reactor	C_1	C_2	C_3	P [barg]	F_P	F_M	B_1	B_2	F_{BM}
PFR-100	0.03881	-0.11272	0.08183	58.8	1.25	1.83	1.63	1.66	3.58

Reactor	c_{BM} (2017) [$]	c^0_{BM} (2017) [$]
PFR-100	395603.57	240439.62

A.1.5 Process vessels

Vessels	Type	K_1	K_2	K_3	A Volume [m^3]	c^0_p (2001) [$]
V-100	Vertical	3.4974	0.4485	0.1074	0.98	3115.11
V-101	Vertical	3.4974	0.4485	0.1074	0.41	2192.45

Vessels	P [barg]	D [m]	F_P	F_M	B_1	B_2	F_{BM}
V-100	56.00	0.61	3.88	3.12	2.25	1.82	24.26
V-101	0.79	0.46	1	3.12	2.25	1.82	7.92

Vessels	c_{BM} (2017) [$]	c^0_{BM} (2017) [$]
V-100	115661.82	19400.97
V-101	26581.65	13654.61

A.1.6 Towers

Columns	Type	K_1	K_2	K_3	A Volume [m^3]	c^0_p (2001) [$]
T-100	Tower	3.4974	0.4485	0.1074	0.09	954.88
T-101	Tower	3.4974	0.4485	0.1074	11.30	12269.99
T-102	Absorber	3.4974	0.4485	0.1074	56.03	40726.88

Columns	P [barg]	D [m]	F_P	F_M	B_1	B_2	F_{BM}
T-100	1.15	0.29	1	3.12	2.25	1.82	7.93
T-101	0.88	0.80	1	3.12	2.25	1.82	7.93
T-102	0.00	6.76	1.13	1	2.25	1.82	4.31

Columns	c_{BM} (2017) [$]	c^0_{BM} (2017) [$]
T-100	11577.11	5947.00
T-101	148763.72	76417.76
T-102	268562.96	253647.91

Trays	Type	K_1	K_2	K_3	A Area [m^2]	c^0_p (2001) [$]
T-101	Sieves	2.9949	0.4465	0.3961	0.50	789.21

Trays	N	F_q	F_{BM}	c_{BM} (2017) [$]	c^0_{BM} (2017) [$]
T-101	35	1	62.45	75416.50	42268.46

Packing	Type	K_1	K_2	K_3	A Volume [m^3]	c^0_p (2001) [$]
T-100	Loose	2.4493	0.9744	0.0055	0.09	27.45
T-102	Loose	2.4493	0.9744	0.0055	56.03	14783.21

Packing	F_{BM}	c_{BM} (2017) [$]	c^0_{BM} (2017) [$]
T-100	7.07	296.90	296.90
T-102	7.07	159872.44	159872.44

A.2. CAPEX for Dimethyl-ether plant

A.2.1 Heat exchangers

Heat Exchanger	Type	K_1	K_2	K_3	A Area [m^2]	c_p^0 (2001) [$]
E-100	Air cooler	4.0336	0.2341	0.0497	3.82	11667.36
E-101	Fixed tube	4.3247	-0.303	0.1634	30.40	17166.79
E-102	Fixed tube	4.3247	-0.303	0.1634	10.96	15356.95
E-103	Air cooler	4.0336	0.2341	0.0497	22.31	27521.44
E-104	Fixed tube	4.3247	-0.303	0.1634	3.08	7559.86
E-105	Fixed tube	4.3247	-0.303	0.1634	119.35	25130.27
E-109	Fixed tube	4.3247	-0.303	0.1634	5.70	10810.99
E-110	Fixed tube	4.3247	-0.303	0.1634	11.60	15392.46
E-111	Fixed tube	4.3247	-0.303	0.1634	15.44	15681.86
E-112	Fixed tube	4.3247	-0.303	0.1634	19.07	16018.17
Reboiler T-100	Kettle	4.46460	-0.5277	0.3955	6.41	16455.85
Reboiler T-101	Kettle	4.46460	-0.5277	0.3955	150.00	154561.06
Reboiler T-103	Kettle	4.46460	-0.5277	0.3955	25.52	31986.11

Heat Exchanger	C_1	C_2	C_3	P [barg]	F_P	F_M	B_1	B_2	F_{BM}
E-100	-0.125	0.15361	-0.02861	29.81	1.09	2.94	0.96	1.21	4.85
E-101	0.03881	-0.11272	0.08183	59.00	1.25	2.74	1.63	1.66	7.29
E-102	0.03881	-0.11272	0.08183	58.90	1.25	1.83	1.63	1.66	5.41
E-103	-0.125	0.15361	-0.02861	56.70	1.14	2.94	0.96	1.21	5.01
E-104	0	0	0	2.00	**1**	1.83	1.63	1.66	4.67
E-105	0	0	0	2.00	1	1.83	1.63	1.66	4.67
E-109	0.03881	-0.11272	0.08183	41.00	1.17	1	1.63	1.66	3.58
E-110	0.03881	-0.11272	0.08183	11.70	1.03	2.74	1.63	1.66	6.30
E-111	0.03881	-0.11272	0.08183	41.00	1.17	1.83	1.63	1.66	5.20
E-112	0.03881	-0.11272	0.08183	7.90	1.01	1.83	1.63	1.66	4.69
Reboiler T-100	0	0	0	1.15	1	2.74	1.63	1.66	6.17
Reboiler T-101	0	0	0	0.88	1	2.74	1.63	1.66	6.17
Reboiler T-103	0.03881	-0.11272	0.08183	9.00	1.01	2.74	1.63	1.66	6.23

Heat Exchanger	**c_{BM} (2017) [$]**	**c^0_{BM} (2017) [$]**
E-100	86420.42	38742.55
E-101	191244.55	86425.25
E-102	126310.16	77313.72
E-103	210895.26	91387.46
E-104	53614.44	38059.71
E-105	178223.59	126516.98
E-109	59218.60	54427.36
E-110	148060.41	77492.50
E-111	123794.95	78949.50
E-112	114241.21	80642.62
Reboiler T-100	155161.40	82846.09
Reboiler T-101	1457348.67	778129.30
Reboiler T-103	304651.62	161032.34

A.2.2 Compressors

Compressors	**Type**	**K_1**	**K_2**	**K_3**	**A Fluid power [kW]**	**c^0_p (2001) [$]**
K-100	Axial	2.2897	1.3604	-0.1027	178.12	86032.63
K-101	Axial	2.2897	1.3604	-0.1027	169.62	83545.93
K-102	Centrifugal	2.2897	1.3604	-0.1027	36.10	33019.03

Compressors	**F_{BM}**	**c_{BM} (2017) [$]**	**c^0_{BM} (2017) [$]**
K-100	8.02	1051741.342	358164.93
K-101	8.02	1021341.718	347812.49
K-102	5.74	292649.703	137462.48

A.2.3 Pumps

Pumps	Type	K_1	K_2	K_3	A Shaft power [kW]	c_p^0 (2001) [$]
P-100	Centrifugal	3.3892	0.0536	0.1538	12.10	4242.05
P-101	Centrifugal	3.3892	0.0536	0.1538	1.84	2594.42
P-102	Centrifugal	3.3892	0.0536	0.1538	1.12	2466.66

Pumps	C_1	C_2	C_3	P [barg]	F_P	F_M	B_1	B_2	F_{BM}
P-100	0	0	0	2.00	1	1.56	1.89	1.35	4.00
P-101	-0.3935	0.3957	-0.00226	19.00	1.28	1.56	1.89	1.35	4.60
P-102	-0.3935	0.3957	-0.00226	11.70	1.06	2.28	1.89	1.35	5.16

Pumps	c_{BM} (2017) [$]	c_{BM}^0 (2017) [$]
P-100	26289.74	25939.92
P-101	18517.27	15864.79
P-102	19588.70	15083.52

A.2.4 Reactors

Reactor	Type	K_1	K_2	K_3	A Area [m²]	c_p^0 (2001) [$]
PFR-100	Fixed tube	4.3247	-0.303	0.1634	464.91	47759.24
GBR-100	Fixed tube	4.3247	-0.303	0.1634	106.89	24131.00

Reactor	C_1	C_2	C_3	P [barg]	F_P	F_M	B_1	B_2	F_{BM}
PFR-100	0.03881	-0.11272	0.08183	58.8	1.25	1.83	1.63	1.66	3.58
GBR-100	0.03881	-0.11272	0.08183	19.00	1.07	1.83	1.63	1.66	4.87

Reactor	c_{BM} (2017) [$]	c_{BM}^0 (2017) [$]
PFR-100	395603.57	240441.31
GBR-100	179894.21	121486.22

A.2.5 Process vessels

Vessels	Type	K_1	K_2	K_3	A Volume [m³]	c_p^0 (2001) [$]
V-100	Vertical	3.4974	0.4485	0.1074	0.98	3115.11
V-101	Vertical	3.4974	0.4485	0.1074	0.41	2192.45

Vessels	P [barg]	D [m]	F_P	F_M	B_1	B_2	F_{BM}
V-100	56.00	0.61	3.88	3.12	2.25	1.82	24.26
V-101	0.79	0.46	1	3.12	2.25	1.82	7.92

Vessels	c_{BM} (2017) [$]	c_{BM}^0 (2017) [$]
V-100	115661.82	19400.97
V-101	26581.65	13654.61

A.2.6 Towers

Columns	Type	K_1	K_2	K_3	A Volume [m³]	c_p^0 (2001) [$]
T-100	Tower	3.4974	0.4485	0.1074	0.08	872.13
T-101	Tower	3.4974	0.4485	0.1074	15.54	15283.61
T-102	Absorber	3.4974	0.4485	0.1074	56.50	41008.29
T-103	Tower	3.4974	0.4485	0.1074	0.17	1414.38

Columns	P [barg]	D [m]	F_P	F_M	B_1	B_2	F_{BM}
T-100	1.15	0.25	1	3.12	2.25	1.82	7.93
T-101	0.88	0.89	1	3.12	2.25	1.82	7.93
T-102	0.00	6.76	1.13	1	2.25	1.82	4.31
T-103	9.00	0.38	1	3.12	2.25	1.82	7.93

Columns	c_{BM} (2017) [$]	c_{BM}^0 (2017) [$]
T-100	10573.85	5431.63
T-101	185301.51	95186.69
T-102	271866.25	255400.58
T-103	17148.20	8808.78

Trays	Type	K_1	K_2	K_3	A Area [m^2]	c_p^0 (2001) [$]
T-101	Sieves	2.9949	0.4465	0.3961	0.62	830.38

Trays	N	F_q	F_{BM}	c_{BM} (2017) [$]	c_{BM}^0 (2017) [$]
T-101	39	1	62.45	88418.99	49555.93

Packing	Type	K_1	K_2	K_3	A Volume [m^3]	c_p^0 (2001) [$]
T-100	Loose	2.4493	0.9744	0.0055	0.08	23.74
T-102	Loose	2.4493	0.9744	0.0055	56.50	14906.41
T-103	Loose	2.4493	0.9744	0.0055	0.17	51.63

Packing	F_{BM}	c_{BM} (2017) [$]	c_{BM}^0 (2017) [$]
T-100	7.07	256.72	256.72
T-102	7.07	161204.80	161204.80
T-103	7.07	558.32	558.32

B Appendix B

B.1. NPV Methanol plant

year	Investment [k$]	Revenues [k$]	Costs [k$]	Depreciation [k$]	Delta [k$]	Taxable income [k$]	Taxation [k$]	Profit [k$]	Discounted cash flow [k$]	Net present value [k$]
0	-9725.41									-9725.41
1		6851.91	2182.77	827.69	4669.14	3841.45	1344.51	3324.63	2968.42	-6756.98
2		6851.91	2182.77	827.69	4669.14	3841.45	1344.51	3324.63	2650.38	-4106.61
3		6851.91	2182.77	827.69	4669.14	3841.45	1344.51	3324.63	2366.41	-1740.20
4		6851.91	2182.77	827.69	4669.14	3841.45	1344.51	3324.63	2112.87	372.67
5		6851.91	2182.77	827.69	4669.14	3841.45	1344.51	3324.63	1886.49	2259.16
6		6851.91	2182.77	827.69	4669.14	3841.45	1344.51	3324.63	1684.36	3943.52
7		6851.91	2182.77	827.69	4669.14	3841.45	1344.51	3324.63	1503.90	5447.41
8		6851.91	2182.77	827.69	4669.14	3841.45	1344.51	3324.63	1342.76	6790.18
9		6851.91	2182.77	827.69	4669.14	3841.45	1344.51	3324.63	1198.90	7989.08
10		8296.67	2182.77	827.69	6117.61	5289.91	1851.47	4266.14	1373.58	**9362.66**

B.2. NPV DME plant

year	Investment [k$]	Revenues [k$]	Costs [k$]	Depreciation [k$]	Delta [k$]	Taxable income [k$]	Taxation [k$]	Profit [k$]	Discounted cash flow [k$]	Net present value [k$]
0	-11983.97									-11983.97
1		13740.91	3164.77	1019.91	10576.14	9556.22	3344.68	7231.46	6456.66	-5527.31
2		13740.91	3164.77	1019.91	10576.14	9556.22	3344.68	7231.46	5764.87	237.56
3		13740.91	3164.77	1019.91	10576.14	9556.22	3344.68	7231.46	5147.21	5384.77
4		13740.91	3164.77	1019.91	10576.14	9556.22	3344.68	7231.46	4595.72	9980.50
5		13740.91	3164.77	1019.91	10576.14	9556.22	3344.68	7231.46	4103.32	14083.82
6		13740.91	3164.77	1019.91	10576.14	9556.22	3344.68	7231.46	3663.68	17747.50
7		13740.91	3164.77	1019.91	10576.14	9556.22	3344.68	7231.46	3271.14	21018.65
8		13740.91	3164.77	1019.91	10576.14	9556.22	3344.68	7231.46	2920.66	23939.31
9		13740.91	3164.77	1019.91	10576.14	9556.22	3344.68	7231.46	2607.74	26547.05
10		15525.76	3164.77	1019.91	12360.98	11341.07	3969.37	8391.61	2701.87	**29248.92**

C Appendix C

In this Appendix Aspen HYSYS material balance for the two alternatives are reported. In each section two tables are present: the first one collects temperature, pressure, vapor fraction, mass flow and molar flow for each stream; the second one reports the mass fraction for every stream present in the simulation.

C.1. Methanol plant workbook

Stream	Temperature [°C]	Pressure [bar]	Vapor fraction [-]	Molar flow [kmol/h]	Mass flow [kg/h]
Vapor outlet	245.00	57.80	1.00	779.08	9583.78
To recycle	49.96	56.90	1.00	706.03	7444.79
Crude methanol	49.96	57.00	0.00	73.05	2138.98
To hydrogen membrane	49.96	56.90	1.00	43.70	460.83
Recycle	49.96	56.90	1.00	662.33	6983.96
compressed 1	135.59	30.62	1.00	226.50	2599.93
compressed 2	138.30	60.00	1.00	226.50	2599.93
mixed	76.23	60.00	1.00	888.78	9583.83
Reactor Inlet	235.00	59.80	1.00	888.78	9583.83
compressed Recycle	56.11	60.00	1.00	662.33	6983.96
R	56.11	60.00	1.00	662.28	6983.90
STEAMreactorIN	255.41	42.00	1.00	9.59	172.82
WATERreactorOUT	255.40	42.00	0.00	9.59	172.82
VAPsatREATTORE	217.24	20.00	1.00	132.18	2381.15
Pre-heated	225.00	59.90	1.00	888.78	9583.83
cooled Reactor OUT	109.97	57.70	0.98	779.08	9583.78
waste water	117.78	1.88	0.00	16.27	293.40
Methanol	75.26	1.40	0.00	54.31	1738.18
cooled 1	50.00	30.52	1.00	226.50	2599.93

Stream	Temperature [°C]	Pressure [bar]	Vapor fraction [-]	Molar flow [kmol/h]	Mass flow [kg/h]
stream to vessel	50.00	57.35	0.91	779.08	9583.78
lightends	40.00	1.90	1.00	3.21	123.46
to MEOH column	90.68	2.15	0.00	69.84	2015.52
washing	25.00	1.79	0.00	0.67	12.00
LE	45.88	1.79	1.00	3.14	119.40
laminated vapor	197.78	6.00	1.00	132.18	2381.15
water make up	65.00	6.00	0.00	8.59	154.66
low P steam	159.05	6.00	0.96	140.76	2535.81
air saturated	21.79	1.00	1.00	15396.07	441595.56
cool water	17.13	1.00	0.00	6381.26	114959.33
dry air	20.00	1.00	1.00	15000.00	434460.70
to first reboiler	159.05	6.00	0.96	14.48	260.78
to second reboiler	159.05	6.00	0.96	126.28	2275.03
Recycle CW	17.20	3.00	0.00	6512.74	117328.02
CW LE column IN	17.20	3.00	0.00	200.35	3609.37
CW MeOH column IN	17.20	3.00	0.00	6311.91	113709.72
CW LE column OUT	30.00	1.00	0.00	200.35	3609.36
CW MeOH column OUT	30.00	1.00	0.00	6311.91	113709.72
CW warm	30.00	1.00	0.00	6512.26	117319.08
humid air	20.00	1.00	1.00	15265.06	439235.81
humidity	99.62	1.00	0.93	265.06	4775.12

Stream	Temperature [°C]	Pressure [bar]	Vapor fraction [-]	Molar flow [kmol/h]	Mass flow [kg/h]
CW make-up	20.00	1.00	0.00	131.48	2368.69
CW to pump	17.19	1.00	0.00	6512.74	117328.02
purge cooling water	17.20	3.00	0.00	0.48	8.67
total CW	17.20	3.00	0.00	6512.75	117328.08
H2 recycled	72.16	15.00	1.00	26.51	181.98
purge	39.96	56.00	0.98	17.20	278.86
initial syngas	43.73	15.00	1.00	226.50	2599.93
membrane recycle	72.16	15.00	1.00	26.50	181.97
out of first reb	133.58	3.00	0.00	14.48	260.78
make up steam for 2nd reb	159.05	6.00	1.00	36.89	664.58
total to second reboiler	159.05	6.00	0.97	163.17	2939.61
out second reboiler	133.58	3.00	0.00	163.17	2939.61
net out of second reboiler	133.58	3.00	0.00	117.65	2119.42
waste water reboiler	133.58	3.00	0.00	45.53	820.19
to be pomped	133.58	3.00	0.00	132.12	2380.20
LIQsatREATTORE	213.41	20.00	0.00	132.18	2381.15
ready for reactor	213.41	20.00	0.00	132.12	2380.20
to LE column	47.54	2.15	0.04	73.05	2138.98
Fresh syngas	40.00	15.00	1.00	200.00	2417.96
to be heated	133.82	20.00	0.00	132.12	2380.20
HP steam IN	255.41	42.00	1.00	29.30	527.78

Stream	Temperature [°C]	Pressure [bar]	Vapor fraction [-]	Molar flow [kmol/h]	Mass flow [kg/h]
HP water OUT	255.40	42.00	0.00	29.30	527.78
methanol recovery	45.88	1.79	0.00	0.73	16.06
inMEOHcol	85.55	1.79	0.02	70.57	2031.59

Stream	Mass fraction [-]								
	CO	CO2	H2	MeOH	H2O	CH4	O2	N2	Ar
Vapor outlet	0.0899	0.3977	0.1006	0.2028	0.0311	0.1779	0	0	0
To recycle	0.1156	0.4982	0.1295	0.0267	0.0017	0.2285	0	0	0
Crude methanol	0.0003	0.0482	0.0001	0.8160	0.1336	0.0017	0	0	0
To hydrogen membrane	0.1156	0.4982	0.1295	0.0267	0.0017	0.2285	0	0	0
Recycle	0.1156	0.4982	0.1295	0.0267	0.0017	0.2285	0	0	0
compressed 1	0.4407	0.3967	0.1205	0	0.0002	0.0419	0	0	0
compressed 2	0.4407	0.3967	0.1205	0	0.0002	0.0419	0	0	0
mixed	0.2038	0.4706	0.1270	0.0195	0.0013	0.1779	0	0	0
Reactor Inlet	0.2038	0.4706	0.1270	0.0195	0.0013	0.1779	0	0	0
compressed Recycle	0.1156	0.4982	0.1295	0.0267	0.0017	0.2285	0	0	0
R	0.1156	0.4981	0.1295	0.0267	0.0017	0.2285	0	0	0
STEAMreactorIN	0	0	0	0	1	0	0	0	0
WATERreactorOUT	0	0	0	0	1	0	0	0	0
VAPsatREATTORE	0	0	0	0	1	0	0	0	0

Stream	Mass fraction [-]								
	CO	CO2	H2	MeOH	H2O	CH4	O2	N2	Ar
Pre-heated	0.2038	0.4706	0.1270	0.0195	0.0013	0.1779	0	0	0
cooled Reactor OUT	0.0899	0.3977	0.1006	0.2028	0.0311	0.1779	0	0	0
waste water	0	0	0	0.0030	0.9970	0	0	0	0
Methanol	0	0	0	0.9985	0.0015	0	0	0	0
cooled 1	0.4407	0.3967	0.1205	0	0.0002	0.0419	0	0	0
stream to vessel	0.0899	0.3977	0.1006	0.2028	0.0311	0.1779	0	0	0
lightends	0.0056	0.8352	0.0018	0.1254	0.0020	0.0299	0	0	0
to MEOH column	0	0	0	0.8584	0.1416	0	0	0	0
washing	0	0	0	0	1	0	0	0	0
LE	0.0058	0.8631	0.0019	0.0759	0.0224	0.0309	0	0	0
laminated vapor	0	0	0	0	1	0	0	0	0
water make up	0	0	0	0	1	0	0	0	0
low P steam	0	0	0	0	1	0	0	0	0
air saturated	0	0	0	0	0.0162	0	0.2277	0.7430	0.0132
cool water	0	0	0	0	1	0	0	0	0
dry air	0	0	0	0	0	0	0.2315	0.7552	0.0134
to first reboiler	0	0	0	0	1	0	0	0	0
to second reboiler	0	0	0	0	1	0	0	0	0
Recycle CW	0	0	0	0	1	0	0	0	0
CW LE column IN	0	0	0	0	1	0	0	0	0

Stream	Mass fraction [-]								
	CO	CO2	H2	MeOH	H2O	CH4	O2	N2	Ar
CW MeOH column IN	0	0	0	0	1	0	0	0	0
CW LE column OUT	0	0	0	0	1	0	0	0	0
CW MeOH column OUT	0	0	0	0	1	0	0	0	0
CW warm	0	0	0	0	1	0	0	0	0
humid air	0	0	0	0	0.0109	0	0.2289	0.7470	0.0132
humidity	0	0	0	0	1	0	0	0	0
CW make-up	0	0	0	0	1	0	0	0	0
CW to pump	0	0	0	0	1	0	0	0	0
purge cooling water	0	0	0	0	1	0	0	0	0
total CW	0	0	0	0	1	0	0	0	0
H2 recycled	0.0439	0.6308	0.2525	0	0.0034	0.0694	0	0	0
purge	0.1624	0.4116	0.0492	0.0441	0.0005	0.3322	0	0	0
initial syngas	0.4407	0.3967	0.1205	0	0.0002	0.0419	0	0	0
membrane recycle	0.0439	0.6308	0.2525	0	0.0034	0.0694	0	0	0
out of first reb	0	0	0	0	1	0	0	0	0
make up stream for 2nd reb	0	0	0	0	1	0	0	0	0
total to second reboiler	0	0	0	0	1	0	0	0	0
out second reboiler	0	0	0	0	1	0	0	0	0
net out of second reboiler	0	0	0	0	1	0	0	0	0
waste water reboiler	0	0	0	0	1	0	0	0	0

Stream	Mass fraction [-]								
	CO	CO2	H2	MeOH	H2O	CH4	O2	N2	Ar
to be pomped	0	0	0	0	1	0	0	0	0
LIQsatREATTORE	0	0	0	0	1	0	0	0	0
ready for reactor	0	0	0	0	1	0	0	0	0
to LE column	0.0003	0.0482	0.0001	0.8160	0.1336	0.0017	0	0	0
Fresh syngas	0.4706	0.3791	0.1105	0	0	0.0398	0	0	0
to be heated	0	0	0	0	1	0	0	0	0
HP steam IN	0	0	0	0	1	0	0	0	0
HP water OUT	0	0	0	0	1	0	0	0	0
methanol recovery	0	0.0041	0	0.3997	0.5962	0	0	0	0
inMEOHcol	0	0	0	0.8547	0.1452	0	0	0	0

C.2. Dimethyl-ether plant workbook

Stream	Temperature [°C]	Pressure [bar]	Vapor fraction [-]	Molar flow [kmol/h]	Mass flow [kg/h]
Vapor outlet	245.00	57.80	1.00	780.41	9593.98
To recycle	49.96	56.90	1.00	707.27	7452.58
Crude methanol	49.96	57.00	0.00	73.14	2141.40
To hydrogen membrane	49.96	56.90	1.00	43.78	461.31
Recycle	49.96	56.90	1.00	663.49	6991.26
compressed 1	136.49	30.81	1.00	226.56	2599.81

Stream	Temperature [°C]	Pressure [bar]	Vapor fraction [-]	Molar flow [kmol/h]	Mass flow [kg/h]
compressed 2	137.40	60.00	1.00	226.56	2599.81
mixed	75.99	60.00	1.00	890.21	9594.03
Reactor Inlet	235.00	59.80	1.00	890.21	9594.03
compressed Recycle	56.11	60.00	1.00	663.49	6991.26
R	56.11	60.00	1.00	663.65	6994.22
STEAMreactorIN	255.41	42.00	1.00	9.61	173.09
WATERreactorOUT	255.40	42.00	0.00	9.61	173.09
VAPsatREATTORE	213.41	20.00	1.00	132.83	2392.95
Pre-heated	225.00	59.90	1.00	890.21	9594.03
cooled Reactor OUT	109.89	57.70	0.98	780.41	9593.98
waste water	118.06	1.88	0.00	43.23	779.23
Methanol	75.17	1.40	0.00	60.91	1950.03
cooled 1	50.00	30.71	1.00	226.56	2599.81
stream to vessel	50.00	57.35	0.91	780.41	9593.98
lightends	40.00	1.90	1.00	3.21	123.48
to methanol col	90.68	2.15	0.00	69.93	2017.92
washing	25.00	1.79	0.00	0.67	12.00
LE	45.88	1.79	1.00	3.14	119.42
methanol recovery	45.88	1.79	0.00	0.73	16.06
laminated vapor	193.65	6.00	1.00	132.83	2392.95
water make up	65.00	6.00	0.00	3.91	70.37

Stream	Temperature [°C]	Pressure [bar]	Vapor fraction [-]	Molar flow [kmol/h]	Mass flow [kg/h]
low P steam	160.28	6.00	1.00	152.48	2746.91
air saturated	23.48	1.00	1.00	15440.39	442394.28
cool water	17.14	1.00	0.00	9012.00	162352.62
dry air	20.00	1.00	1.00	15000.00	434460.70
to first reboiler	160.28	6.00	1.00	13.94	251.11
to second reboiler	160.28	6.00	1.00	138.54	2495.80
Recycle CW	17.21	3.00	0.00	9187.97	165522.64
CW LE column OUT	30.00	1.00	0.00	200.17	3606.03
CW MeOH column OUT	30.00	1.00	0.00	7749.07	139600.61
humid air	20.00	1.00	1.00	15265.06	439235.81
humidity	99.62	1.00	0.93	265.06	4775.12
CW make-up	20.00	1.00	0.00	175.96	3170.01
CW to pump	17.19	1.00	0.00	9187.97	165522.64
purge cooling water	17.21	3.00	0.00	0.67	12.14
total CW	17.21	3.00	0.00	9188.00	165523.23
H2 recycled	72.15	15.00	1.00	26.56	182.21
Purge	39.96	56.00	0.98	17.22	279.10
initial syngas	43.73	15.00	1.00	226.56	2599.81
membrane recycle	72.15	15.00	1.00	26.56	182.21
Fresh syngas	40.00	15.00	1.00	200.00	2417.60
out of first reb	133.58	3.00	0.00	13.94	251.11

Stream	Temperature [°C]	Pressure [bar]	Vapor fraction [-]	Molar flow [kmol/h]	Mass flow [kg/h]
make up steam for 2nd reb	133.58	3.00	1.00	53.08	956.19
total to second reboiler	149.36	3.00	1.00	191.62	3451.99
out second reboiler	133.58	3.00	0.00	191.62	3451.99
net out of second reboiler	133.58	3.00	0.00	134.75	2427.46
waste water reboiler	133.58	3.00	0.00	56.87	1024.53
to be pomped	133.58	3.00	0.00	148.68	2678.57
to be heated	133.82	20.00	0.00	148.68	2678.57
LIQsatREATTORE	213.41	20.00	0.00	132.83	2392.95
ready for reactor	213.41	20.00	0.00	148.68	2678.57
to LE column	47.55	2.15	0.04	73.14	2141.40
pumped methanol	75.45	12.70	0.00	60.91	1950.03
Pre-heated methanol	148.01	12.60	0.65	60.91	1950.03
Heated methanol	230.00	12.50	1.00	60.91	1950.03
crude DME	81.00	10.15	0.49	60.91	1950.04
DME	40.29	8.90	0.00	27.45	1255.03
MEOH to be recycled	158.25	10.10	0.00	33.47	695.01
R methanol	158.25	10.10	0.00	33.47	695.01
purge MEOH recycle	158.25	10.10	0.00	0.00	0.00
recycled methanol	101.26	1.89	0.15	33.48	695.27
laminated recycle	101.26	1.89	0.15	33.47	695.01
CW DME column OUT	30.00	1.00	0.00	1238.09	22304.44

Stream	Temperature [°C]	Pressure [bar]	Vapor fraction [-]	Molar flow [kmol/h]	Mass flow [kg/h]
HP in DME	255.41	42.00	1.00	30.71	553.29
HP out DME	255.40	42.00	0.00	30.71	553.29
vapor outlet 2nd reactor	230.00	10.50	1.00	60.91	1950.04
liquid products	230.00	10.50	0.00	0.00	0.00
VAPsatDME	213.41	20.00	1.00	15.74	283.59
CW LE column IN	17.21	3.00	0.00	200.17	3606.03
CW methanol column IN	17.21	3.00	0.00	7749.07	139600.61
CW DME column IN	17.21	3.00	0.00	1238.09	22304.44
CW warm	30.00	1.00	0.00	9187.33	165511.09
laminated vapor DME	193.65	6.00	1.00	15.74	283.59
LIQsatToDME	213.41	20.00	0.00	15.74	283.59
purge vapor cycle	213.41	20.00	0.00	0.11	2.03
HP steam IN	255.41	42.00	1.00	32.97	593.96
HP water OUT	255.40	42.00	0.00	32.97	593.96
inMEOHcol	88.94	1.79	0.06	104.14	2729.26

Stream	Mass fraction [-]									
	CO	CO2	H2	MeOH	DME	H2O	CH4	O2	N2	Ar
Vapor outlet	0.0899	0.3977	0.1007	0.2028	0	0.0311	0.1777	0	0	0
To recycle	0.1156	0.4981	0.1296	0.0267	0	0.0017	0.2283	0	0	0

Stream	**Mass fraction [-]**									
	CO	**CO2**	**H2**	**MeOH**	**DME**	**H2O**	**CH4**	**O2**	**N2**	**Ar**
Crude methanol	0.0003	0.0482	0.0001	0.8160	0	0.1337	0.0017	0	0	0
To hydrogen membrane	0.1156	0.4981	0.1296	0.0267	0	0.0017	0.2283	0	0	0
Recycle	0.1156	0.4981	0.1296	0.0267	0	0.0017	0.2283	0	0	0
compressed 1	0.4407	0.3966	0.1205	0	0	0.0002	0.0419	0	0	0
compressed 2	0.4407	0.3966	0.1205	0	0	0.0002	0.0419	0	0	0
mixed	0.2037	0.4707	0.1271	0.0195	0	0.0013	0.1777	0	0	0
Reactor Inlet	0.2037	0.4707	0.1271	0.0195	0	0.0013	0.1777	0	0	0
compressed Recycle	0.1156	0.4981	0.1296	0.0267	0	0.0017	0.2283	0	0	0
R	0.1156	0.4982	0.1296	0.0267	0	0.0017	0.2282	0	0	0
STEAMreactorIN	0	0	0	0	0	1	0	0	0	0
WATERreactorOUT	0	0	0	0	0	1	0	0	0	0
VAPsatREATTORE	0	0	0	0	0	1	0	0	0	0
Pre-heated	0.2037	0.4707	0.1271	0.0195	0	0.0013	0.1777	0	0	0
cooled Reactor OUT	0.0899	0.3977	0.1007	0.2028	0	0.0311	0.1777	0	0	0
waste water	0	0	0	0.0013	0	0.9987	0	0	0	0
Methanol	0	0	0	0.9985	0.0002	0.0012	0	0	0	0
cooled 1	0.4407	0.3966	0.1205	0	0	0.0002	0.0419	0	0	0
stream to vessel	0.0899	0.3977	0.1007	0.2028	0	0.0311	0.1777	0	0	0
lightends	0.0056	0.8353	0.0018	0.1254	0	0.0020	0.0299	0	0	0
to methanol col	0	0	0	0.8582	0	0.1418	0	0	0	0

Stream	**Mass fraction [-]**									
	CO	**CO2**	**H2**	**MeOH**	**DME**	**H2O**	**CH4**	**O2**	**N2**	**Ar**
washing	0	0	0	0	0	1	0	0	0	0
LE	0.0058	0.8632	0.0019	0.0759	0	0.0224	0.0309	0	0	0
methanol recovery	0	0.0041	0	0.3997	0	0.5962	0	0	0	0
laminated vapor	0	0	0	0	0	1	0	0	0	0
water make up	0	0	0	0	0	1	0	0	0	0
low P steam	0	0	0	0	0	1	0	0	0	0
air saturated	0	0	0	0	0	0.0179	0	0.2273	0.7416	0.0131
cool water	0	0	0	0	0	1	0	0	0	0
dry air	0	0	0	0	0	0	0	0.2315	0.7552	0.0134
to first reboiler	0	0	0	0	0	1	0	0	0	0
to second reboiler	0	0	0	0	0	1	0	0	0	0
Recycle CW	0	0	0	0	0	1	0	0	0	0
CW LE column OUT	0	0	0	0	0	1	0	0	0	0
CW MeOH column OUT	0	0	0	0	0	1	0	0	0	0
humid air	0	0	0	0	0	0.0109	0	0.2289	0.7470	0.0132
humidity	0	0	0	0	0	1	0	0	0	0
CW make-up	0	0	0	0	0	1	0	0	0	0
CW to pump	0	0	0	0	0	1	0	0	0	0
purge cooling water	0	0	0	0	0	1	0	0	0	0
total CW	0	0	0	0	0	1	0	0	0	0

Stream	Mass fraction [-]									
	CO	**CO2**	**H2**	**MeOH**	**DME**	**H2O**	**CH4**	**O2**	**N2**	**Ar**
H2 recycled	0.0439	0.6306	0.2527	0	0	0.0034	0.0694	0	0	0
Purge	0.1624	0.4117	0.0493	0.0441	0	0.0005	0.3320	0	0	0
initial syngas	0.4407	0.3966	0.1205	0	0	0.0002	0.0419	0	0	0
membrane recycle	0.0439	0.6306	0.2527	0	0	0.0034	0.0694	0	0	0
Fresh syngas	0.4706	0.3790	0.1105	0	0	0	0.0399	0	0	0
out of first reb	0	0	0	0	0	1	0	0	0	0
make up steam for 2nd reb	0	0	0	0	0	1	0	0	0	0
total to second reboiler	0	0	0	0	0	1	0	0	0	0
out second reboiler	0	0	0	0	0	1	0	0	0	0
net out of second reboiler	0	0	0	0	0	1	0	0	0	0
waste water reboiler	0	0	0	0	0	1	0	0	0	0
to be pomped	0	0	0	0	0	1	0	0	0	0
to be heated	0	0	0	0	0	1	0	0	0	0
LIQsatREATTORE	0	0	0	0	0	1	0	0	0	0
ready for reactor	0	0	0	0	0	1	0	0	0	0
to LE column	0.0003	0.0482	0.0001	0.8160	0	0.1337	0.0017	0	0	0
pumped methanol	0	0	0	0.9985	0.0002	0.0012	0	0	0	0
Pre-heated methanol	0	0	0	0.9985	0.0002	0.0012	0	0	0	0
Heated methanol	0	0	0	0.9985	0.0002	0.0012	0	0	0	0
crude DME	0	0	0	0.1122	0.6374	0.2504	0	0	0	0

Stream	Mass fraction [-]									
	CO	CO2	H2	MeOH	DME	H2O	CH4	O2	N2	Ar
DME	0	0.0001	0	0.0072	0.9900	0.0028	0	0	0	0
MEOH to be recycled	0	0	0	0.3018	0.0006	0.6975	0	0	0	0
R methanol	0	0	0	0.3018	0.0006	0.6975	0	0	0	0
purge MEOH recycle	0	0	0	0.3018	0.0006	0.6975	0	0	0	0
recycled methanol	0	0	0	0.3018	0.0006	0.6975	0	0	0	0
laminated recycle	0	0	0	0.3018	0.0006	0.6975	0	0	0	0
CW DME column OUT	0	0	0	0	0	1	0	0	0	0
HP in DME	0	0	0	0	0	1	0	0	0	0
HP out DME	0	0	0	0	0	1	0	0	0	0
vapor outlet 2nd reactor	0	0	0	0.1122	0.6374	0.2504	0	0	0	0
liquid products	0	0	0	0.1122	0.6374	0.2504	0	0	0	0
VAPsatDME	0	0	0	0	0	1	0	0	0	0
CW LE column IN	0	0	0	0	0	1	0	0	0	0
CW methanol column IN	0	0	0	0	0	1	0	0	0	0
CW DME column IN	0	0	0	0	0	1	0	0	0	0
CW warm	0	0	0	0	0	1	0	0	0	0
laminated vapor DME	0	0	0	0	0	1	0	0	0	0
LIQsatToDME	0	0	0	0	0	1	0	0	0	0
purge vapor cycle	0	0	0	0	0	1	0	0	0	0
HP steam IN	0	0	0	0	0	1	0	0	0	0

Stream	**Mass fraction [-]**									
	CO	**CO2**	**H2**	**MeOH**	**DME**	**H2O**	**CH4**	**O2**	**N2**	**Ar**
HP water OUT	0	0	0	0	0	1	0	0	0	0
inMEOHcol	0	0	0	0.7138	0.0002	0.2860	0	0	0	0

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List of abbreviations

Abbreviation	Description
Al_2O_3	Alumina
Ar	Argon
CAPEX	Capital expenditure
C_2H_6O	Dimethyl-ether
CH_3OH	Methanol
CH_4	Methane
CO	Carbon monoxide
CO_2	Carbon dioxide
CO_x	CO and CO_2
CORO	CAPEX OPEX Robust Optimizer
Cr	Chromium
Cr_2O_3	Chromium oxide
Cu	Copper
CW	Cooling water
CZA	Copper-zinc-alumina catalyst
DME	Dimethyl-ether
GHG	Greenhouse gas
GHSV	Gas hourly space velocity
GWP	Global warming potential
H_2	Hydrogen
HP	High-pressure
IRR	Internal rate of return
KPI	Key performance indicator
LHV	Lower heating value
LP	Low-pressure
LPG	Liquified petroleum gas
MeOH	Methanol
MgO	Magnesium oxide
MP	Medium-pressure
MTBE	Methyl tert-butyl ether
MSW	Municipal solid waste
N_2	Nitrogen

N_2O	Nitrous oxide
NO_x	Nitrogen oxides
NPV	Net Present Value
O_2	Oxygen
OPEX	Operative expenditure
PBT	Payback time
PFD	Process flow diagram
PFR	Plug flow reactor
PM	Particulate matter
r-WGS	Reverse water gas shift
SO_x	Sulphur oxide
SRK	Soave-Redlich-Kwong
WGS	Water gas shift
Zn	Zinc
ZnO	Zinc oxide

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