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CHEMICAL ENGINEERING DEPARTMENT

MASTER IN HYDROCARBON PROCESSING ENGINEERING

METHANOL SYNTHESIS VIA DIRECT METHANE OXIDATION

SIMULATION AND EVALUATION OF ENERGETIC VIABILITY

LEILA DEIZY ARMANDO PARRUQUE JOSSIAS

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A DISSERTATION BY

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2023

DECLARATION OF ORIGINALITY

I declare that this thesis is an original report of my research, has been written by me and has not been submitted for any previous degree. The collaborative contributions have been indicated clearly and acknowledged. Due references have been provided on all supporting literature and resources.

(Leila Deizy Armando Parruque Jossias)

“(…) how much more will those who receive God’s abundant provision of grace and of the gift of righteousness reign in life through the one man, Jesus Christ”

Rom 5, 17

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ABSTRACT

Direct conversion of methane to methanol (DMTM) has been attracting significant attention since it was found possible in the early 20th century because of its great industrial potential for the efficient utilization of abundant natural gas reserves. Apart from producing methanol, which is an important intermediate in the chemical industry, direct methane oxidation should facilitate transportation as natural gas can be converted into a product, which is a liquid under ambient temperature and pressure. There is considerable literature on the process chemistry of direct methane to methanol conversion, but very few papers discuss the process engineering. In this thesis it was proposed to design, simulate and to evaluate the energetic viability of DMTM. It is a general understanding that at **a conversion per pass of 10% and a selectivity of at least 80%, even at low yields direct methane to methanol can compete with conventional processes based in synthesis gas (syngas)**.

Two flowsheets were built in COCO simulator. **The first for methanol synthesis based on autothermal reforming (ATR) and the second for direct methanol synthesis through methane oxidation.** Parametric studies were performed and the optimization of variables (Molar ratio, H_2\CO ratio, methane conversion, methanol overall methanol overall selectivity and yield, energy requirement) was done using a Scilab code. The inputs that gave the lowest energy usage were set for the flowsheets for a better comparison. In this simulation 1642.9 mol/s of methane were converted into 1360.21 mol/s of methanol through the syngas route and 1302.84 mol/s of methanol through direct methane oxidation. The carbon efficiency of the classical process is 83%. The energy required to convert methane into methanol through the classical route is **229 kJ/mol while for the direct route is 185 kJ/mol under the same conditions**. The results indicate the DMTM can be energetically viable. In this study the energy requirement was minimised at 13% methane per pass conversion and 87% methanol per pass selectivity.

Key words: Methane, ATR, Syngas, Methanol synthesis, Energy requirement.

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ABBREVIATIONS

ABBREVIATIONS

Syngas	Synthesis gas
SMR	Steam Reforming
POX	Partial Oxidation
ATR	Autothermal reforming,
DMR	Dry Reforming of methane
CMR	Combined Reforming of methane
GHR	Gas heated reforming
WGS	Water Gas Shift
GCR	Gas-Cooled Reactor
BWR	Boiling Water Reactor
DMTM	Direct conversion of methane to methanol
COCO	Cape-open to Cape-open

SYMBOLS

X_{CH4}	Methane conversion
S_{CH3OH}	Methanol Selectivity
F_i	Flow rate of compound i
F_{CO}	Carbon monoxide flowrate
F_{CO2}	Carbon dioxide flowrate
F_{H2}	Hydrogen flowrate
F_{H2O}	Water flowrate
F_{CH4}	Methane flowrate
F_{CH3OH}	Methanol flowrate

$X_{overall}$	Overall conversion
$S_{overall}$	Overall selectivity
C_E	Carbon efficiency
S_{ratio}	H_2\CO ratio
M_{ratio}	Molar ratio (H_2-CO_2/ CO_2+CO)
Q	Heat duty
X_1	Oxygen conversion in methane oxidation
X_2	Oxygen conversion in methane combustion
O_2 rate	Oxygen rate (O_2/CH_4)
S_1	Split factor
Y_{CH3OH}	Methanol yield
$Y_{overall}$	Methanol overall yield

CHAPTER I

1. INTRODUCTION

1.1. Background and context of the study

Methanol is a clear, colourless and flammable poisonous liquid which is nowadays considered one of the most useful chemical compounds (Palma, *et al.*, 2018). This alcohol, can be used as a solvent, e.g. as paint and varnish remover, but also as an intermediate in the production of valuable chemical products such as formaldehyde, acetic acid, methyl chloride, methyl tert-butyl ether, dimethyl terephthalate and methyl methacrylate used every day in industrial applications. On the other hand, it can be used in the energy sector where it is directly blended into petroleum fuel or converted into dimethyl ether, olefins, gasoline and biodiesel. (Boyd, 2012 *apud* Guo, 2015). Methanol has an octane number of 113 and its energy density is about half of that of gasoline. The blend of 10% / 90% methanol/gasoline can lead to an octane of up to 130. The fact that methanol is liquid at ambient temperature, easy to store and transport makes it attractive for new fuel and energy applications (Bozzano and Maneti 2016). Therefore, it is a key compound in the global economy of the future, as the world moves from crude oil towards gas reserves and renewable sources (Ali *et al*, 2015). Figures. 1.1 and 1.2 illustrate the worldwide methanol consumption and its industrial demand.

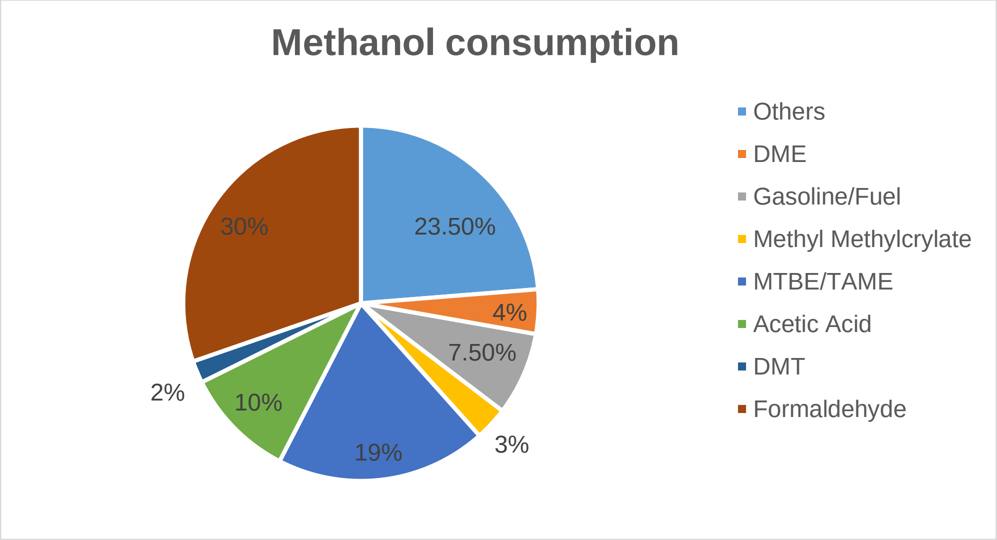


Figure 1. 1: Methanol worldwide consumption (adapted from Ali, 2015)

The methanol industry spans the entire globe, with production in Asia, North and South America, Europe, Africa and the Middle East. Worldwide, over 90 methanol plants have a combined production capacity of about 110 million metric tons. (Methanol Institute, 2022). Figure 1.2 shows that the Asia-Pacific region dominated the global market share in 2020 due to the growing petrochemical industry and increasing usage of methanol-based fuel in countries, such as China and Japan. It is expected that methanol consumption will expand until 2030, due to increased demand from sectors like the construction and automotive industries. (Mandaokar, 2023)

Figure 1. 2: World methanol demand by region (adapted HIS Chemical, 2019)

Methanol is a clean and sustainable energy resource that can be produced from different sources, traditional or renewable: natural gas, coal, biomass, landfill gas and power plant/industrial emissions. An important source is CO_2, which can be recovered from industrial sites and, eventually, from the atmosphere. This production pathway would mitigate global warming due to the increasing presence of greenhouse gases in the atmosphere. Actually, the dominant feedstock for methanol production is natural gas, and this will likely continue to be the case for many years, especially due to the large strides recently made in shale gas production. Using this feedstock, methanol is generated indirectly via syngas, which is a common procedure. In this process, the first step is the conversion of methane into a gas mixture of CO and H_2, (syngas), a very energy - expensive phase, and the second step is the catalytic conversion of syngas into methanol.

Another route is direct methane oxidation which is a new catalytic and challenging process. DMTM has been a research topic for more than a century and lies in the activation of the H_3C-H bond in methane, which implies the use of extreme conditions or a very active catalyst for its activation. On the other hand, due to the lower H_2OHC-H dissociation energy, the desired product, methanol is more readily converted to consecutive oxidation products such as CO and CO_2 (Guo, 2015).

1.2. Problem statement

There is considerable literature on the process chemistry of DMTM, but studies that consider the engineering aspects are less abundant. Therefore, in this study it is proposed to design two flowsheets for methanol synthesis processes, one through syngas route based in ATR and other through direct methane oxidation in order to compare the energy input for both and evaluate viability. On the other hand, it is important to consider that Mozambique is one of the countries, where huge gas fields have been discovered (150 trillion cubic feet) (Hanlon and Nuvunga, 2015), thus direct conversion of methane to methanol should represent an economical alternative to make feasible more natural gas reserves since transportation of liquefied natural gas is also rather costly.

1.3. Aim and objectives

The general objective of this research is to:

- Evaluate of the energetic viability of methanol synthesis via direct methane oxidation.

As specific objectives the following were considered:

- Determine and compare the energy input of the two routes of methanol synthesis;
- Analyse how the energy requirement of DMTM varies with recycle ratio, methanol selectivity and yield.

1.4. Research questions

The key questions considered in this research were:

- What is the carbon efficiency in the classical methanol synthesis?
- How much energy is required to produce methanol (including all recycles)?
- How does the recycle ratio in the DMTM affect the overall energy requirement of this process?
- How does reactor selectivity and overall yield affect the energy requirement for the process?

1.5. Hypothesis

The interest in the direct methane to methanol process arises because it avoids the energy intensive step of syngas production which is typically the largest cost of methanol production, making up 54% operating cost of a methanol plant. By avoiding this costly step, it is thought that even if methanol production is less efficient DMTM may be energetically competitive. The literature reports that the DMTM may become competitive energetically at a conversion larger than 10% and a selectivity to oxygen methanol of at least 80% thus energy minimisation can be used a way measuring the performance of the process

1.6. Research methodology

The elaboration of the thesis was based in the following methodology:

- Literature Review, specifically in methanol synthesis routes, process design and operational conditions;
- Flowsheets design and simulation in COCO simulator V3.6, based in parametric studies done in Scilab V6.1.1;
- Data analysis and report writing.

1.7. Scope of the research

This study was limited to design, simulate methanol synthesis processes and determine the energy requirement in order to evaluate DMTM energetic viability, no physical experiments were performed. Due to a lack of literature about DMTM flowsheet and reliable kinetic data the design was exploratory in nature, based in parametric studies and a fixed conversion reactor was used as a key simplification.

CHAPTER II

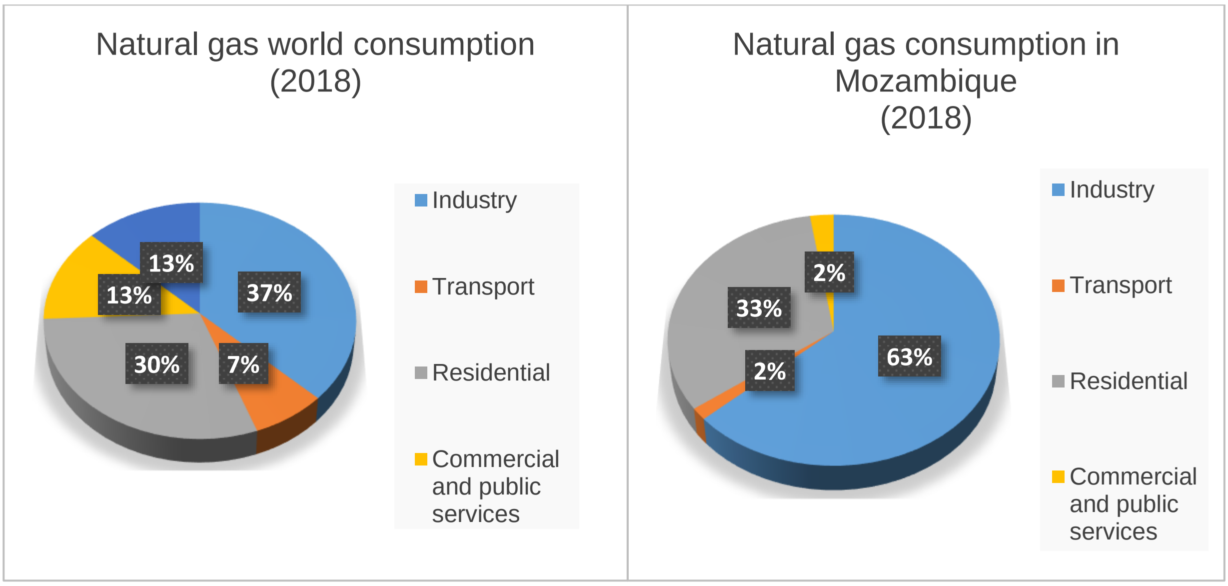
2. LITERATURE REVIEW

This chapter brings the main concepts for better understanding of this thesis. Firstly, the discussion about classical methanol synthesis, with more emphasis in autothermal reforming (ATR) and finally, the theoretical aspects about DMTM.

2.1. Natural gas as an energy-feedstock

Natural gas is a mixture of gaseous hydrocarbons mainly CH_4, and C_2H_6, with also C_3H_8 and C_4H_{10} some higher alkanes such (C_5+), N_2, O_2, CO_2, H_2S, and sometimes He. The process of natural gas formation began millions of years ago, when microscopic plants and animals living in the ocean absorbed energy from the sun, which was stored as carbon molecules in their bodies. When they died, they sank to the bottom of the sea. Over millions of years, layer after layer of sediment and other plants and bacteria were formed. As they became buried ever deeper, heat and pressure began to rise and allowed the conversion of the organic material. After oil and natural gas formation, they tended to migrate through tiny pores in the surrounding rock. Some oil and natural gas migrated to the surface and escaped, others migrated until they were caught under impermeable layers of rock or clay where they were trapped. These trapped deposits are where we find oil and natural gas wells today (Bakar and Ali, 2010). Natural gas is normally produced far away from the consumption regions, and it is transported either by pipeline pressure or liquefied with ships and land vehicles from the origin to areas of demand (Bakar and Ali, 2010; Deligeorgiou and Gounaris, 2014).

Natural gas was firstly used in the 19th century for illumination of roads and public buildings but nowadays it’s being used in almost all sectors, residential, industry, transport and others. The charts below illustrate natural gas consumption in the world (figure 2.1a and in Mozambique (figure 2. b) in 2018.



(a) (b)

Figure 2. 1: Natural gas consumption by sector in the world (a) and in Mozambique (b) (IEA, 2018)

Natural gas is one of the abundant, cleanest, safest and most useful of all energy sources since it also emits lower levels of potentially harmful by-products into the air after burning (Arthur, 2018). The uses of natural gas in different sectors are listed below (ENI, 2015; Deligeorgiou and Gounaris, 2014):

- **Production of electric power**: is used as a main fossil fuel to generate electricity also as a fuel in electric plants;
- **Transport sector**: is used as a fuel for vehicles;
- **Industrial sector**: is used in food, glass, steel, petroleum, metallurgic, plastic and chemicals industries for heating, cooling and electricity. It is also used as a raw material to produce important chemical such as methanol
- **Residential sector**: is used in gas ovens, and with the advancements in technology is gradually replacing electricity in fireplaces, air-condition devices, grills, clothes dryers, outdoor lighting, etc.
- **Commercial sector**: is used for heating, water boiling, space cooling, conditioning and refrigeration, cloth drying and preparing food in public buildings, schools, churches, hospitals, restaurants, hotels.

2.2. Methanol production via synthesis gas

The three basic steps for producing methanol are summarized in fig 2.2: syngas generation, methanol synthesis, methanol purification.

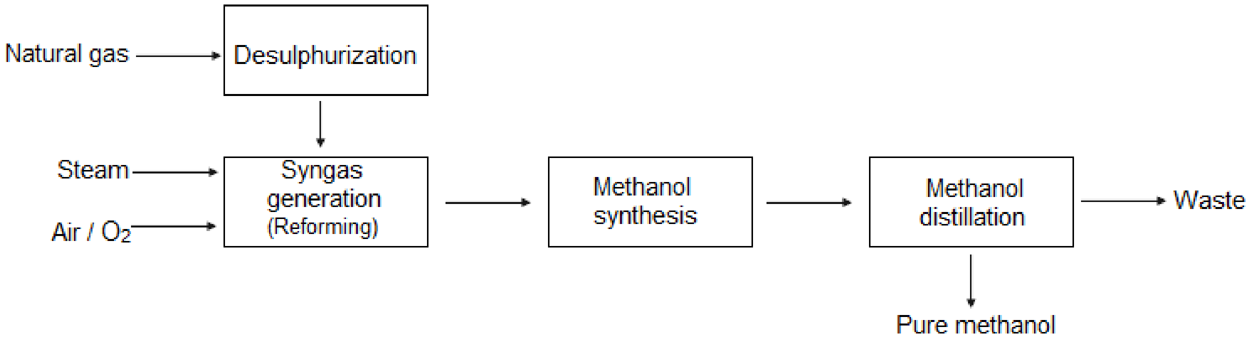


Figure 2. 2: Basic steps of methanol production (De Klerk and Prasad, 2012)

2.2.1. Syngas generation from Natural Gas

Syngas is a general term used in describing a mixture mainly composed of H_2 and CO and very often some CO_2 and H_2O. In the methanol synthesis, its production occupies the major investment and compression typically accounts for about 54% of the investment, so almost all energy is consumed in this process section. The syngas for methanol synthesis should have a balanced composition of CO, CO_2, and H_2. This composition can be simply expressed by H_2/CO ratio (S_{ratio}), (eq. 2.1) but considering that methanol synthesis is 100 times faster in CO_2 presence, another parameter called Module M or Molar ratio (M_{ratio}), (eq. 2.2) is used. For methanol synthesis syngas S_{ratio} and M_{ratio} has to be approximately equal to 3 and 2 respectively (Blumberg, *et al.*, 2017).

$$S_{ratio} = \frac{F_{H2}}{F_{CO}} \qquad \text{(eq. 2.1)}$$

$$M_{ratio} = \frac{F_{H2} - F_{CO2}}{F_{CO} + F_{CO2}} \qquad \text{(eq. 2.2)}$$

Natural gas contains other components than CH_4, that affect reforming processes, causing catalyst deactivation and decreasing the performance of the overall plant for this reason before syngas conversion, it needs to pass through the pre-treatment section. The pre-treatment basically consists in sulphur removal with a small stream of H_2 that converts all the sulphur components into H_2S which is then removed and also in pre-reforming on which higher hydrocarbons are catalytically converted with steam in CH_4 (De Klerk and Prasad, 2012). After feedstock purification, it becomes ready to be reformed into syngas. A variety of technologies is available to produce syngas from natural gas. The choice of an adequate syngas production technology has to consider a number of factors such as feedstock availability composition, cost, plant location, integration with existing facilities, environmental constraints and capital cost considerations. However, the common objective to all production technologies is the provision of a syngas with a stoichiometric composition for the respective synthesis (Blumberg, 2018).

The main technologies used for syngas production are summarized below and the respective reactions are presented Table 2.1:

- **Steam Reforming (SMR)**: Is the industrially most common used technology for synthesis gas production from natural gas. In SMR, CH_4 reacts in a highly endothermic reaction with steam over a catalyst, (typically based on nickel), at temperatures between 800-1000°C and pressures in the range of 20–30 bar (Blumberg *et al*., 2017).

- **Partial Oxidation (POX) / Catalytic partial oxidation (CPOX)**: In POX the feedstock and a sub-stoichiometric amount of pure O_2 react together, producing syngas. This process can be carried out with or without a catalyst. Non-catalytic process takes place at high temperatures (around 1200-1500^{o}C) while the use of catalyst lowers the required reaction temperature (to around 800˚C -900˚), however this catalytic process can be used if the sulphur content of natural gas is below 50 ppm (Ghoneim, *et al*., 2016).

- **Autothermal reforming, (ATR)**: ATR, combines steam reforming and partial oxidation in a single reactor operating in a pressure range of 30 - 50 bar with outlet stream temperatures between 950 - 1100^{o}C. The hydrocarbon feedstock is mixed with steam and reacts sub-stoichiometrically with O_2. Partial oxidation, which is exothermic, produces energy for endothermic steam reforming (Brett *et al.* 2012).

- **Dry Reforming of methane (DMR):** also called CO_2-reforming, is a well-known conversion process in which CH_4 is catalytically reformed by CO_2 at high temperatures (around 800 - 1000 ◦C) instead of steam. DMR is a new promising technology which attracts many research efforts as it contributes to the conversion of the most abundant carbon containing greenhouse gases (CO_2 and CH_4) into useful chemical products (Arora and Prasad, 2016). Dry reforming can also be combined with steam reforming, and partial oxidation in a process called **combined reforming of methane (CMR**). A combined use of O_2, CO_2, and H_2O in CH_4 reforming is also called mixed reforming or **bi-reforming** and **tri-reforming**, respectively (Storch *et al.,* 2018 and Blumberg, 2018).

- **Gas Heated Reforming (GHR):** is a new technology for the production of syngas in which heat is obtained by convective heat transfer with the hot gases leaving a secondary reformer in contrast with common SMR, where natural gas fired burners are used to supply the heat required for the endothermic reactions, and additional heat is then recovered by generating high pressure steam. (Nia, *et al.,* 2016).

Table 2. 1: Methane reforming reactions (Arthur, 2018)

Process	Reaction	Heat of reaction (ΔH^o_{298}, kJ/mol)
SMR	$CH_4 + H_2O = CO + 3\ H_2$ (2.3)	206
	$CO + H_2O = CO_2 + H_2$ (2.4)	- 41
ATR	$CH_4 + 1½\ O_2 = CO + 2\ H_2O$ (2.5)	- 520
	$CH_4 + H_2O = CO + 3\ H_2$ (2.6)	206
	$CO + H_2O = CO_2 + H_2$ (2.7)	- 41
	$2CO = C + CO_2$ (2.8)	-172.5
CPO	$CH_4 + ½\ O_2 = CO + 2\ H_2$ (2.9)	-38
DMR	$CH_4 + CO_2 = 2\ CO + 2\ H_2$ (2.10)	247

The first three methods are well established and are widely employed in industry, the last represent innovations to minimise greenhouse gases emissions, energy consumption and improve the reforming process yields. These methods differ in the composition of syngas produced ratio as shown in Figure 2.3.

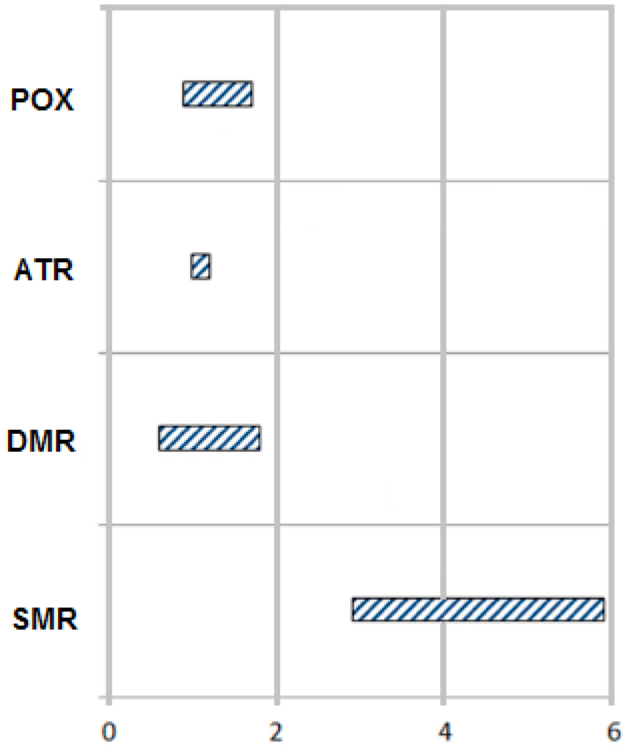


Figure 2. 3: Range of stoichiometric module M for synthesis gas from different reforming processes (Blumberg, *et al.*, 2017)

The syngas obtained in the various reforming processes is initially a mixture of H_2, CO, CO_2, minimal amount of unreacted CH_4 and other trace components. In general, the M/S ratio needs to be adjusted to meet the requirements of the downstream processes, for that reason, the syngas is typically conditioned and purified by reverse water gas shift or acid gas removal for CO_2 separation (Blumberg, 2018).

2.2.2. Autothermal Reforming (ATR)

ATR is a process developed by Haldor Topsoe in the 1950s which combines both POX and SMR technologies. The reformer (Figure 2.4) basically consists of a combustion chamber (combustion zone) and a fixed catalyst bed within a refractory lined pressurised shell (catalytic zone). The mixture of hydrocarbon feedstock and steam and reacts sub - stoichiometrically with O_2 (eq. 2.5) and, after leaving the combustion zone, steam reforming and the shift reaction (eqs. 2.6 and 2.7 respectively) take place in catalytic section (Pei *et al*., 2016).

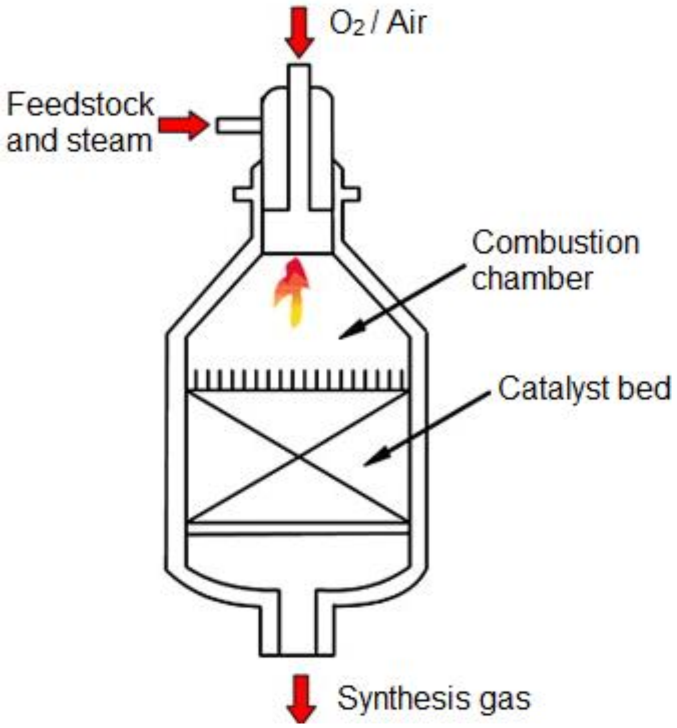


Figure 2. 4: Design of a autothermal reformer (Ghoneim *et al.*, 2016)

The syngas produced by ATR has a module M in the range of 1 - 2, and this ratio can be changed by varying the amounts of oxidant and steam in the feed (de Klerk and Prasad, 2012) or by syngas conditioning steps to increase hydrogen content while lowering the carbon dioxide fraction. These steps include hydrogen recovery from the purge gas to the synthesis loop through application of a pressure swing absorption unit or a WGS unit in conjunction with the carbon dioxide removal process (Bonh, 2011).

Typically, the ATR operates in a pressure range of 30 - 50 bar at high temperatures ca. 1200-1300°C in the combustion zone and 950-1200°C in the catalytic zone. This results in a lower oxygen consumption however, with a certain amount of steam added to eliminate the undesired carbon formation (Boudouard reaction, eq. 2.8) in the combustion zone, as this leads to carbon deposition on downstream tubes causing equipment damage, pressures losses and heat transfer problems (Studiorum, 2013).

2.2.3. Methanol synthesis

2.2.3.1. Chemistry and catalysts

The syngas is catalytically converted to produce raw methanol by equations 2.11 and 2.12. Raw methanol is a mixture of methanol, water and by-products, predominantly higher alcohols, ethers, acetone and methyl ethyl-ketone.

$$CO + 2H_2 \leftrightarrow CH_3OH \qquad \Delta H^o_{298K} = -90.64 \text{ kJ/mol} \qquad (2.11)$$

$$CO_2 + 3H_2 \leftrightarrow CH_3OH + H_2O \qquad \Delta H^o_{298K} = -49.67 \text{ kJ/mol} \qquad (2.12)$$

In addition to the two methanol forming reactions, the water gas shift reaction (WGS), (eq. 2.7) also takes place. Since methanol synthesis reactions are exothermic and involve a decrease in the number of moles, this process is favoured at low temperature and high pressure (Sheldon, 2017).

The first industrial production of methanol from syngas employed a catalyst system consisting of ZnO and Cr_2O_3. The processes were performed at high pressure, 250–350 bar and temperatures between 320–450^{o}C. This catalyst was highly stable to the sulphur and chlorine compounds present in synthesis gas. The harsh experimental conditions required by the BASF process induced strong efforts to realise methanol synthesis at lower pressures. This was achieved by ICI Company, in the 1960s which proposed a Cu-based ($CuO/ZnO/Al_2O_3$) catalysts for methanol synthesis process in the pressure range from 35-100 bar and at temperatures from 200 to 300^{o}C, that is still used today in industrial methanol production. Generally, the methanol synthesis catalyst is highly selective, a value of 99.9% is commonly achieved (Dalena, *et al*., 2018), however the conversion rate of the reactants is restricted by chemical equilibrium and the kinetic characteristics of the synthesis. The conversion per pass is typically limited in the order of 10 % (De Klerk and Prasad, 2012).

A simplified flow diagram for low pressure methanol synthesis is shown in figure 2.5. The syngas is compressed to the desired pressure (50–100 bar) and mixed with the unreacted recycle gas and routed to a heat exchanger in which energy from the hot gas leaving the reactor is transferred to the gas entering the reactor. The exothermic formation of methanol takes place in the reactor and the gas mixture leaving the reactor is cooled further. After passing through the heat exchanger, crude methanol is separated from the gas phase in a separator at temperatures around 30-40^{o}C (Luyben, 2010 and De Maria, 2013), part of the gas from the separator is recycled and the remaining gas containing H_2, CH_4 and inerts is sent to the purge (Ott *et al*., 2012).

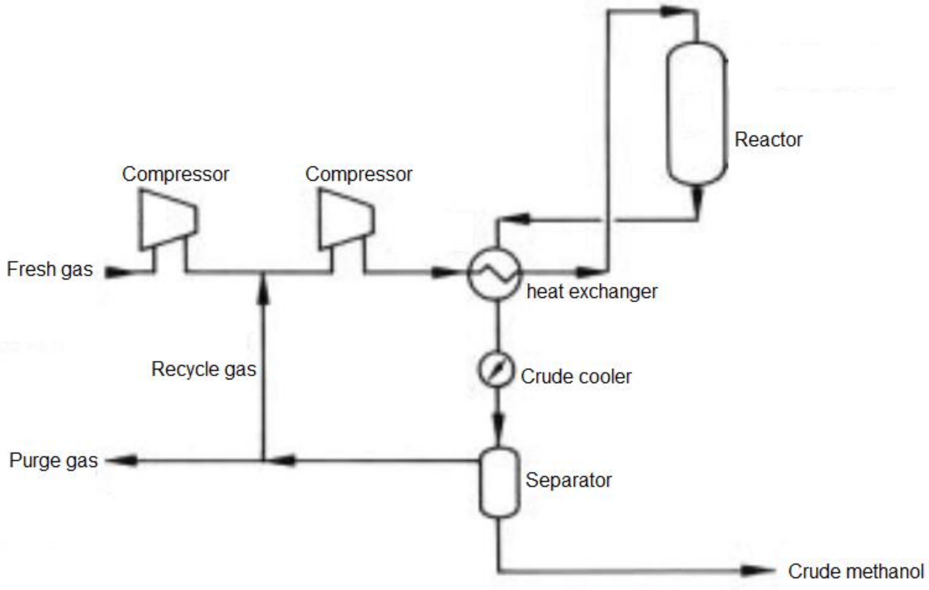


Figure 2. 5: Flow diagram for the methanol synthesis (adapted from Ott, *et al.*, 2012)

2.2.3.2. Methanol synthesis reactors

For the methanol synthesis two main reactor types are being used: adiabatic reactors and isothermal reactors. They differ in how the developed heat is controlled since the temperature within the reactor affects the conversion profile, the production of unwanted by-products and the recycle rate.

The adiabatic reactor is composed of a number of catalyst beds installed in a series within a common pressure shell designed to allow the synthesis reaction to reach equilibrium. They are characterised by the absence of an external cooling system within their reaction zone and the temperature in adiabatic reactors is automatically controlled by the limit set by thermodynamic equilibrium. The adiabatic systems can be divided in two groups: a series of adiabatic reactors with indirect cooling by application of intermediate heat exchangers and a series of catalyst beds with direct cooling through injection of cold syngas called quench gas (Bozzano and Manenti, 2016).

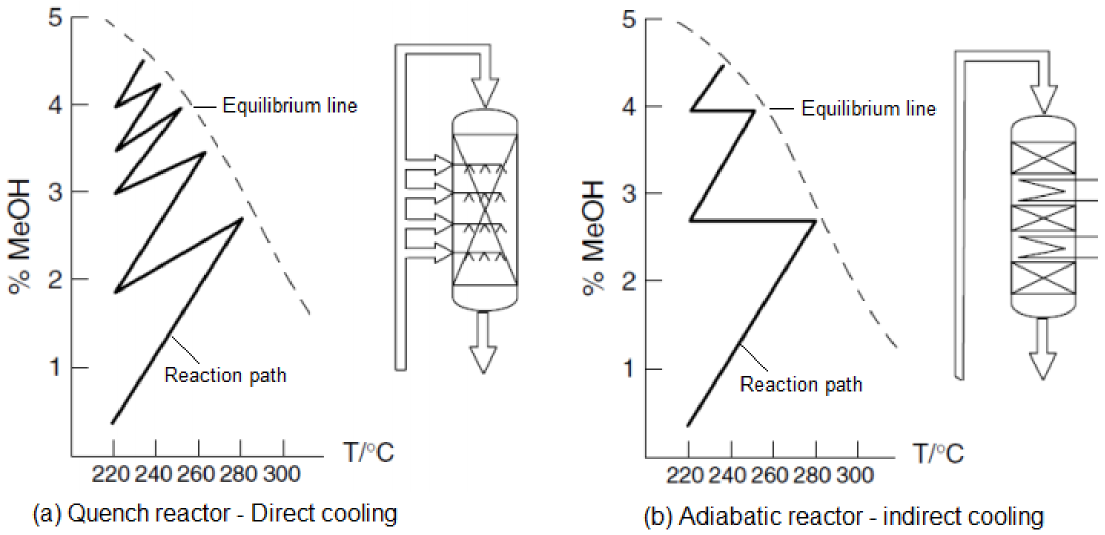


Figure 2. 6: Adiabatic reactors and their conversion profile (adapted from Hansen and Nielsen, 2008 and Lücking, 2017). Left: injection of cold synthesis gas. Right: interstage cooling

In Figure 2.6 (a) the conversion profile shows the injection points of the quench gas, through which the methanol concentration is reduced by the fresh syngas injection through the distributors while in figure 2.6 (b) the reactor with intermediate cooling only reduces the temperature keeping the methanol fraction constant. Worldwide, the quench converter is the most widespread technology among the low-pressure methanol synthesis processes. Compared with other designs, the catalyst utilisation is poor since not the entire amount of reactants passes through the total catalyst volume (Blumberg *et al.*, 2017).

Adiabatic reactors are very simple in design but increase in temperature levels within the reactors leads to a reduction in production and shortening of the catalyst's lifetime due to sintering (Zhong *et al.*, 2020), a maximum operating temperature of 300ºC is considered to be acceptable (Lücking, 2017).

In an isothermal reactor, the temperature is kept constant at a low level through a cooling process done indirectly to avoid reaction dilution. The most common cooling technologies include: gas-cooling (gas-cooled reactor- GCR) and cooling through steam generation (boiling water reactor -BWR). The GCR is often placed into a feed or effluent around a BWR (figure 2.7). On one side of the heat exchanger the BWR feed is preheated while on the other side of the heat exchanger the BWR-effluent is brought to a lower temperature. A GCR in series with a BWR allows a very high per pass conversion (Bohn, 2011).

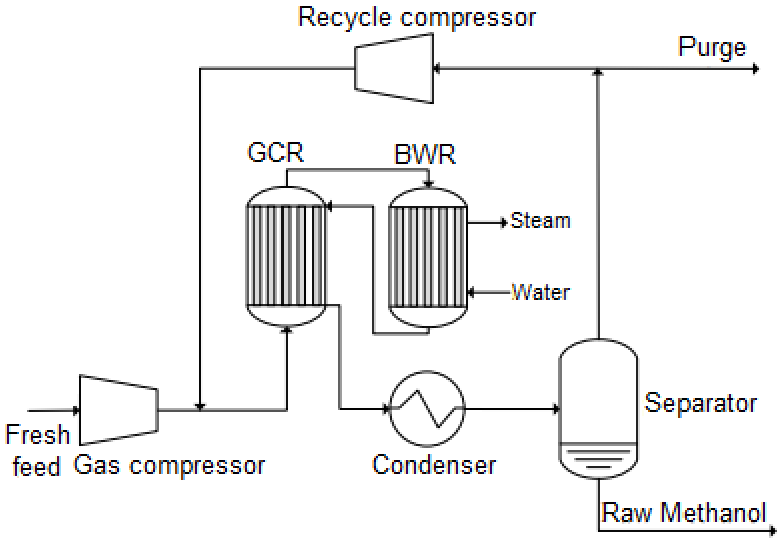


Figure 2. 7: Gas-cooled reactor in series with a boiling water reactor (Bohn, 2011)

The BWR is composed of a shell and tube heat exchanger with a catalyst inside the tube side. The heat of reaction is continuously removed through indirect heat exchange and recovered as steam on the shell side. The cooling medium typically has a pressure in the range of 30 - 50 bar to ensure an operation temperature between 240 – 260ºC for high reaction rates (Bozzano and Manenti, 2016).

In figure 2.8 the reactor never reaches high temperatures due to the continuous cooling process. By controlling the pressure of the circulating boiling water, the temperature of the reaction is controlled and optimised (Arthur, 2018). Isothermal BWR have a complex mechanical design, and consequently incurs a high investment costs, however the near isothermal behaviour of the reactor ensures high conversion and catalyst stability, due to the low operating temperature that minimises catalyst sintering (Zhong *et al.*, 2020).

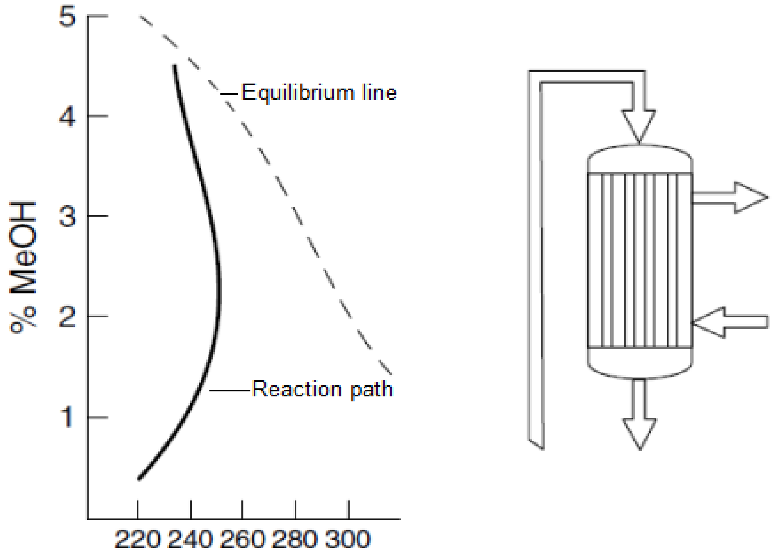


Figure 2. 8: Tubular boiling water reactor -BWR and conversion profile (Hansen and Nielsen, 2008 and Lücking, 2017, adapted)

2.2.4. Methanol purification

Crude methanol leaving the reactor contains water and other impurities such as dimethyl ether, methyl formate, acetone, heavy ends (higher chained hydrocarbons higher alcohols), light ends as dissolved gases (CH_4, CO, CO_2). The amount of by-products depends on the type and the lifetime of the catalyst and the operation conditions of the synthesis (Ott *et al*., 2012).

The objective of methanol purification is to remove these impurities in order to meet the final specifications. Three different qualities of methanol can be distinguished: fuel grade, used as burner or motor fuel, grade A (99.85% of methanol content), used as a solvent, grade AA (>99.85% of methanol content), used as industrial intermediate for chemicals production (Arthur, 2018).

According to the amount of impurities and the desired product quality, different distillation systems can be applied (Bonh, 2011):

- **Two-column system**: illustrated in figure 2.9, composed by a topping column for preliminary treatment with a purpose of separating the more volatile components contained in the crude methanol (light ends at the top and an aqueous solution at the bottom) and a refining column which carries out the actual distillation obtaining:

refined methanol at the top, a prevalently aqueous stream at the bottom, a side stream known as “fusel oil” mainly containing water, residual methanol and most of the by-products of the synthesis reaction.

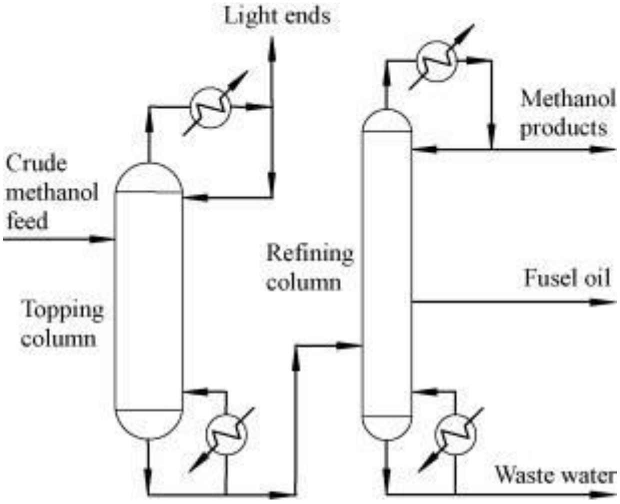


Figure 2. 9: Flowsheet of a two-column distillation system (Zhang, *et al.*, 2010)

- **Three-column system**: illustrated in figure 2.10, the refining column often is split into a first stage operating at elevated pressure called pressure column and a second atmospheric stage (atmospheric column). The three-column system therefore represents an energy-saving alternative. The topping column serves for the overhead removal of light ends present in the crude product, while methanol, water and heavy ends are withdrawn from the bottom. This bottom product is subsequently fed to the pressure column to separate the water and the heavier ends from the methanol vapour, which leaves the column at the top. Since the bottom product from the pressure column may still contain a considerable amount of methanol, it is fed to the atmospheric column for further recovery. Generally, the methanol vapour of the pressure column is condensed in the reboiler of the atmospheric column which represents a reduction in energy consumption.

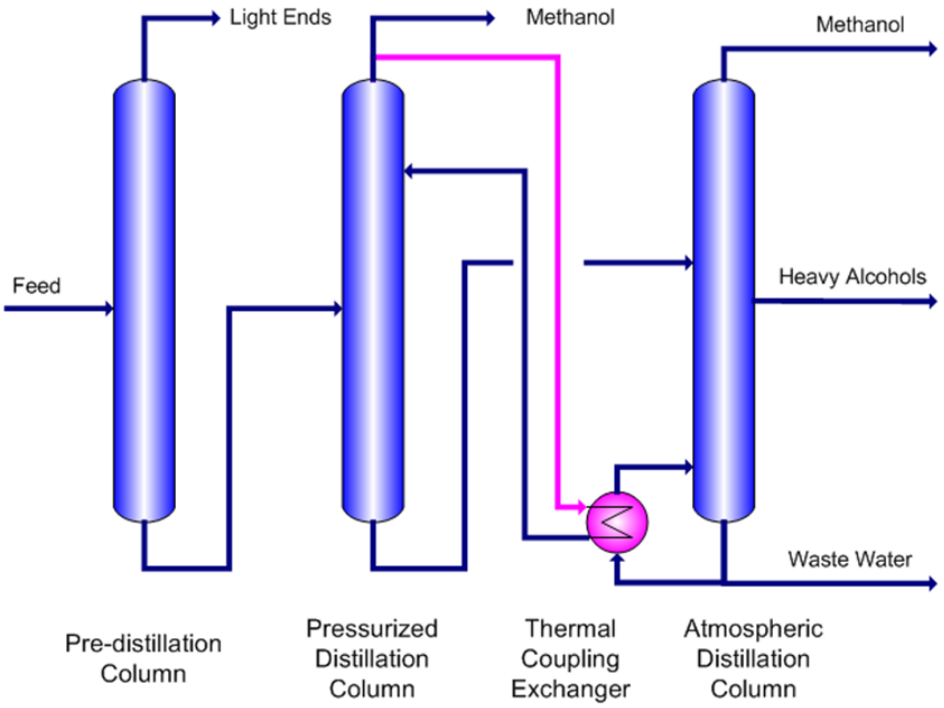


Figure 2. 10: Flowsheet of a three-column distillation system

2.3. Methanol synthesis via direct methane oxidation

This subchapter brings the main concepts related to direct methanol synthesis.

2.3.1. Historical Aspects

Research on DMTM began at the start of the last century with studies carried out by Bone and co-workers in 1902-1903 which demonstrated in principle the possibility of obtaining valuable oxygen-containing products (oxygenates) in the direct oxidation of methane. However, real interest arose only in the 1920s and 1930s, with the advent of industrial processes for the production of methanol and other oxygenates by means of the direct oxidation of natural gas. In the early 1930s, different researchers (Yoshikawa, 1931, Newitt and Huffner, 1932, Pichler and Reder, 1933; Newitt and Szego, 1934; Newitt, 1937) almost simultaneously demonstrated the possibility of the occurrence of a high selectivity of the gas-phase oxidation of methane to methanol at high pressures and this has stimulated further efforts to increase the yield of oxygenates and to develop industrial processes for their production by the direct oxidation of natural gas (Arutyunov, 2014). These studies demonstrated the possibility of obtaining a high yield of alcohols and aldehydes directly by the oxidation of alkanes. In fact, already in the works in the 1930s, a range of optimal conditions for DMTM were identified: high pressure (Newitt and Huffner, 1932; Newitt and Szego, 1934; Wiezevich and Frolich, 1934), moderate temperature (Paris, 1934), and a low concentration of oxygen (Pichler and Reder, 1933; Paris, 1934). In the 1940s in the United States and Canada, the industrial processes of POM became widespread, but the rapid progress of a competing large-capacity technology based syngas, the development of the market for propane and butane as domestic fuels and raw materials for a number of petrochemical processes, the difficult in isolating individual components from a wide variety of products of the nonselective gas phase oxidation, a very limited number of fundamental studies and the lack of clear ideas about the mechanism of the process have become a serious obstacle on the progress of this process. Although research continued to introduce new industrial processes, none of them has found practical implementation. In the mid-1980s, interest in the direct production of oxygenates from methane re-emerged due to the increasing role of natural gas in the global energy sector, the oil crisis of the 1970s, and the need for environmentally friendly motor fuels. Many works (Gesser et al., 1985; Gesser and Hunter, 1992) with very high yields of methanol were reported however, these reviews elucidated the absence, at the time, of clear ideas about the actual mechanism of the DMTM process and except for Gesser et al. 1985, they do not contain new data, being largely based on a compilation of the results of previous work. Later, many researchers have summarised and published the available literature data based on the existing theoretical understanding of the mechanism DMTM and since then and up to now, the main goal is to identify conditions that would ensure a stable highest-yield production of the desired product, so that DMTM could compete with other technological processes (Arutyunov, 2017).

3.3.2. DMTM reaction

The direct partial oxidation of methane to methanol is an exothermic reaction that is energetically more efficient than the endothermic steam reforming reaction (eq. 2.13).

$$CH_4 + \frac{1}{2} O_2 \rightarrow CH_3OH \quad \Delta H^o_{298} = -127.19 \text{ kcal/mol} \qquad (2.13)$$

The reaction proceeds via a free radical mechanism, the conversion of CH_4 in the reaction is typically less than 15%, with the selectivity varying considerably. Side products include CO, CO_2, CH_2O and C_2H_6. This process can reduce the capital and operating cost (Zhang *et al*., 2002) as it avoids the step of syngas production which is typically the largest cost of methanol production. (Turan, 2020). According to the available economic assessments (figure 2.11), for the DMTM process to successfully compete with the traditional technologies, it is necessary a reasonable conversion (X_{CH4}) of 7.5%–10.0%, and a selectivity of methanol (S_{CH3OH}) (or the total of organic products) greater than 80% (Edwards and Foster, 1986; Foulds and Gray, 1995 *apud* Arutyunov, 2018). However, until now, the experimental studies about the conditions of which DMTM can be transferred to the industrial scale, have shown a methane conversion of more than 5%, and a methanol selectivity of 50% (Arutyunov, 2014). The difficulties in DMTM lies in the activation of the H_3C-H bond in CH_4, which has a dissociation energy of 440 kJ/mol, meaning that extreme conditions or a very active catalyst are required for its activation. On the other hand, the H_2OHC-H dissociation energy is 47 kJ/mol less at 393 kJ/mol which implies that the desired product methanol is more readily activated than CH_4, leading to the formation of consecutive oxidation products such as CO and CO_2 (Caballero and Pérez, 2013).

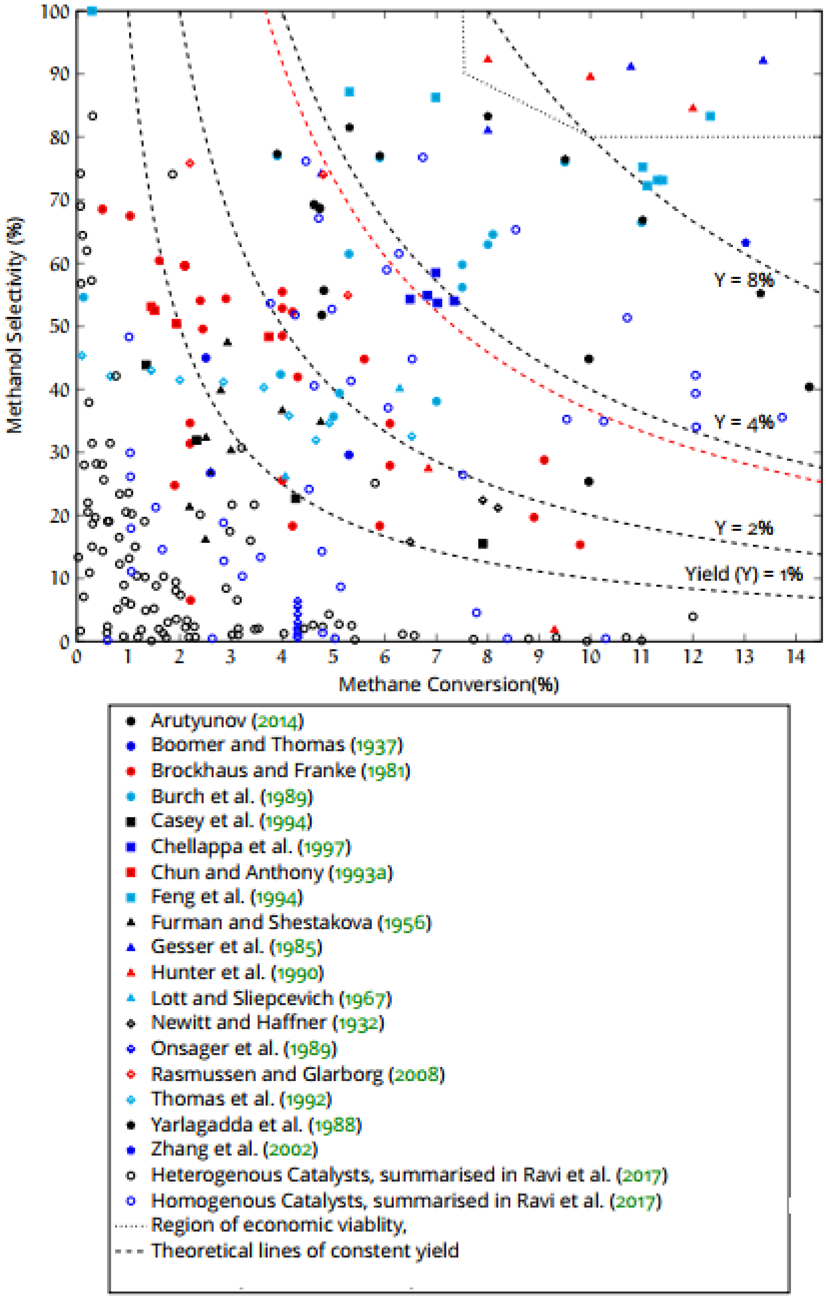


Figure 2. 11: Comparison of experimental selectivities of methanol (S_{CH3OH}), as a function of the methane conversion, (X_{CH4}), reported in the literature for the DMTM (Turan, 2020)

Currently, processes for conversion methane to methanol include (Guo, 2015):

- **Gas phase partial oxidation**: a non-catalytic partial oxidation involves reacting excess methane in oxygen at elevated temperatures (400°C – 600°C) at high pressures. This reaction is hard to control and the selectivity and yield of methanol cannot be improved by changing the reaction conditions. The selectivity to useful products reduces dramatically as methane conversion increases, due to the elevated reactivity of the oxygenated products compared to the reactant methane.

Some parameters such as reactor materials, reaction conditions and natural gas additives may influence the methanol yield (Han, *et al.,* 2016).

- **High temperature catalytic oxidation**: many heterogeneous catalysts have been tested to improve the selectivity of methanol in the partial oxidation of methane. Systems mentioned in literature include molybdenum and iron based catalysts.
- **Low temperature catalytic oxidation**: where activation of the strong C-H bond in methane takes place at low temperatures and reaction is assisted by methanotrophic bacteria which contains an enzyme system called methane monooxygenase, capable of selectively oxidizing methane to methanol at ambient conditions using oxygen. Homogeneous catalysts such Pt, Pd and Hg have been used in literature to study methane partial oxidation (Zakaria and Kamarudin, 2016).

CHAPTER III

3. FLOWSHEET DESIGN AND SIMULATION

This chapter presents all the methodology followed to design and simulate methanol flowsheets. The flowsheets were designed and simulated in COCO Software V 3.6 and to perform parametric studies optimization, Scilab V 6.1.1. was used.

3.1. Methanol synthesis via syngas

For process simulation some choices and assumptions were made and the descriptions are given below:

- Methane, water and oxygen were considered as process feed;
- Authothermal reforming was chosen as reforming technology to produce syngas. The ATR reformer was modelled as an adiabatic Gibbs reactor which performs equilibrium reactions for a single phase. Operational conditions, reaction phase and reactive compounds were specified.
- Methanol reactor was modelled as a tubular reactor which performs kinetic reactions in a single specified phase with full heat balance and pressure drop. The heat of reaction was removed by evaporation water to make steam and control the exothermic temperature rise.
- The raw methanol separation columns were modelled as one distillation column
- The model set in the property package definition is Peng Robinson equation of state

The methanol flow sheet includes units below:

- Autothermal reactor;
- Methanol reactor;
- Methanol distillation units.

3.1.1. Autothermal reactor

The autothermal reactor receives one stream of CH_4 mixed with steam and another stream of O_2. Before entering the reactor CH_4 (50ºC, 20 bar) is compressed (comp 4), H_2O (25ºC, 1 bar) is pumped (Pump 1) and heated (Hx3) to generate steam and O_2 (25ºC, 1 bar) passes through an interstage-cooling compression section (Comp 1, Hx1, Comp 2, Hx2, Comp 4). The feed enters the reactor at 600ºC and 50bar. In ATR exothermic partial oxidation and endothermic steam reforming take place adiabatically. The main specifications about the reactor are shown in the table 3.1, further details can be found in appendix 1.

Table 3. 1: ATR specifications

Parameter	Value
Temperature (ºC)	1002.79
Pressure (bar)	50
Phase	Vapour
Heat duty (W)	0

The syngas produced leaves the reactor at 1000ºC and 50 bar and since it needs further treatment for the adjustment of the composition required for methanol synthesis, it goes to flash 1 where it is separated into two streams, one liquid and other gaseous. The vapour stream is split (S1) in two streams and the small fraction is heated (Hx5) to subsequently carbon dioxide separation (CS1). A gas expander (Gas expander 1) is placed in the purged CO_2 stream to recover the energy as it comes out at 50 bar.

3.1.2. Syngas to methanol

After passing through the separation units, syngas is compressed (Comp 5), mixed with the recycle stream and heated (Hx6) to enter reactor. In these simulation is considered that the reactor has the catalyst in the shell, the cooling fluid in the tubes. The methanol reactor has 8000 tubes (with a diameter of 0.06m), a length of 12m and diameter of approximately 7.59 m. The tube temperature is 240ºC and the tube heat transfer coefficient is 400 $W/m^2\,^oC$.

The feed enters the reactor at 200°C, 50 bar, the product leaves the reactor at approximately 227°C, 48 bar and since it needs to be purified, is cooled (Hx7) to pass to the distillation section. The units MU3. and MU4. are placed in the reactor's feed stream in order to measure the F_{CO} and F_{CO2}, which are introduced into the calc1 unit to determine the M_{ratio} at the reactor's inlet. Inside reactor, syngas is catalytically converted to methanol. The reactions considered in simulation are methanol synthesis (eq. 2.10) and WGS (eq. 2.5). The main specifications about the reactor are shown in the table 3.2, further details can be found in appendix 1.

Table 3. 2 Methanol reactor specifications

Parameter	**Value**
Temperature (°C)	240
Pressure (bar)	50
Phase	vapor
Heat duty (W)	0
Catalyst loading (kg/m3)	1000
Porosity	0.5
Particle diameter (m)	0.004
Cooling tubes	8000
Cooling tubes diameter (m)	0.06
Cooling tube temperature (°C)	220
Tube heat transfer coefficient (W/m^2 °C)	400

The catalyst has a density of 2000 kg/m3, the reactor void volume is 0.5 and the particle diameter is 0.004m. The tubes inside the reactor have a diameter of 0.06m. The catalyst properties, reactions and kinetics need to be specified (appendix 2).

3.1.3. Methanol distillation units

The methanol distillation section is composed of 4 purification units. The reactor effluent is cooled to a temperature low enough (90°C) to separate out liquid crude methanol product in HP-flash 2 (48 bar), and the vapours from the flash enter the splitter (S2) and are separated in two streams, one that is compressed (comp 6) and recycled back to the reactor and other that is purged to keep the inerts from building up in the loop. The split factor set is 98%. A gas expander (Gas expander 2) is placed in the purge stream in order recover the energy as the purge comes out at 50 bar. The liquid phase from HP Flash 2, contains significant amounts of light components (H_2, CO_2, CH_4, CO) because of the high pressure in the separator. If this stream were fed directly into the distillation column, these inert components would build up in the condenser, thus the stream is expanded through a turbine, which generates energy from the pressure difference, to 2 bar and enter LP Flash 3, that operates at 40ºC, where most of the light components are removed before feeding into the column. The liquid from the flash tank enters a 20-stage distillation column on stage 10. The column operates at 1 bar and the design can be assumed to have ideal trays, which means assuming the tray efficiency to be 1. Since the feed to the distillation column contains gases which can only be condensed at very low temperatures (< -50°C), it is necessary to use a partial condenser with a vapour product stream. The vapour stream from the methanol column, which is mainly composed by methanol enters Flash 4 for further separation which results in a liquid stream of methanol at 40ºC and 1 bar. The specifications about methanol column are shown in the table 3.3, further details about separation units can be found in appendix 1.

Table 3. 3: Methanol column and specifications

Parameter	**Value**
Pressure (bar)	1
Efficiency	1
Reflux ratio	2
Water recovery	0.99
Methanol recovery	0.99
Feed stage	10

3.1.4. Parametric study on the reformer operation

The measurement units MU3, MU4 and MU5 are used to measure carbon oxides (F_{CO2}, F_{CO}) and hydrogen (F_{H2}) flowrates. These measured values are subsequently introduced in the calculators (calc1 and calc2) to determine S_{ratio} and M_{ratio} through eq. 2.1 and 2.2. In order to optimise syngas ratios for methanol synthesis, a parametric study was performed in COCO software and finalised through a programming code (appendix 3) and an objective function (eq. 3.1). For optimization methane flowrate (F_{CH4}) was considered constant, F_{O2} and F_w were considered as input variables. The objective is to find the closest values for S_{ratio} equals to 3, M_{ratio} equals to 2,05 and high methane conversion (X_{CH4}) equals to 0.99.

$$\text{Obj.} = \log\left[\left(1-\frac{M_{ratio}}{2.05}\right)^2+\left(1-\frac{S_{ratio}}{3}\right)^2+(X_{XCH4}-0.99)^2\right] \quad (3.1)$$

The plot of the objective function as a function of input variables is illustrated below (figure 3.1). The objective function goes to a minimum at high flowrates of water and low flowrates of oxygen. The results that give the best operating point are presented in table 3.4. These values were used in the methanol flowsheet to define the feed flowrates and consequently adjust syngas ratios. The other results of simulation are presented in appendix 4.

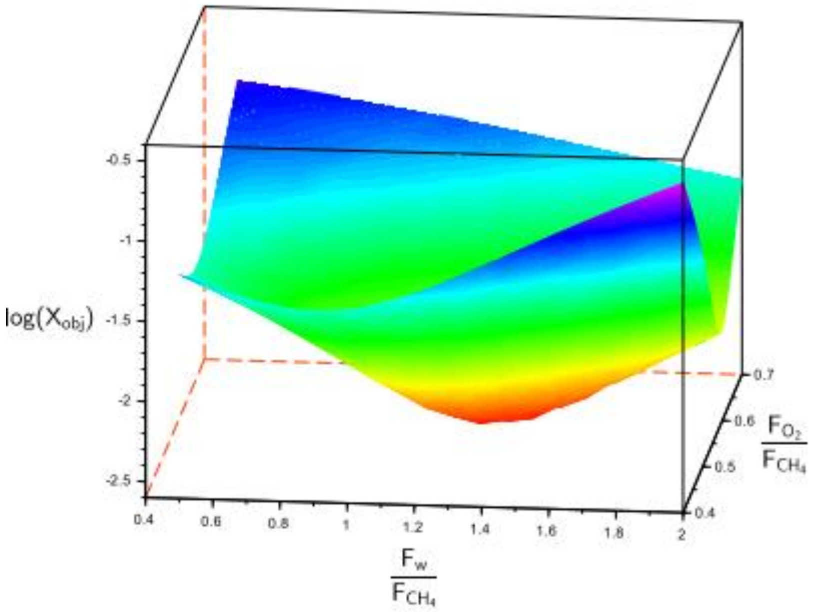


Figure 3. 1: Objective function vs. F_{O2} and F_w

Table 3. 4: Optimization results

Parameter	Value	Parameter	Value
F_W / F_{CH4}	1.40	F_{CO} (mol/s)	0.69
F_{O2} /F_{CH4}	0.54	F_{CO2} (mol/s)	0.27
M_{ratio}	1.89	F_{O2} (mol/s)	0.00
S_{ratio}	2.99	F_W (mol/s)	1.24
T_{OUT} (^OC)	975.85	X_{CH4}	0.95
P_{OUT} (bar)	30	X_{O2}	1
F_{CH4} (mol/s)	0.04	X_W	0.11

In order to determine the methane overall conversion ($X_{overall}$) and methanol overall selectivity ($S_{overall}$), the inlet F_{CH4}, outlet F_{CH4}, F_{CH3OH} are measured through MU1, MU2, MU7, MU6 and MU8 units. The measured values are inserted in the calculators calc3 and calc4. The values of $X_{overall}$ and $S_{overall}$ are determined by equations 3.2 and 3.3.

$$X_{overall} = \frac{F_{CH4,in} - F_{CH4,out}}{F_{CH4,in}} \qquad (3.2)$$

$$S_{overall} = \frac{F_{CH3,out}}{F_{CH4,in} - F_{CH4,out}} \qquad (3.3)$$

The complete flowsheet of methanol via syngas is shown in the figure 3.2

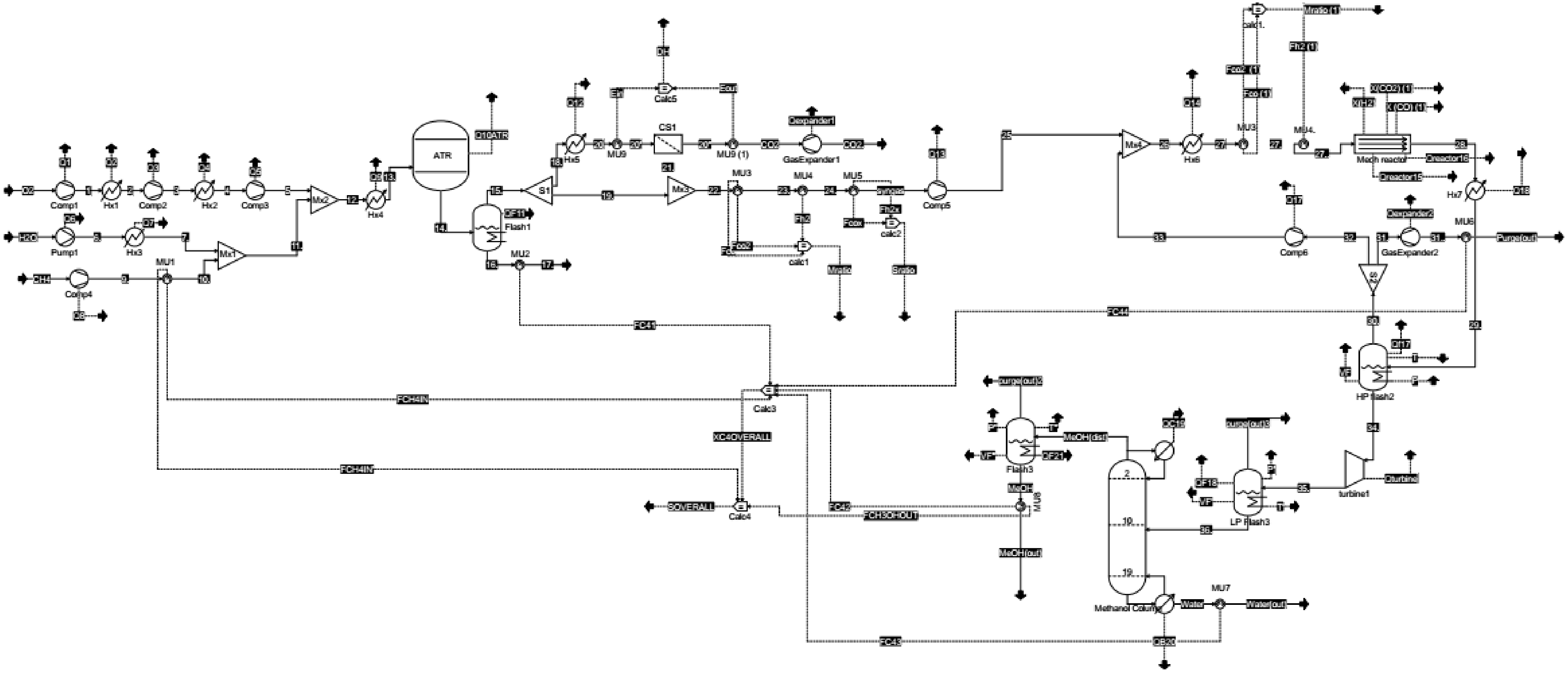


Figure 3. 2: Simulation of methanol synthesis via syngas

3.2. Methanol synthesis via direct methane oxidation

For process simulation some choices and assumption were made and the descriptions are given below:

- Methane and oxygen were considered as process feed;
- Methanol reactor was modelled as a fixed conversion reactor, which performs one or more reactions using a specified conversion. In this model reactor is considered to operate isothermally. Operational conditions, reactions, and component conversions were specified;
- The distillation column is the same used for raw methanol separation in syngas flowsheet;
- The model set in the property package definition is Peng Robinson equation of state

The flowsheet which includes units below:

- Methanol reactor;
- Methanol distillation units.

3.2.1. Methane to methanol reactor

Methane at 20 bar and 50°C is compressed (comp1) to 50 bar and added to a recycle stream to enter the reactor. O_2 stream (1bar and 25°C) passes through a interstage-cooling compression section (comp 2, Hx1, comp 3, Hx2, comp4) until it is at 50 bar to enter the reactor. The methanol reactor operates isothermally at 400°C and 50 bar, inside, methane oxidation (eq. 2.11) and methane complete combustion (eq. 3.4) take place.

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O \qquad \Delta H^o_{298K} = -802.7 \text{ kJ/mol} \qquad (3.4)$$

The oxygen conversions (X_1 and X_2) are set to be 80% and 20% for oxidation and combustion reaction respectively. The main specifications about the reactor are shown in the table 3.5, further details can be found in appendix 5.

Table 3. 5: Methanol reactor specifications

Parameter	**Value**
Temperature (ºC)	400
Pressure (bar)	50
X_{O2}	1
X_1	0.8
X_2	0.2

The conversions set for the reactions determines the amount of O2 necessary in the process. The O_2 added is defined by the measurement loop composed by the measurement unit (MU3) and the controller (C1). The values of CH_4 and O_2 flowrates measured by the unit MU3 are used to calculate the O_2/CH_4 ratio in the calculator (calc1) and this information is send to the controller that defines the amount of O_2 that enters the process. The units MU1, MU2 are used to measure in inlet and outlet F_{CH4} and F_{CH3OH}, and these information is sent to the calculator (calc 2), that gives the methanol selectivity (S_{CH3OH}) in the reactor. The reactions selectivity and the amount of O_2 added determine methane per-pass conversion (X_{CH4}) of 10% and the methanol production.

The product of the direct oxidation of CH_4 is methanol while in the complete combustion the typical products obtained are CO_2 and H_2O. The product leaves the reactor and passes through a valve (valve 1) that helps in reducing the pressure and then is cooled (Hx4) to proceed to the purification units.

3.2.2. Methanol distillation units

The reactor effluent is cooled to a temperature low enough (50ºC) to separate out liquid crude methanol product in a HP-flash (48 bar). The vapours from the separator enter the splitter (S1) and are separated in two streams, one that is compressed (comp 5) and recycled back to the reactor and other that is purged to keep the inerts from building up in the loop. The split factor set is 99.5%. A gas expander is placed in the purge stream to recover the energy as the purge comes out at 50 bar. The methanol-rich liquid stream from the HP flash is expanded through a turbine, which generates energy from the pressure difference, and enters the distillation column which is the same used in syngas route. The specifications about the purification units can be found in appendix 5.

3.2.3. Parametric study on the process

In order to optimise process variables, a parametric study was performed in COCO software and finalised through a programming code (appendix 6) and an objective function (eq. 3.6). For optimization O_2 rate (O_2/CH_4), O_2 conversion (X_1) and split factor (S_1) were set as input variables. The objective is to find the point that give the minimum heat duty (Q), high $X_{overall}$ (0.95) and $S_{overall}$ (0.95).

$$\text{Obj} = \log\left[\left(1 - \frac{X_{overall}}{0.95}\right)^2 + \left(1 - \frac{S_{overall}}{0.95}\right)^2 + \left(1 - \frac{\text{sumQ}}{\min(\text{sumQ})}\right)^2\right] \qquad (3.6)$$

The plot (figure 3.6) illustrates the variation of objective function with conversion and oxygen ratio at different values of split factor. The objective function goes to a minimum at high values of X_1 and low O_2 rates. The results that give the best operating point are presented in table 3.2, other simulation results can be found in appendix 7.

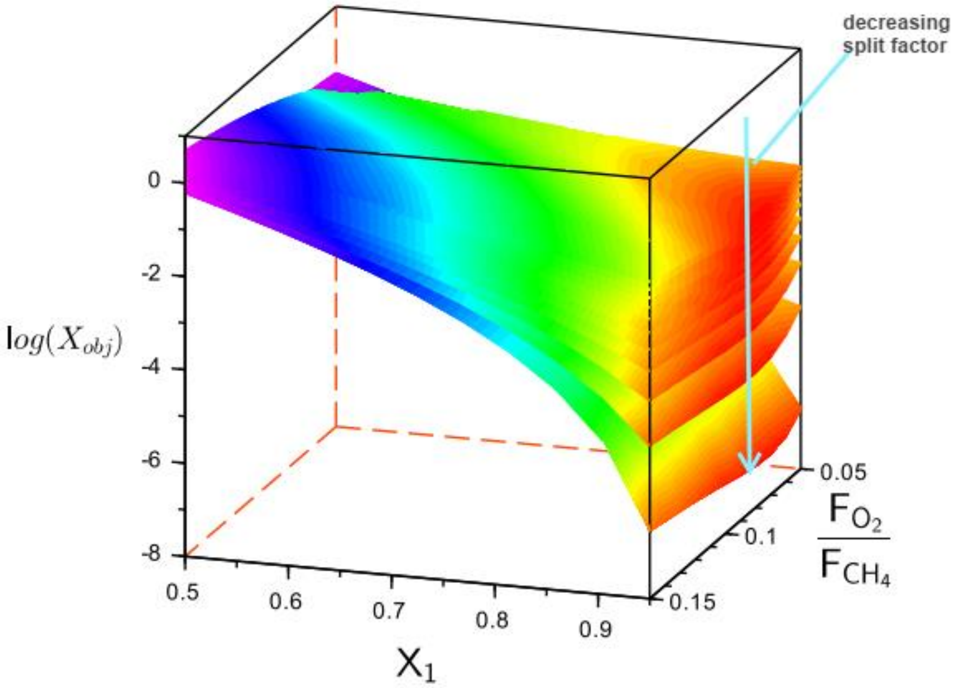


Figure 3. 3: Objective function vs. O_2 ratio and X_1 at different split factors

In order to determine $X_{overall}$ and $S_{overall}$, the inlet and outlet F_{CH4}, F_{CH3OH} are measured through the units MU6, MU7, MU8 and MU9. The measured values are inserted in the calculators (calc3, calc4, calc5, calc 6). The values of $X_{overall}$ cha and $S_{overall}$ are determined by the equations 3.2 and 3.3.

Table 3. 6: Optimization results

Parameter	Result	Parameter	Result
O_2 ratio	0.070	Q_5 (kW)	-3083.395
X_1	0.950	Q_6 (kW)	3154.554
S_1	0.995	Q_7 (kW)	-3365.083
X_{CH4}	0.134	Q_8 (kW)	-201068.940
F_{CH3OH} (mol/s)	1431.282	Q_9 (kW)	268171.635
S_{CH3OH}	0.987	Q_{rctr10} (kW)	211110.287
$X_{overall}$	0.935	Q_{c11} (kW)	120463.308
$S_{overall}$	0.931	Q_{b12} (kW)	-179567.335
F_{O2} (mol/s)	798.245	Q_{f13} (kW)	0
Q_1 (kW)	- 5803.790	Q_{414} (kW)	56343.094
Q_2 (kW)	-5891.965	$Q_{turbine}$ (kW)	236.707
Q_3 (kW)	5340.458	$Q_{expander}$(kW)	228.550
Q_4 (kW)	-3083.394	SumQ (kW)	264876

The complete flowsheet of methanol synthesis via direct methane oxidation is shown in the figure 3.4

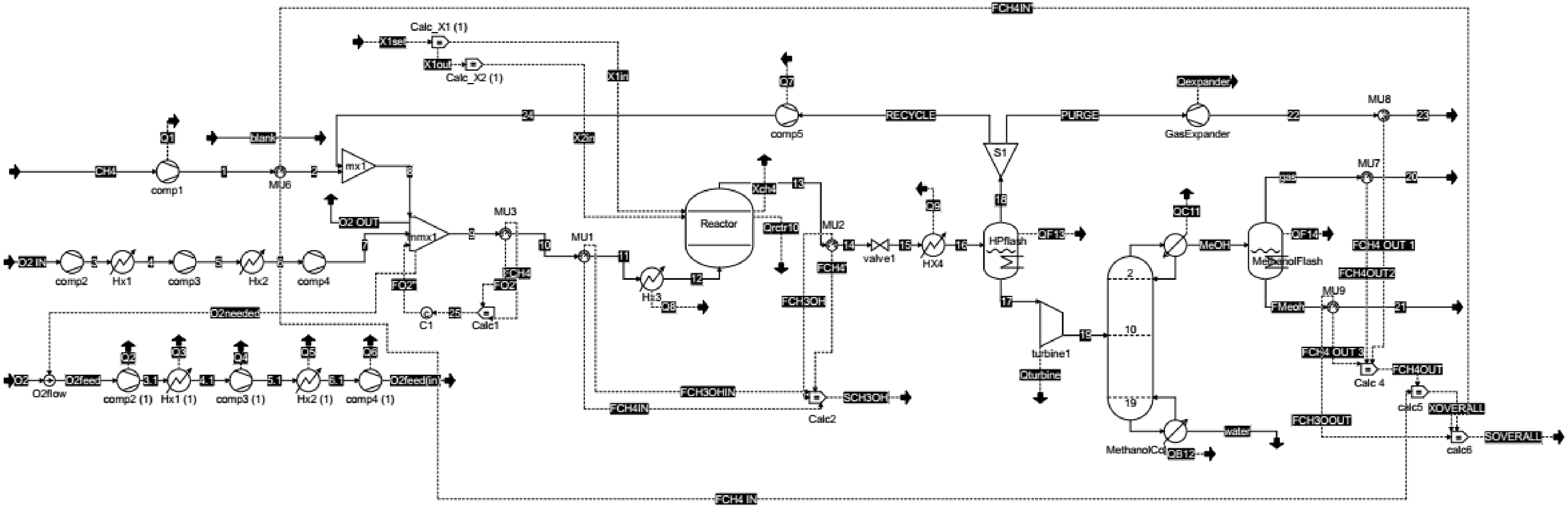


Figure 3. 4: Simulation of methanol synthesis via direct methane oxidation

CHAPTER IV

4. RESULTS AND DISCUSSION

This chapter presents the main results of the research: firstly, the simulation results of the main units and then the discussion, which is also based on other published results on the same subject.

4.1. Simulation of methanol synthesis via syngas

4.1.1. Autothermal reactor

Autothermal reactor converts CH_4, H_2O and O_2 into syngas (figure 4.1). In this unit 1642.9 mol/s of CH_4 is mixed with 2300 mol/s of steam and reacts with 878.9 mol/s of O_2. After all the separation process 4867.78 mol/s of syngas is produced.

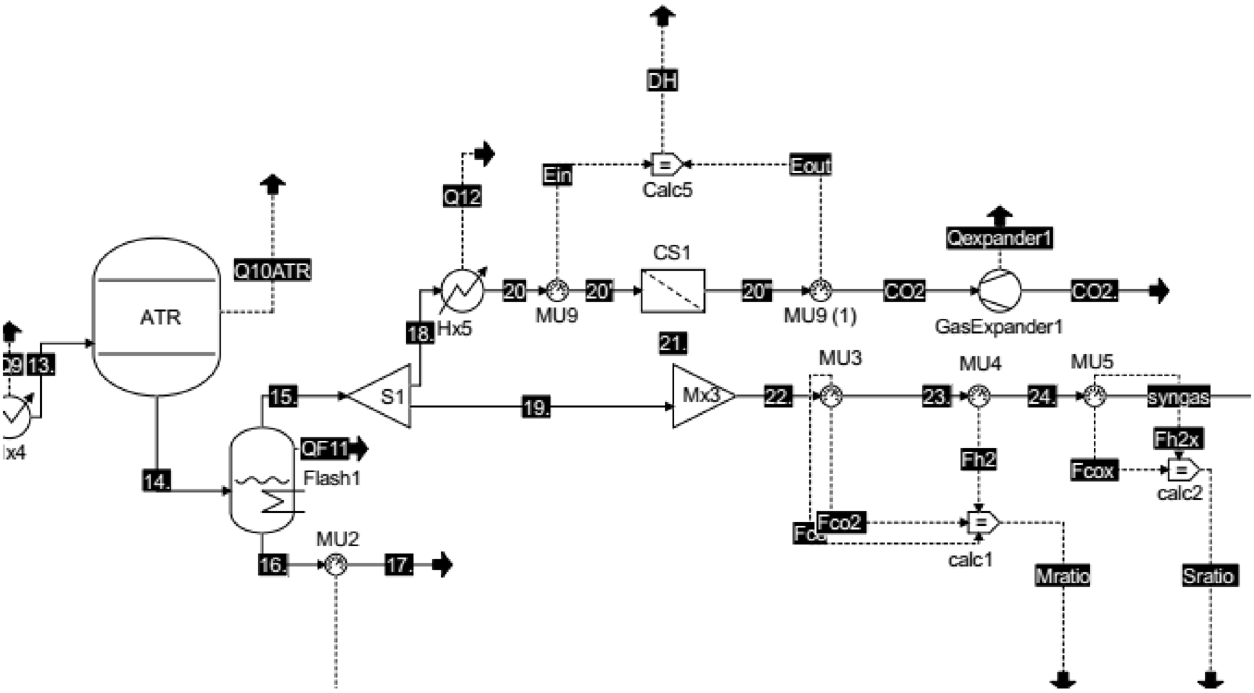


Figure 4. 1: Simulation of autothermal reactor

The composition of the product and the description of reactor inlets and outlets are presented in table 4.1

Table 4. 1: Results of Simulation in autothermal reactor

Stream	ATR inlet	ATR outlet	Syngas
Pressure (atm)	50	50	49
Temperature (ºC)	600	1002.79	63.55
Flowrate (mol/s)	4821.91	7023.38	4867.78
Molar Composition			
CH_4	0.3407	0.0146	0.0211
CO	0	0.1588	0.2292
CO_2	0	0.0605	0.0697
H_2	0	0.4681	0.6753
O_2	0.1823	0	0
H_2O	0.4770	0.2980	0.0047

The results show that CH_4 and O_2 conversion are 94% and 100%. According to Wurzel, 2006 *apud* Blumberg 2018, ATR processes can achieve high CH_4 conversion rates, often exceeding 90% and high O_2 conversion is desirable in ATR to ensure efficient utilisation of the oxygen and maximise the production of syngas. The flash tank separates almost all the water in the product. The flash unit is also used by Arthur, 2010 to remove water in reactor products in his study about methanol synthesis using autothermal reforming. After separation, the syngas produced has a M_{ratio} of 1.86, and this value was reported by Dahl *et al.,* 2014. If M_{ratio} is less than 2, the syngas is deficient in H_2 and this calls for some adjustment in before methanol production. This adjustment is either done by removing CO_2 from the syngas or recovering H_2 from the synthesis loop purge gas and recycling the recovered H_2 to the syngas. In this project M_{ratio} was adjusted to 2.03 and S_{ratio} (H_2/CO) to 2.95 by removing carbon dioxide and by optimization through the objective function (eq. 3.1).

4.1.2. Syngas to methanol reactor

The syngas is compressed to 50 bar and added at 21466.5 mol/s of recycle. This feed is preheated to enter the methanol reactor (figure 4.2). In the reactor, 23600 mol/s of product are generated and cooled to proceed to the purification units. The cooled product from the reactor is sent to a two stage flash system. The purpose of the flash drums is to prevent the gases from reaching the distillation column.

The flash drum pressures are varied in order to improve the process. In the distillation column, operating at atmospheric pressure, methanol is separated from water. After all the separation process 1320.61 mol/s of methanol is produced.

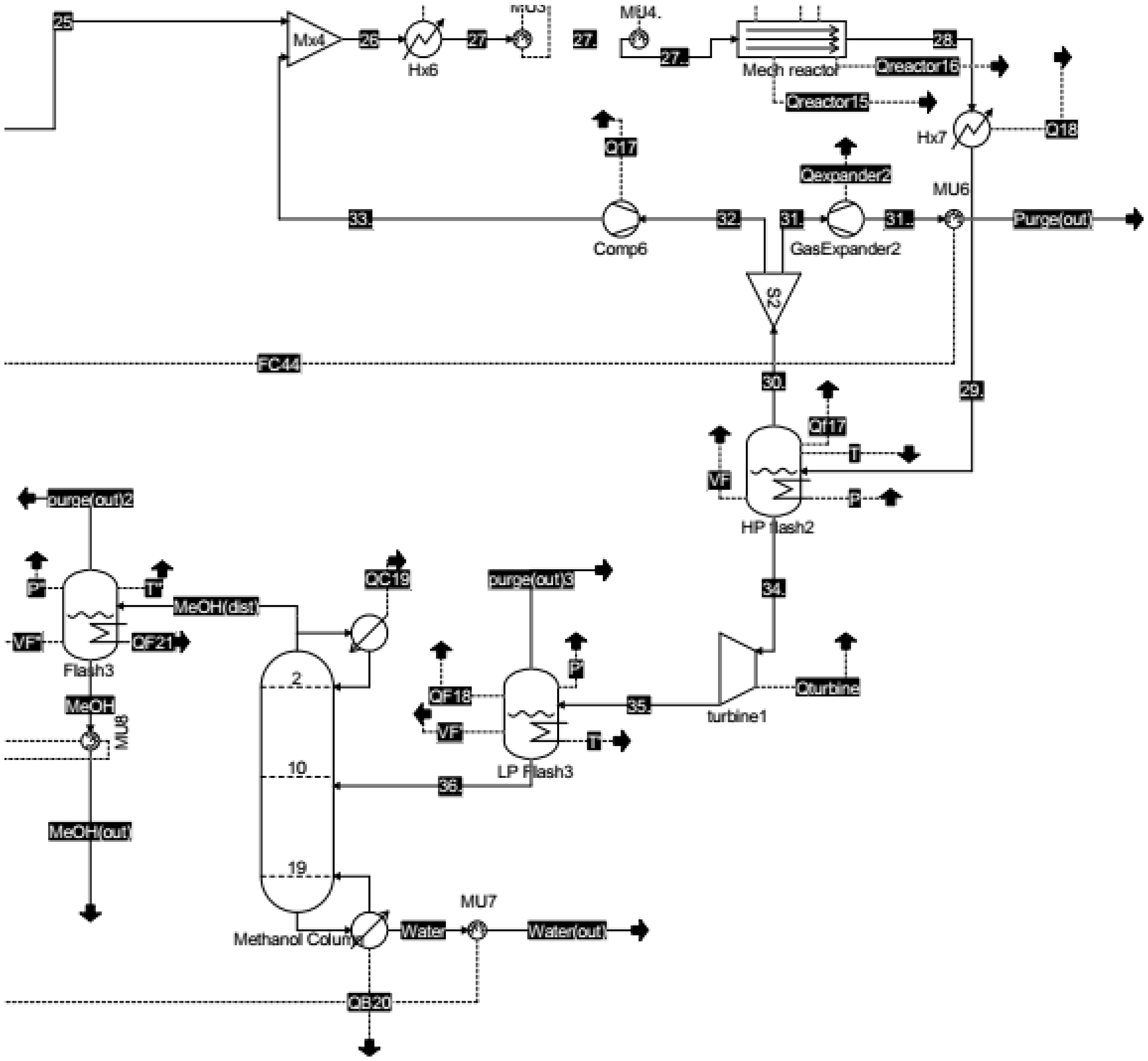


Figure 4. 2: Simulation of syngas to methanol reactor

The composition of the product and the description of reactor inlets and outlets are presented in table 4.2 The conversion per pass of CO, CO_2 and H_2 in methanol reactor are 56%, 11% and 18% respectively. Luyben, 2010 simulated methanol plant from syngas at 110 bar and reported a per-pass conversion of 25% for H_2, 64% for CO and 17% for CO_2. De, Maria *et al.*, 2015 also simulated a methanol plant from syngas at a 76.98 bar and found a per –pass conversion is 22% for H_2, 39% for CO and 15% CO_2

Table 4. 2: Results of Simulation in methanol reactor

Stream	R. inlet	R. outlet	Methanol out
Pressure (atm)	50	47.6	1
Temperature (ºC)	200	90	40
Flowrate (mol/s)	26334.3	23600	1360.21
Molar Composition			
CH_4	01793	0.2001	0
CO	0.0725	0.0343	0
CO_2	0.0896	0.0886	0.0043
H_2	0.6461	0.5937	0
O_2	0	0	0
H_2O	0.0016	0.0131	0.0002
CH_3OH	0.0109	0.0702	0.9954

. The conversion of syngas into methanol synthesis can be influenced by several factors. Because the synthesis reactions are exothermic with a net decrease in molar volume, equilibrium conversions of the carbon oxides to methanol are favoured by high pressure and low temperature as can be conserved in figure 4.3.

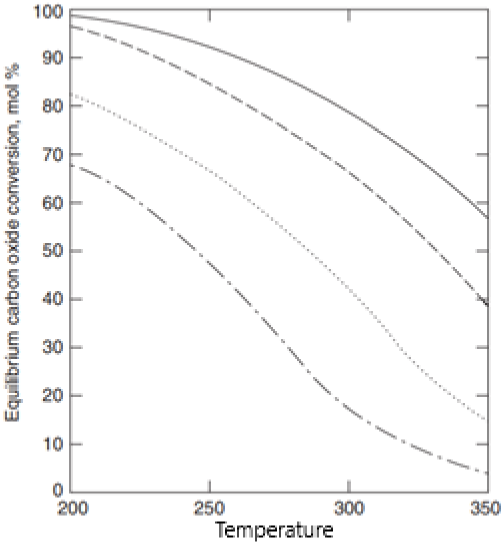


Figure 4. 3: Equilibrium conversion of carbon oxides to methanol based on reformed natural gas composition of 73% H2, 15% CO, 9% CO2, and 3% CH4 where (—) is at 300 bar, (– – –) is at 200 bar (. . .) is at 100 bar, and (— – —) is at 50 bar. (English *et al.,* 2022)

In this simulation the overall conversion of carbon oxides is 94%, the yield of the carbon (CO + CO2) converted to CH_3OH is 93%. These values are close to the ones reported by Luyben 2010 (96%).

Mignard and Prithchard, 2016 considered the kinetic model of Vanden Bussche and Froment in their study and reported a conversion of 95% at 50-60 bar. English *et al*., 2022 reports carbon oxides conversions between 50-60% which is lower than the obtained in this simulation but conversion can also be influenced by the difference of M_{ratio} at reactor inlet. The recycle purge and the degree of overall recycle greatly affect the overall conversion and yield. Methanol selectivity (S_{CH3OH}) over carbon oxides is 99%, close to the commercial value (99.5-99.9%). This value of selectivity is also reported by Dahl, *et al.*, 2005 and Machado *et al.*, 2014.

The pictures 4.4- 4.7 illustrate the reactor profiles. Hydrogen flowrate is high at begging of the process as since most of it is recycled back to the reactor and tends to decreases with reactor length as it is consumed in the methanol synthesis reaction (figure 4.4). The flow rate of carbon dioxide decreases with the length but at a certain position (around 4m) it becomes constant while carbon monoxide flow rate is continuously decreasing (figure 4.5). On the other hand, methanol flowrate increases with the reactor length as it being formed while hydrogen and carbon oxides are being consumed. The reactor temperature is initially low but is tends to increase with the length and achieves a maximum (around 266^{o}C), from this point the temperature decreases until 226^{O}C (figure 4.6). This behaviour can be explained by the system of cooling used to control the reactor temperature. This trend for reactants, product and reactor temperature plots is very similar to that observed in the reactor profiles obtained by De Maria *et al.*, 2013 in their study.

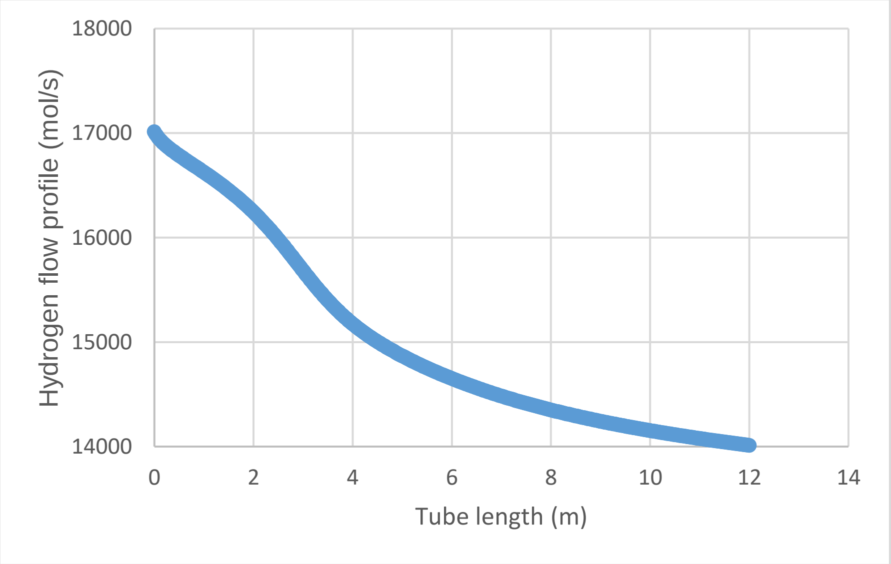


Figure 4. 4: Hydrogen flow profile vs. reactor position

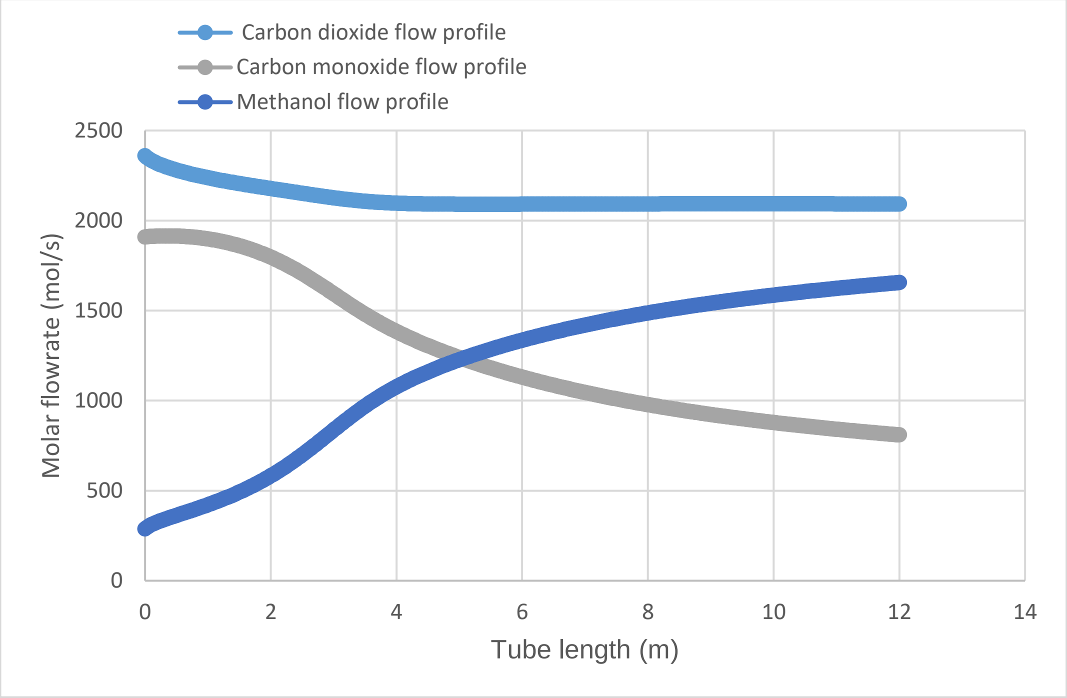


Figure 4. 5: Carbon oxides and methanol flowrates vs. reactor length.

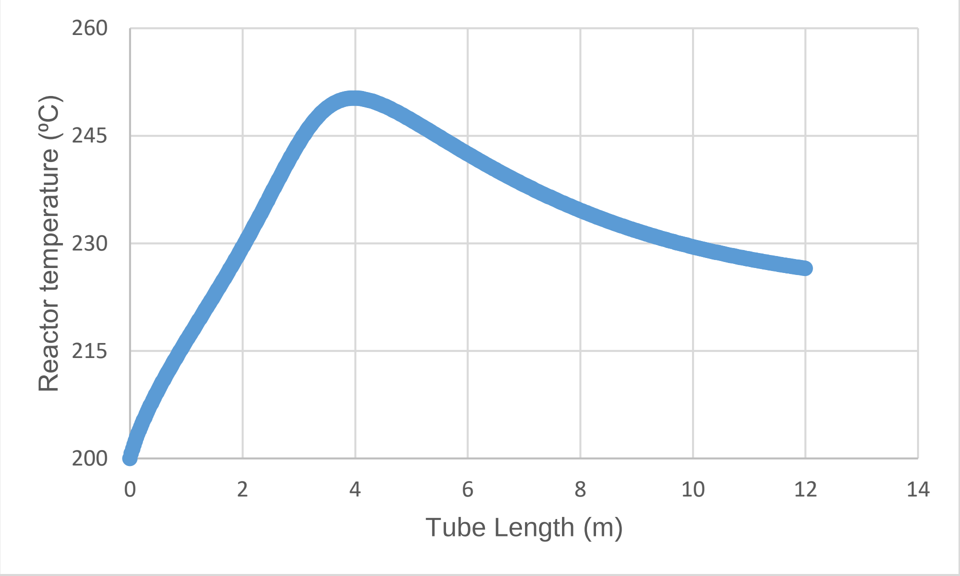


Figure 4. 6: Reactor temperature vs reactor length

Analysing the plot in figure 4.7 it can be observed that methanol flowrate is increasing with reactor temperature, but at a certain point the temperature starts to decrease due to the cooling system, however the methanol flowrate keeps increasing. As mentioned before the reaction of methanol synthesis is exothermic and is favoured by temperature decrease.

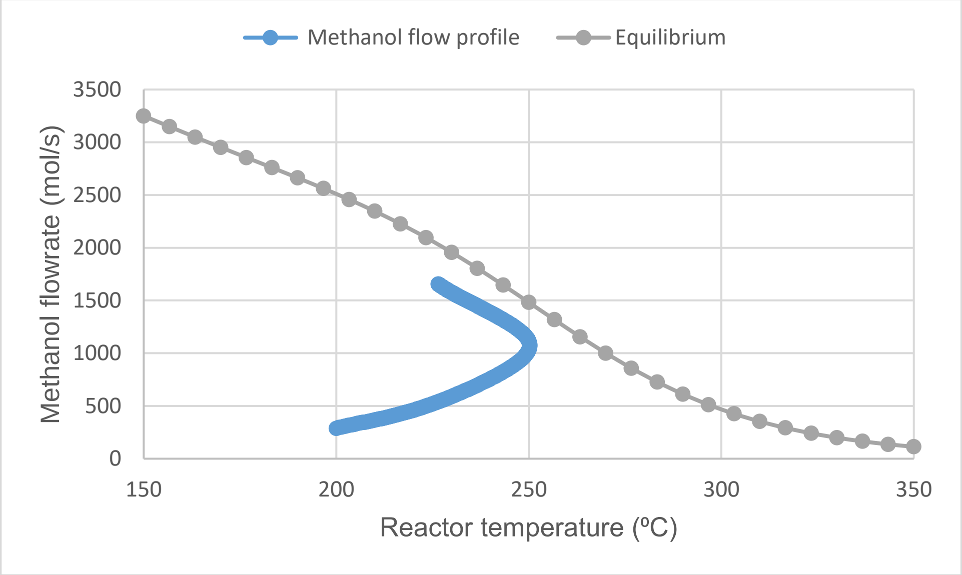


Figure 4. 7: Methanol flowrate vs reactor temperature

4.2. Simulation of methanol synthesis via direct methane oxidation

In the methanol reactor 1642.9 mol/s of CH$_4$ reacts with 878.9 mol/s of O$_2$. After all separations 1302.84 mol/s of methanol is produced (figure 4.8). The composition of the product and the description of reactor inlets and outlets presented in table 4.3

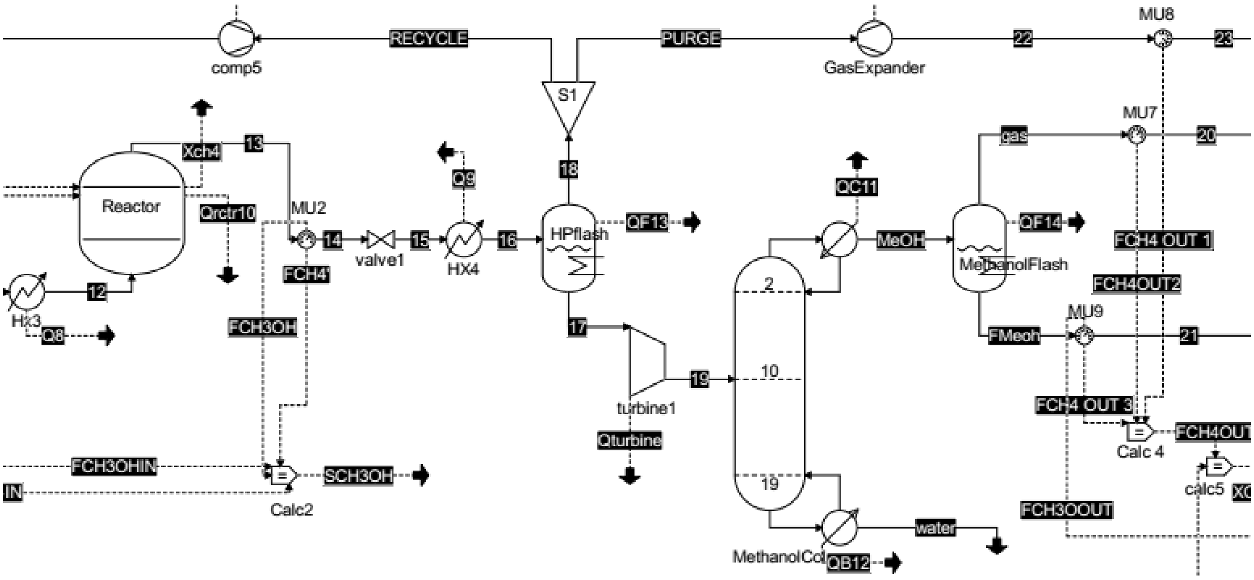


Figure 4. 8: Simulation of methanol reactor with purification units

The composition of the product and the description of reactor inlets and outlets are presented in table 4.3.

Table 4. 3: Results of Simulation in methanol reactor

Stream	R. inlet	R. outlet	Methanol out
Pressure (atm)	50	50	1
Temperature (°C)	400	400	50
Flowrate (mol/s)	18875.9	18156.5	1302.84
Molar Composition			
CH_4	0.7939	0.7412	0.0004
CO_2	0.1414	0.1519	0.0028
O_2	0.0476	0	0
H_2O	0.0014	0.0113	0.0001
CH_3OH	0.0157	0.0096	0.9970

In this simulation the CH_4 per pass and overall conversion are 10% and 93% respectively. The per pass CH_4 conversion is achieved by controlling O_2 flowrate, and reactor selectivity. In this process 99.5 % of the vapour exiting the flash is recycled to the reactor, this amount represents the unconverted material, and 9 passes are required to achieve overall CH_4 conversion. The methanol per pass yield is 8%, and overall selectivity ($S_{overall}$) is 85%. Zhang *et al.,* 2022 reported the same yield (7-8%), a methanol selectivity of 60% and a methane per-pass conversion of 13% at 50 bar. These results are close to the commercial target range according to Ramussen 2008 and Turan, 2020.

4.3. Carbon efficiency in methanol synthesis

Carbon efficiency (C_E) is an important operating parameter, defined as the moles of methanol in the outlet stream to the moles of inlet carbon. It is a measure of how effectively carbon is utilised in a particular process. The C_E measures the incorporation of carbon atoms of the reactant into the final product. This parameter is given by equation 4.1

$$C_E = \frac{\text{molar flow of } CH_3OH}{\text{molar flow of carbon contents in natural gas for the plant}} \qquad (4.1)$$

In this simulation the only carbon containing feed is CH_4 thus, C_E is the same as methanol overall yield ($Y_{overall}$). The carbon efficiency for indirect and direct routes are 83% and 79% respectively, the calculations are presented in appendix 8.

According to Turan, 2020, the current industrial process of methanol production achieves a C_E of methanol above 60%. In his study he reported a methanol C_E of 37.7% for DMTM. De Klerk, 2015 reported a C_E of 65-68% for industrial process and 35 % for direct process.

4.4. Energy requirement in methanol synthesis

The energy required to produce methanol for both flowhseets was calculated considering all the heat required by the process (for compression, heating) and the heat generated by the system that can be recovered (coolers, separators, reactions, expanders, turbines). The energy streams considered for each flowsheet are presented in table 4.4 and 4.5 and all the calculations are presented in appendix 9. For direct route, the minimum energy requirement was obtained by though optimization (see table 3.2).

Table 4. 4: Energy stream of syngas route flowsheet

Energy streams	Value (KW)	Energy streams	Value (KW)
Q_1	262.76	Q_{14}	-125647.00
Q_2	4069.59	$Q_{reactor}$	100802.00
Q_3	-4913.73	Q_{17}	-3370.90
Q_4	5013.48	$Q_{Flash\ 17}$	73446.80
Q_5	3872.33	Q_{18}	136579.00
Q_6	-274.17	$Q_{19Condenser}$	106390.00
Q_7	-131628.00	$Q_{20Boiler}$	-165049.00
Q_8	-5803.79	$Q_{21Flash}$	55033.70
Q_9	-73575.20	$Q_{Turbine}$	223.40
Q_{10ATR}	0	$Q_{Expander1}$	262.76
$Q_{11Flash}$	320503.00	$Q_{Expander}$	1939.23
Q_{12}	-608.63	Q_{13}	-369.94
DH	25832.30		

Table 4. 5: Energy streams of direct route flowsheet

Energy streams	Value (KW)	Energy streams	Value (KW)
Q_1 (J/s)	-5803.790	Q_9 (J/s)	268171.635
Q_2 (J/s)	-5891.965	Q_{rctr10} (J/s)	211110.635
Q_3 (J/s)	5340.458	Q_{c11} (J/s)	120463.308
Q_4 (J/s)	-3083.394	Q_{b12} (J/s)	-179567.335
Q_5 (J/s)	-3083.395	Q_{f13} (J/s)	0
Q_6 (J/s)	3154.554	Q_{14} (J/s)	56343.70
Q_7 (J/s)	-3365.083	$Q_{turbine}$ (J/s)	236.707
Q_8 (J/s)	-201068.940	$Q_{expander}$(J/s)	228.550

The energy required to convert 1642.9 mol/s of CH_4 into 1360.21 mol/s of methanol via syngas in this simulation is 229 kJ/mol. This value is higher than that mentioned by Patel, *et al.*, 2010 in their study about methanol synthesis (58.74 KJ/mol), however it is generally agreed that energy requirements for methanol synthesis can vary depending on the specific process technology used and the operating conditions. For direct conversion, the energy required to convert 1642.9 mol/s into 1302.84 mol/s at a per pass CH_4 conversion of 13% and a S_{CH3OH} of 99 % is 132 kJ/mol.

4.5. Comparison between the two methanol synthesis routes

This section compares the simulation results of the two methanol synthesis routes. The variables used for comparison are: methanol flowrate (F_{CH3OH}), overall methane conversion ($X_{overall}$), overall methanol selectivity ($S_{overall}$), overall methanol yield ($Y_{overall}$)/carbon efficiency (C_E) and energy requirement (Q). The values are presented in the table 4.6.

Table 4. 6: Comparision of simulation results

Variables	Syngas route	Direct route	Direct route (optimized)
F_{CH3OH} (mol/s)	1360.21	1302.84	1431
$X_{overall}$ (	0.94	0.93	0.94
$S_{overall}$	0.87	0.84	0.93
$Y_{overall}$ /C_e	0.83	0.79	0.87
Q(kJ/mol)	229	238	185

From this table it can be concluded that the syngas route has the best values than direct methane oxidation (not optimized) in terms of yield (83%) and also a low energy requirement (229 kJ/mol). The difference in C_E can be explained by the separation and high recycle that ensures the overall yield to be high. For the two flowsheets the HP flash operate at the same temperature and pressure but there is difference the recycle and purge streams (98% for syngas route and 99.5% for direct route). On the other hand comparing syngas route with the results of optimization for direct route, it can be observed that the yield for the second route becomes the best (87%) and energy requirement decreases (185 kJ/mol) what indicates that DMTM can be energetically competitive.

4.6. Effect of purge ratio and yield in DMTM energy requirement

This chapter describes the analysis of energy requirement variation with purge ratio, methanol overall selectivity ($S_{overall}$) and yield ($Y_{overall}$) for DMTM.

The increase in purge ratio means that more unreacted feed is recycled back. The plots in figure 4.9 and 4.10 illustrates that energy requirement decreases with purge ratio and methane overall conversion, thus, according to this simulation maintaining the minimum energy requirement means setting the high purge ratio and conversions.

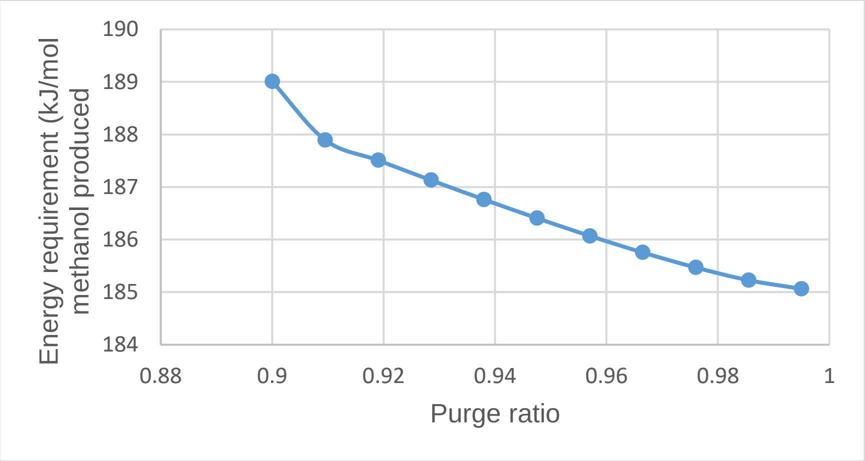


Figure 4. 9: Energy requirement vs. purge ratio

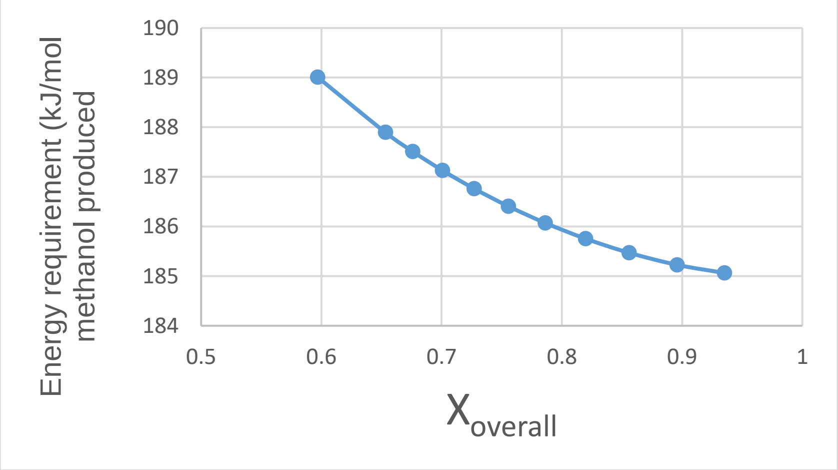


Figure 4. 10: Energy requirement vs. $X_{overall}$

The selectivity represents the amount of methanol produced based in the amount of methane converted. It is given by the amount of methanol produced divided by the amount of methane reacted.

The plot in figure 4.11 shows that energy varies with no change in selectivity, thus the energy requirement does not affect the overall methanol selectivity.

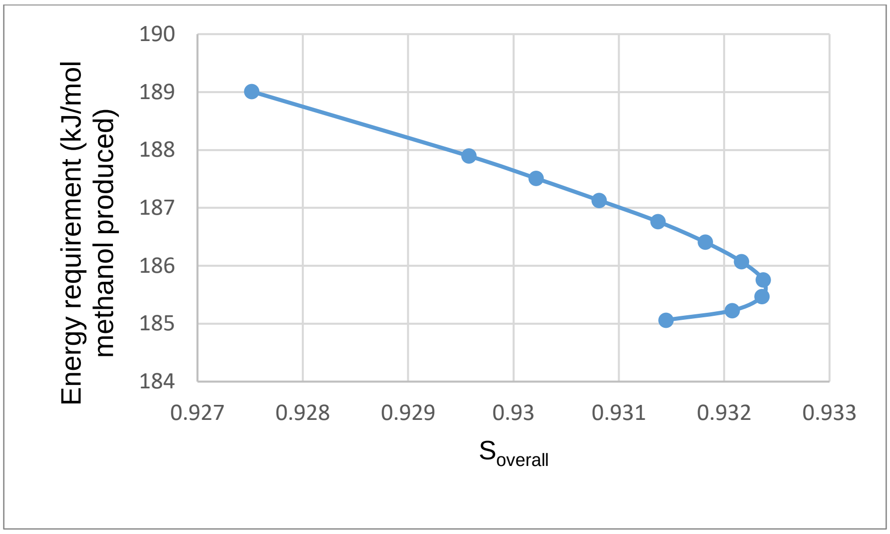


Figure 4. 11: Energy requirement vs. $S_{overall}$

The yield represents the amount of methanol that is formed per mole of methane feed to the process. The plot in figure 4.12 illustrates that the energy requirement decreases with an increase in the yield what means that less energy would be required, to increase the amount of the desired product. Comparing the two routes at the same yield (83%) it can be observed that the energy requirement of direct route (185 kJ/mol) remains lower than the required for syngas route (229kJ/mol).

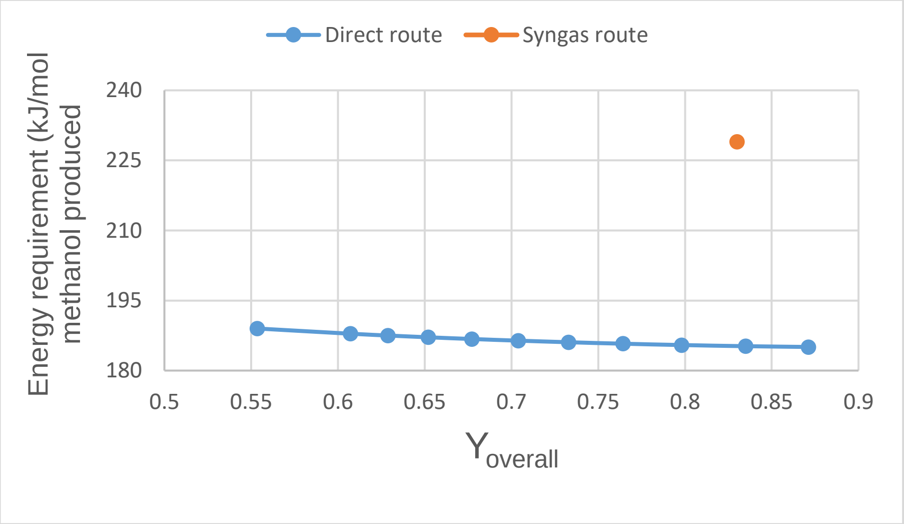


Figure 4. 12: Energy requirement vs. Y_{overal}

CHAPTER V

5. CONCLUSIONS AND RECOMENDATIONS

5.1. Conclusions

The objective of the present research was to evaluate the energetic viability of DMTM, thus design and simulation of classical and direct processes were made, and at the same conditions the two flowsheets were analysed and compared. The overall conclusions of this study are summarised below:

- 1642.9 mol/s of methane were converted into 1360.21 mol/s of methanol by syngas route (94% of methane overall conversion and 87 % of methanol overall selectivity) and 1302.84 mol/s of methanol through direct methane oxidation (93% of methane overall conversion and 85 % of methanol overall selectivity);
- The carbon efficiency/overall yield of classical process is (83%) slightly higher than the direct process (79%), without optimization, however the value obtained for direct methane in this simulation is higher than those mentioned in literature as a result of different operating conditions for the overall process;
- The energy required to convert methane in methanol trough the indirect route is 229 kJ/mol while for the direct route the energy required is 185 kJ/mol at the same yield (83%);
- For DMTM the energy requirement decreases with purge ratio, methane overall conversion, methanol overall yield and but does not affect methanol overall selectivity;
- In this study the energy requirement was minimised at 13% methane per pass conversion and 87% methanol per pass selectivity, this corresponds to a yield of 87%. The results obtained in this simulation indicate that DMTM can be energetically viable.

5.2. Recommendations

For future studies it is recommended to:

- Evaluate the feasibility of DMTM using natural gas as feedstock;
- Study the energetic optimisation of the direct conversion plant;
- Test the kinetic models proposed in the literature for the direct conversion process;
- Study the methanol and other by-products separation processes;

CHAPTER VI

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APPENDIXES

Appendix 1: Units report (Syngas route)

- **ATR reformer**

```
Last run for unit ATR:

+++ specifications +++

Heat duty:      0 W
Pressure drop:  0 Pa
Tolerance:      0.000001
Maximum iterations:     1000
Solution converged in 15 iterations
Re-calculating assuming total conversion of Oxygen

+++ solution +++

Solution converged in 6 iterations
Extent of reaction "0.0182286 Carbon dioxide + 0.408893 Carbon monoxide + 0.75114
Hydrogen + 0.103103 Water=0.427122 Methane + 0.274227 Oxygen":  -605.511 mol/s
Extent of reaction "0.636723 Carbon dioxide + 0.245892 Water=0.520753 Carbon
monoxide + 0.0139514 Hydrogen + 0.11597 Methane + 0.499293 Oxygen":     -210.158
mol/s
Extent of reaction "0.239602 Carbon dioxide + 0.463187 Hydrogen + 0.121014
Methane + 0.293313 Oxygen=0.360616 Carbon monoxide + 0.705215 Water":   -923.849
mol/s

+++ optional parameters +++

Temperature:    1275.94268098669 K
```

- **MeoH reactor**

```
Last run for unit Meoh reactor:

+++ specifications +++

Using enthalpyF in enthalpy calculations
Length: 12 m
Diameter:       7.58946638440411 m
Cross section area:     45.2389 m²
Total reactor volume:   542.867 m³
Number of heating/cooling tubes:        8000
Heating/cooling tube diameter:  0.06 m
Total tube cross section area:  22.6195 m²
Total tube perimeter:   1507.96 m
Tube heat transfer coefficient: 400 W/m²/K
Heating/Cooling tube temperature:       493.15 K
Nett cross section area:        22.6195 m²
Net reactor volume:     271.434 m³
Hydraulic diameter:     0.0590661 m
Catalyst loading:       1000 kg/m³
Packing porosity:       0.5
Packing particle diameter:      0.004 m
Heat duty:      0 W/m
Wall heat transfer coefficient: 0 W/m²/K
```

```
Flow direction: Horizontal
Reaction phase: Vapor
Tolerance:      0.00001
Report Intervals:       500
kinetic reaction "rxn1":        heterogeneous
kinetic reaction "rxn2":        heterogeneous
Compound equations:     5
Inert compounds:        2
Number of equations:    8

+++ solution +++

Solution obtained using 640 function evaluations

+++ Heat Transfer results +++

Minimum temperature:    473.15 K
Maximum temperature:    523.41790318 K
Heat duty heating/cooling tubes:        -100802139.618 W
```

- **Methanol column**

Results

Stream	**Feed1**	**L.Feed1**	**Top**	**Bottom**
Stage	10	10	1	20
Pressure (N/m2)	202650	101325	101325	101325
Vapour fraction (-)	0	0	1	0
Temperature (K)	313.15	313.176	337.627	374.523
Enthalpy (J/kmol)	-3.98E+07		1.66E+06	-3.95E+07
Entropy (J/kmol/K)	-112316		5768.66	-104520
Total molar flow (kmol/s)	1.65517	1.65517	1.36496	0.290216
Total mass flow (kg/s)	49.0582	49.0582	43.8299	5.22825
Vapour std.vol.flow (m3/s)			32.3366	
Liquid std.vol.flow (m3/s)	0.060437	0.060437		0.005242
Mole flows (kmol/s)				
Methane	3.27E-04	3.27E-04	3.27E-04	0
Carbon monoxide	3.40E-06	3.40E-06	3.40E-06	0
Carbon dioxide	0.00869877	0.00869877	0.00869877	0
Hydrogen	2.83E-05	2.83E-05	2.83E-05	9.75E-21
Oxygen	0	0	0	0
Water	0.290507	0.290507	2.91E-04	0.290216
Methanol	1.35561	1.35561	1.35561	1.93E-08
Mole fractions (-)				
Methane	1.98E-04	1.98E-04	2.40E-04	0

Carbon monoxide	2.05E-06	2.05E-06	2.49E-06	0
Carbon dioxide	0.0052555	0.0052555	0.00637292	0
Hydrogen	1.71E-05	1.71E-05	2.07E-05	3.36E-20
Oxygen	0	0	0	0
Water	0.175514	0.175514	2.13E-04	1
Methanol	0.819013	0.819013	0.993151	6.66E-08
Mass flows (kg/s)				
Methane	0.00524662	0.00524662	0.00524662	0
Carbon monoxide	9.53E-05	9.53E-05	9.53E-05	0
Carbon dioxide	0.382824	0.382824	0.382824	0
Hydrogen	5.70E-05	5.70E-05	5.70E-05	1.96E-20
Oxygen	0	0	0	0
Water	5.23348	5.23348	0.00523348	5.22824
Methanol	43.4365	43.4365	43.4364	6.20E-07
Mass fractions (-)				
Methane	1.07E-04	1.07E-04	1.20E-04	0
Carbon monoxide	1.94E-06	1.94E-06	2.17E-06	0
Carbon dioxide	0.00780347	0.00780347	0.00873431	0
Hydrogen	1.16E-06	1.16E-06	1.30E-06	3.76E-21
Oxygen	0	0	0	0
Water	0.106679	0.106679	1.19E-04	1
Methanol	0.885407	0.885407	0.991023	1.19E-07
Combined feed and product f				
Total molar	1	1	0.824661	0.175339
Total mass	1	1	0.893428	0.106572
Component molar				
Methane	1	1	1	0
Carbon monoxide	1	1	1	0
Carbon dioxide	1	1	1	0
Hydrogen	1	1	1	3.45E-16
Oxygen	0	0	0	0
Water	1	1	0.001	0.999
Methanol	1	1	1	1.43E-08
Vapour:				
Mole weight (kg/kmol)			32.1107	
Density (kg/m3)			1.1806	
Std.density (kg/m3)			1.35543	
Viscosity (N/m2.s)			1.10E-05	
Heat capacity (J/kmol/K)			48008.4	
Thermal cond. (J/s/m/K)			0.0191245	

Liquid:				
Mole weight (kg/kmol)	29.6392	29.6392		18.0153
Density (kg/m3)	795.654	795.581		946.314
Std.density (kg/m3)	811.724	811.724		997.457
Viscosity (N/m2.s)	4.59E-04	4.59E-04		2.74E-04
Heat capacity (J/kmol/K)	82440.7	82445.6		76010.7
Thermal cond. (J/s/m/K)	0.267995	0.267951		0.667936
Surface tension (N/m)	0.0294107	0.0294082		0.058807

- **Flash Units**

```
Last run for unit HP flash2:
+++ specifications +++
Pressure drop:  0 Pa
Heat duty:      -73446812.7829399 W
+++ optional parameters +++
Pressure:       4822810.93553476 Pa
Heat duty:      -73446828.5776689 W
Vapor fraction: 0.928164397247971
```

```
Last run for unit LP Flash3:

++ specifications ++Pressure drop:  0 Pa
Heat duty:      -1519227.67905368 W
+++ optional parameters +++
Pressure:       202650 Pa
Heat duty:      -1519227.95715423 W
Vapor fraction: 2.36799496361414E-02
```

```
Last run for unit Flash3:
+++ specifications +++
Pressure drop:  0 Pa
Heat duty:      -55033667.1095047 W
+++ optional parameters +++
Pressure:       101325 Pa
Heat duty:      -55033675.5250981 W
Vapor fraction: 3.48072504621371E-03
```

Appendix 2: Kinetics of methanol reactor and catalyst properties

Methanol synthesis is described by 3 reversible reactions (2.5, 2.8 and 2.9), however in this research, it was considered that the kinetics are given by Vanden Bussche and Froment (1996) that makes use of only two reactions (2.9 and 2.5). The kinetic expressions for these reactions are:

$$R_1=R_{CH_3OH}=k_1P_{CO_2}P_{H_2}\frac{\left(1-\frac{P_{H_2O}P_{CH_3OH}}{K_{E1}P_{H_2}^3PCO_2}\right)}{\left(1+k_2\frac{PH_2O}{PH_2}+k_3P_{H2}^{0.5}+k_4P_{H_2O}\right)^3}$$

$$R_1=R_{CH3OH}=k_5P_{CO_2}\frac{\left(1-\frac{P_{H_2O}P_{CO}}{K_{E2}PH_2PCO_2}\right)}{1+k_2\frac{PH_2O}{PH_2}+k_3P_{H2}^{0.5}+k_4P_{H_2O}}$$

The reaction rate is given in [mol/(kgcat .s)] and the partial pressures are in [bar]. The constants are given by:

$K_{E1}=10^{(\frac{3066}{T}-10.592)}$ $K_{E1}=10^{(\frac{3066}{T}+2.029)}$ $k_1=1.07EXP^{(\frac{36696}{RT})}$ $k_2=3453.38$ $k_3=0.499EXP^{(\frac{17197}{RT})}$
$k_4=6.62x10^{-11}EXP^{(\frac{124119}{RT})}$ $k_5=1.22x10^{10}EXP^{(\frac{-94765}{RT})}$

Catalyst properties

The catalyst properties	
Catalyst particle density (kg/m^3)	1775
Diameter of catalyst particles (mm)	2
Catalyst bed porosity	0.5

Appendix 3: Scilab Programming Code (Syngas route)

```
clear;clc()

//variable ranges
//Fw=3:15:20
//Fo2=1:7:20
Fch40=10  //flow of methane, mol/s
n=21   //number of parametric points, 20 intervals, 21 points

//read data
sheets=readxls("ParametricStudy_v2.xls")
Fw0=sheets(1)(3:$,3)
Fo20=sheets(1)(3:$,4)
Tin=sheets(1)(3:$,5)
Mratio=sheets(1)(3:$,6)
Sratio=sheets(1)(3:$,7)
Tout=sheets(1)(3:$,8)
Pout=sheets(1)(3:$,9)
Fch4=sheets(1)(3:$,10)
Fco=sheets(1)(3:$,11)
Fco2=sheets(1)(3:$,12)
Fh2=sheets(1)(3:$,13)
Fo2=sheets(1)(3:$,14)
Fw=sheets(1)(3:$,15)
XXch4=sheets(1)(3:$,16)
XXo2=sheets(1)(3:$,17)
XXw=sheets(1)(3:$,18)
OK=sheets(1)(3:$,19)

k=find("OK"<>OK)
if k<>[] then
   disp("Some COCO runs have failed, not OK, abort")
   abort
end
Fw0=Fw0/Fch40
Fo20=Fo20/Fch40
Fch4=Fch4/Fch40
Fco=Fco/Fch40
Fco2=Fco2/Fch40
Fh2=Fh2/Fch40
Fo2=Fo2/Fch40
Fw=Fw/Fch40
Xch4=1-Fch4

//feed temperature
printf("\nFeed Temperature: Tin(C)=%f\n",Tin(1))
printf("all flows normalised to methane feed: F(i)/Fch40 \n\n")
```

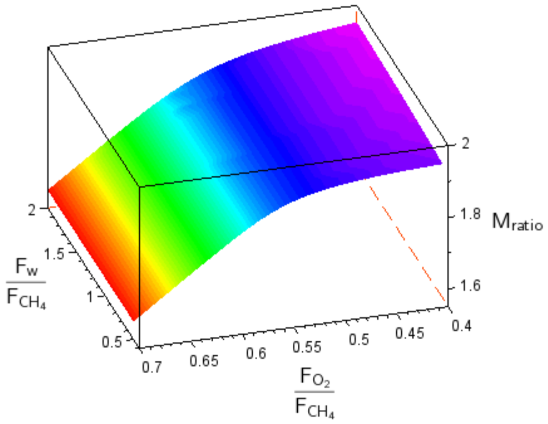
```
//max values
[Mmax,k]=max(Mratio)
printf("conditions and outputs at maximum Mratio\n")
printf("Mratio(max)=%f\n",Mmax)
printf("Fw(max)=%f\n",Fw0(k))
printf("Fo2(max)=%f\n",Fo20(k))
printf("Sratio(max)=%f\n",Sratio(k))
printf("Tout(max)=%f\n",Tout(k))
printf("Pout(max)=%f\n",Pout(k))
printf("Fch4(max)=%f\n",Fch4(k))
printf("Fco(max)=%f\n",Fco(k))
printf("Fco2(max)=%f\n",Fco2(k))
printf("Fh2(max)=%f\n",Fh2(k))
printf("Fo2(max)=%f\n",Fo2(k))
printf("Fw(max)=%f\n",Fw(k))
printf("Xch4(max)=%f\n",Xch4(k))
printf("XXch4(max)=%f\n",XXch4(k))
printf("XXo2(max)=%f\n",XXo2(k))
printf("XXw(max)=%f\n",XXw(k))

//matrices for surface plotting
Fw0=matrix(Fw0,n,n)
Fo20=matrix(Fo20,n,n)
Mratio=matrix(Mratio,n,n)
Sratio=matrix(Sratio,n,n)
Tout=matrix(Tout,n,n)
Pout=matrix(Pout,n,n)
Fch4=matrix(Fch4,n,n)
Fco=matrix(Fco,n,n)
Fco2=matrix(Fco2,n,n)
Fh2=matrix(Fh2,n,n)
Fo2=matrix(Fo2,n,n)
Fw=matrix(Fw,n,n)
Xch4=matrix(Xch4,n,n)
XXch4=matrix(XXch4,n,n)
XXo2=matrix(XXo2,n,n)
XXw=matrix(XXw,n,n)

//finding the closest values for Mratio=2.05 and Sratio=3
//obj=(1-Mratio/2.05).^2 + (1-Sratio/3).^2
//any one of the parameters above can be added
obj=(1-Mratio/2.05).^2 + (1-Sratio/3).^2 + (Xch4-0.99).^2

obj=sqrt(obj)
[objmin,pos]=min(obj)
printf("\nconditions and outputs which minimise the objective function\n")
printf("obj(min)=%f\n",objmin)
printf("Fw0(min)=%f\n",Fw0(pos(1),pos(2)))
printf("Fo20(min)=%f\n",Fo20(pos(1),pos(2)))
printf("Mratio(min)=%f\n",Mratio(pos(1),pos(2)))
printf("Sratio(min)=%f\n",Sratio(pos(1),pos(2)))
printf("Tout(min)=%f\n",Tout(pos(1),pos(2)))
printf("Pout(min)=%f\n",Pout(pos(1),pos(2)))
printf("Fch4(min)=%f\n",Fch4(pos(1),pos(2)))
printf("Fco(min)=%f\n",Fco(pos(1),pos(2)))
printf("Fco2(min)=%f\n",Fco2(pos(1),pos(2)))
printf("Fh2(min)=%f\n",Fh2(pos(1),pos(2)))
printf("Fo2(min)=%f\n",Fo2(pos(1),pos(2)))
printf("Fw(min)=%f\n",Fw(pos(1),pos(2)))
printf("Xch4(min)=%f\n",Xch4(pos(1),pos(2)))
printf("XXch4(min)=%f\n",XXch4(pos(1),pos(2)))
printf("XXo2(min)=%f\n",XXo2(pos(1),pos(2)))
printf("XXw(min)=%f\n",XXw(pos(1),pos(2)))

obj=log(obj)

//plot Mratio
angle=[47.75,-196.5]  //change this to make graph look good
```

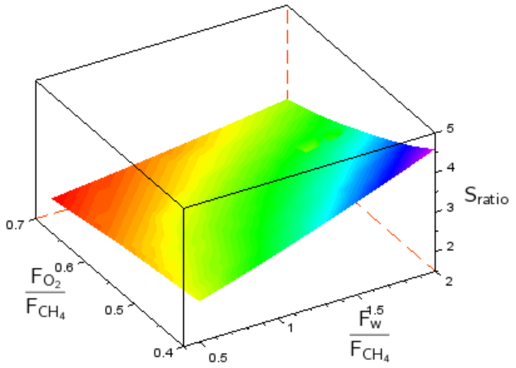
```
scf(1)
drawlater()
clf
gcf.figure_size=[500 500]
gcf.color_map = rainbowcolormap(64);
gca.margins = [0.17,0.17,0.1,0.17]
surf(Fw0,Fo20,Mratio)
gce.color_mode=-1
gce.color_flag=3
xlabel("$\mathsf{\dfrac{F_w}{F_{CH_4}}}$","fontsize",4)
ylabel("$\mathsf{\dfrac{F_{O_2}}{F_{CH_4}}}$","fontsize",4)
zlabel("$\mathsf{M_{ratio}}$","fontsize",4)
gca.rotation_angles = angle
gca.font_size=2
drawnow()

//Plot Sratio
scf(2)
drawlater()
clf
gcf.figure_size=[500 500]
gcf.color_map = rainbowcolormap(64);
gca.margins = [0.17,0.17,0.1,0.17]
surf(Fw0,Fo20,Sratio)
gce.color_mode=-1
gce.color_flag=3
xlabel("$\mathsf{\dfrac{F_w}{F_{CH_4}}}$","fontsize",4)
ylabel("$\mathsf{\dfrac{F_{O_2}}{F_{CH_4}}}$","fontsize",4)
zlabel("$\mathsf{S_{ratio}}$","fontsize",4)
gca.rotation_angles = angle
drawnow()

//Plot methane conversion
scf(3)
drawlater()
clf
gcf.figure_size=[500 500]
gcf.color_map = rainbowcolormap(64);
gca.margins = [0.17,0.17,0.1,0.17]
surf(Fw0,Fo20,Xch4)
gce.color_mode=-1
gce.color_flag=3
xlabel("$\mathsf{\dfrac{F_w}{F_{CH_4}}}$","fontsize",4)
ylabel("$\mathsf{\dfrac{F_{O_2}}{F_{CH_4}}}$","fontsize",4)
zlabel("$\mathsf{X_{CH_4}}$","fontsize",4)
gca.rotation_angles = [54.25,-159.75]
drawnow()

//plot objective function
scf(4)
drawlater()
clf
gcf.figure_size=[500 500]
gcf.color_map = rainbowcolormap(64);
gca.margins = [0.17,0.17,0.1,0.17]
surf(Fw0,Fo20,obj)
gce.color_mode=-1
gce.color_flag=3
xlabel("$\mathsf{\dfrac{F_w}{F_{CH_4}}}$","fontsize",4)
    •   ylabel("$\mathsf{\dfrac{F_{O_2}}{F_{CH_4}}}$","fontsizeatr",4)
zlabel("$\mathsf{X_{obj}}$","fontsize",4)
gca.rotation_angles = angle
drawnow()

//xs2svg(1,"fig1.svg")
//xs2svg(2,"fig2.svg")
//xs2svg(3,"fig3.svg")
//xs2svg(4,"fig4.svg")
```

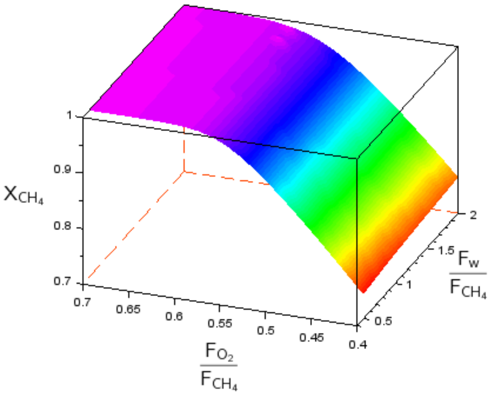
Appendix 4: Results of Simulation in Scilab (Syngas route)

```
conditions and outputs at maximum Mratio
Mratio(max)=1.953624
Fw(max)=2.000000
Fo2(max)=0.400000
Sratio(max)=4.597561
Tout(max)=823.623033
Pout(max)=30.000000
Fch4(max)=0.235457
Fco(max)=0.403421
Fco2(max)=0.361122
Fh2(max)=1.854753
Fo2(max)=0.000000
Fw(max)=1.674334
Xch4(max)=0.764543
XXch4(max)=0.764543
XXo2(max)=1.000000
XXw(max)=0.162833
```

```
conditions and outputs which minimise the objective function
obj(min)=0.086100
Fw0(min)=1.400000
Fo20(min)=0.535000
Mratio(min)=1.884967
Sratio(min)=2.991005
Tout(min)=975.852659
Pout(min)=30.000000
Fch4(min)=0.040387
Fco(min)=0.693673
Fco2(min)=0.265940
Fh2(min)=2.074779
Fo2(min)=0.000000
Fw(min)=1.244447
Xch4(min)=0.959613
XXch4(min)=0.959613
XXo2(min)=1.000000
XXw(min)=0.111109
```







Appendix 5: Units report (Direct route)

- **Reactor**

```
Last run for unit Reactor:
+++ specifications +++
Using enthalpyF in enthalpy calculations
Heat duty type: Isothermal
Temperature:    673.15 K
Pressure drop:  0 Pa
+++ optional parameters +++
Heat duty:      -257241574.776976 W
```

- **Flash Units**

```
Last run for unit HPflash:

+++ specifications +++

Pressure drop:  0 Pa
Heat duty:      0 W

+++ optional parameters +++

Pressure:       4863600 Pa
Vapor fraction: 0.904130807365233
Temperature:    323.15 K
```

Appendix 6: Scilab Programming Code (Direct route)

```
clear;clc()

//read data
sheets=readxls("Leila(CH42MEOH)km_parametric_v1-6.xls")
```

```
//the data here is in a different format, you have many 11 x 11 studies at 11
//purge ratios, thus 11 x 11 x 11 data
//its best to read one purge ratio at a time
//you can store then each in a sheet
i=1  //choose sheet
Ratio=sheets(i)(3:$,3)        //O2 to CH4
X1=sheets(i)(3:$,4)           //CH4 conversion to methanol in the reactor
S1=sheets(i)(3:$,5)           //purge ratio
Xch4=sheets(i)(3:$,6)           //methane conversion per pass
Fmeoh=sheets(i)(3:$,7)           //methanol flow rate reactor
Smeoh=sheets(i)(3:$,8)           //methanol selectivity reactor
Xoverall=sheets(i)(3:$,9)       //overall CH4 conversion
Soverall=sheets(i)(3:$,10)      //overall methanol selectivity
Fo2=sheets(i)(3:$,11)           //O2 supplied to the process
Q1=sheets(i)(3:$,12)            //methane compressor
Q2=sheets(i)(3:$,13)            //O2 compressor 1
Q3=sheets(i)(3:$,14)            //O2 cooler 1
Q4=sheets(i)(3:$,15)            //O2 compressor 2
Q5=sheets(i)(3:$,16)            //O2 cooler 2
Q6=sheets(i)(3:$,17)            //O2 compressor 3
Q7=sheets(i)(3:$,18)            //recycle compressor
Q8=sheets(i)(3:$,19)            //reactor feed preheater
Q9=sheets(i)(3:$,20)            //reactor product cooler
Qrctr10=sheets(i)(3:$,21)       //reactor isothermal heat duty
Qc11=sheets(i)(3:$,22)          //column condenser
Qb12=sheets(i)(3:$,23)          //column reboiler
Qf13=sheets(i)(3:$,24)          //reactor product flash
Qf14=sheets(i)(3:$,25)          //column distillate flash
Qturbine=sheets(i)(3:$,26)      //turbine power
Qexpander=sheets(i)(3:$,27)     //expander power
OK=sheets(i)(3:$,28)

printf("\npurge ratio = %f\n\n",S1(1))

//disp(length(Ratio))
//the idea is that you can add the energy streams here and you can then
//get build the objective function based on energy, in this way you can
//find the operating point with the lowest energy
//this migh be quicker to do that a Pinch analysis for each run
//here there are 121 (11 by 11) runs, each would need a pinch analysis
//to do this you would need to automate the pinch analysis

k=find("OK"==OK)
//if k<>[] then
//    disp("Some COCO runs have failed, not OK, abort")
//    abort
//end
Ratio=Ratio(k)
X1=X1(k)
S1=S1(k)
Xch4=Xch4(k)
Fmeoh=Fmeoh(k)
Smeoh=Smeoh(k)
Xoverall=Xoverall(k)
Soverall=Soverall(k)
Fo2=Fo2(k)
Q1=Q1(k)
Q2=Q2(k)
Q3=Q3(k)
Q4=Q4(k)
Q5=Q5(k)
Q6=Q6(k)
Q7=Q7(k)
Q8=Q8(k)
Q9=Q9(k)
Q1=Q1(k)
Qrctr10=Qrctr10(k)
Qc11=Qc11(k)
```

```
Qb12=Qb12(k)
Qf13=Qf13(k)
Qf14=Qf14(k)
Qturbine=Qturbine(k)
Qexpander=Qexpander(k)
sumQ=Q1+Q2+Q3+Q4+Q5+Q6+Q7+Q8+Q9+Qrctr10+Qc11+Qb12+Qf13+Qf14+Qturbine+Qexpander
n=length(Ratio)
n=int(round(sqrt(n)))

//max values
[Mmax,k]=max(Xoverall)
printf("conditions and outputs at maximum Xoverall\n")
printf("Ratio(max)=%f\n",Ratio(k))
printf("X1(max)=%f\n",X1(k))
printf("S1(max)=%f\n",S1(k))
printf("Xch4(max)=%f\n",Xch4(k))
printf("Fmeoh(max)=%f\n",Fmeoh(k))
printf("Smeoh(max)=%f\n",Smeoh(k))
printf("Xoverall(max)=%f\n",Xoverall(k))
printf("Soverall(max)=%f\n",Soverall(k))
printf("Fo2(max)=%f\n",Fo2(k))
printf("Q1(max)=%f\n",Q1(k))
printf("Q2(max)=%f\n",Q2(k))
printf("Q3(max)=%f\n",Q3(k))
printf("Q4(max)=%f\n",Q4(k))
printf("Q5(max)=%f\n",Q5(k))
printf("Q6(max)=%f\n",Q6(k))
printf("Q7(max)=%f\n",Q7(k))
printf("Q8(max)=%f\n",Q8(k))
printf("Q9(max)=%f\n",Q9(k))
printf("Qrctr10(max)=%f\n",Qrctr10(k))
printf("Qc11(max)=%f\n",Qc11(k))
printf("Qb12(max)=%f\n",Qb12(k))
printf("Qf13(max)=%f\n",Qf13(k))
printf("Qf14(max)=%f\n",Qf14(k))
printf("Qturbine(max)=%f\n",Qturbine(k))
printf("Qexpander(max)=%f\n",Qexpander(k))
printf("sumQ(max)=%f\n",sumQ(k))

//matrices for surface plotting
Ratio=matrix(Ratio,n,n)
X1=matrix(X1,n,n)
S1=matrix(S1,n,n)
Xch4=matrix(Xch4,n,n)
Fmeoh=matrix(Fmeoh,n,n)
Smeoh=matrix(Smeoh,n,n)
Xoverall=matrix(Xoverall,n,n)
Soverall=matrix(Soverall,n,n)
Fo2=matrix(Fo2,n,n)
Q1=matrix(Q1,n,n)
Q2=matrix(Q2,n,n)
Q3=matrix(Q3,n,n)
Q4=matrix(Q4,n,n)
Q5=matrix(Q5,n,n)
Q6=matrix(Q6,n,n)
Q7=matrix(Q7,n,n)
Q8=matrix(Q8,n,n)
Q9=matrix(Q9,n,n)
Qrctr10=matrix(Qrctr10,n,n)
Qc11=matrix(Qc11,n,n)
Qb12=matrix(Qb12,n,n)
Qf13=matrix(Qf13,n,n)
Qf14=matrix(Qf14,n,n)
Qturbine=matrix(Qturbine,n,n)
Qexpander=matrix(Qexpander,n,n)
sumQ=matrix(sumQ,n,n)

//Objective function
```

```
//any one of the parameters above can be added
obj=(1-Xoverall/0.95).^2 + (1-Soverall/0.95).^2 + (1-sumQ/min(sumQ)).^2
//
//obj=sqrt(obj)
obj=log(obj)   //use log scale to separate the small values
//obj=sumQ
[objmin,pos]=min(obj)
printf("\nconditions and outputs which minimise the objective function\n")
printf("obj(min)=%f\n",objmin)
printf("Ratio(min)=%f\n",Ratio(pos(1),pos(2)))
printf("X1(min)=%f\n",X1(pos(1),pos(2)))
printf("S1(min)=%f\n",S1(pos(1),pos(2)))
printf("Xch4(min)=%f\n",Xch4(pos(1),pos(2)))
printf("Fmeoh(min)=%f\n",Fmeoh(pos(1),pos(2)))
printf("Smeoh(min)=%f\n",Smeoh(pos(1),pos(2)))
printf("Xoverall(min)=%f\n",Xoverall(pos(1),pos(2)))
printf("Soverall(min)=%f\n",Soverall(pos(1),pos(2)))
printf("Fo2(min)=%f\n",Fo2(pos(1),pos(2)))
printf("Q1(min)=%f\n",Q1(pos(1),pos(2)))
printf("Q2(min)=%f\n",Q2(pos(1),pos(2)))
printf("Q3(min)=%f\n",Q3(pos(1),pos(2)))
printf("Q4(min)=%f\n",Q4(pos(1),pos(2)))
printf("Q5(min)=%f\n",Q5(pos(1),pos(2)))
printf("Q6(min)=%f\n",Q6(pos(1),pos(2)))
printf("Q7(min)=%f\n",Q7(pos(1),pos(2)))
printf("Q8(min)=%f\n",Q8(pos(1),pos(2)))
printf("Q9(min)=%f\n",Q9(pos(1),pos(2)))
printf("Qrctr10(min)=%f\n",Qrctr10(pos(1),pos(2)))
printf("Qc11(min)=%f\n",Qc11(pos(1),pos(2)))
printf("Qb12(min)=%f\n",Qb12(pos(1),pos(2)))
printf("Qf13(min)=%f\n",Qf13(pos(1),pos(2)))
printf("Qf14(min)=%f\n",Qf14(pos(1),pos(2)))
printf("Qturbine(min)=%f\n",Qturbine(pos(1),pos(2)))
printf("Qexpander(min)=%f\n",Qexpander(pos(1),pos(2)))
printf("SumQ(min)=%f\n",sumQ(pos(1),pos(2)))
//obj=log(obj)

//plot Methane conversion in the reactor
angle=[43,-154]  //change this to make graph look good
scf(1)
drawlater()
clf
gcf.figure_size=[500 500]
gcf.color_map = rainbowcolormap(64);
gca.margins = [0.2,0.2,0.1,0.2]
surf(Ratio,X1,Xch4)
gce.color_mode=-1
gce.color_flag=3
xlabel("$\mathsf{\dfrac{F_{O_2}}{F_{CH_4}}}$","fontsize",4)
ylabel("$\mathsf{X_1}$","fontsize",4)
zlabel("$\mathsf{X_{CH_4}}$","fontsize",4)
gca.rotation_angles = angle
gca.font_size=2
drawnow()

//Plot Fmeoh in the reactor
scf(2)
drawlater()
clf
gcf.figure_size=[500 500]
gcf.color_map = rainbowcolormap(64);
gca.margins = [0.2,0.2,0.1,0.2]
surf(Ratio,X1,Fmeoh)
gce.color_mode=-1
gce.color_flag=3
xlabel("$\mathsf{\dfrac{F_{O_2}}{F_{CH_4}}}$","fontsize",4)
ylabel("$\mathsf{X_1}$","fontsize",4)
zlabel("$\mathsf{F_{MeOH}}$","fontsize",4)
```

```
gca.rotation_angles = angle
drawnow()

//Plot selectivity in the reactor
scf(3)
drawlater()
clf
gcf.figure_size=[500 500]
gcf.color_map = rainbowcolormap(64);
gca.margins = [0.2,0.2,0.1,0.2]
surf(Ratio,X1,Smeoh)
gce.color_mode=-1
gce.color_flag=3
xlabel("$\mathsf{\dfrac{F_{O_2}}{F_{CH_4}}}$","fontsize",4)
ylabel("$\mathsf{X_1}$","fontsize",4)
zlabel("$\mathsf{S_{MeOH}}$","fontsize",4)
gca.rotation_angles = angle
drawnow()

//plot Xoverall
scf(4)
drawlater()
clf
gcf.figure_size=[500 500]
gcf.color_map = rainbowcolormap(64);
gca.margins = [0.2,0.2,0.1,0.2]
surf(Ratio,X1,Xoverall)
gce.color_mode=-1
gce.color_flag=3
xlabel("$\mathsf{\dfrac{F_{O_2}}{F_{CH_4}}}$","fontsize",4)
ylabel("$\mathsf{X_1}$","fontsize",4)
zlabel("$\mathsf{X_{overall}}$","fontsize",4)
gca.rotation_angles = angle
drawnow()

//Plot Soverall in the reactor
scf(5)
drawlater()
clf
gcf.figure_size=[500 500]
gcf.color_map = rainbowcolormap(64);
gca.margins = [0.2,0.2,0.1,0.2]
surf(Ratio,X1,Soverall)
gce.color_mode=-1
gce.color_flag=3
xlabel("$\mathsf{\dfrac{F_{O_2}}{F_{CH_4}}}$","fontsize",4)
ylabel("$\mathsf{X_1}$","fontsize",4)
zlabel("$\mathsf{S_{overall}}$","fontsize",4)
gca.rotation_angles = angle
drawnow()

//plot Fo2
scf(6)
drawlater()
clf
gcf.figure_size=[500 500]
gcf.color_map = rainbowcolormap(64);
gca.margins = [0.2,0.2,0.1,0.2]
surf(Ratio,X1,Fo2)
gce.color_mode=-1
gce.color_flag=3
xlabel("$\mathsf{\dfrac{F_{O_2}}{F_{CH_4}}}$","fontsize",4)
ylabel("$\mathsf{X_1}$","fontsize",4)
zlabel("$\mathsf{F_{O2}}$","fontsize",4)
gca.rotation_angles = angle
drawnow()

//plot Qc
```

```
scf(7)
drawlater()
clf
gcf.figure_size=[500 500]
gcf.color_map = rainbowcolormap(64);
gca.margins = [0.2,0.2,0.1,0.2]
surf(Ratio,X1,Qc11)
gce.color_mode=-1
gce.color_flag=3
xlabel("$\mathsf{\dfrac{F_{O_2}}{F_{CH_4}}}$","fontsize",4)
ylabel("$\mathsf{X_1}$","fontsize",4)
zlabel("$\mathsf{Q_{c}}$","fontsize",4)
gca.rotation_angles = angle
drawnow()

//plot Qb
scf(8)
drawlater()
clf
gcf.figure_size=[500 500]
gcf.color_map = rainbowcolormap(64);
gca.margins = [0.2,0.2,0.1,0.2]
surf(Ratio,X1,Qb12)
gce.color_mode=-1
gce.color_flag=3
xlabel("$\mathsf{\dfrac{F_{O_2}}{F_{CH_4}}}$","fontsize",4)
ylabel("$\mathsf{X_1}$","fontsize",4)
zlabel("$\mathsf{Q_{b}}$","fontsize",4)
gca.rotation_angles = angle
drawnow()

//plot Qrctr
scf(9)
drawlater()
clf
gcf.figure_size=[500 500]
gcf.color_map = rainbowcolormap(64);
gca.margins = [0.2,0.2,0.1,0.2]
surf(Ratio,X1,Qrctr10)
gce.color_mode=-1
gce.color_flag=3
xlabel("$\mathsf{\dfrac{F_{O_2}}{F_{CH_4}}}$","fontsize",4)
ylabel("$\mathsf{X_1}$","fontsize",4)
zlabel("$\mathsf{Q_{rctr}}$","fontsize",4)
gca.rotation_angles = angle
drawnow()

//plot Q7 recycle stream
scf(10)
drawlater()
clf
gcf.figure_size=[500 500]
gcf.color_map = rainbowcolormap(64);
gca.margins = [0.2,0.2,0.1,0.2]
surf(Ratio,X1,Q7)
gce.color_mode=-1
gce.color_flag=3
xlabel("$\mathsf{\dfrac{F_{O_2}}{F_{CH_4}}}$","fontsize",4)
ylabel("$\mathsf{X_1}$","fontsize",4)
zlabel("$\mathsf{Q_{recycle}}$","fontsize",4)
gca.rotation_angles = angle
drawnow()

//Plot Qturbine
scf(11)
drawlater()
clf
gcf.figure_size=[500 500]
```

```
gcf.color_map = rainbowcolormap(64);
gca.margins = [0.2,0.2,0.1,0.2]
surf(Ratio,X1,Qturbine)
gce.color_mode=-1
gce.color_flag=3
xlabel("$\mathsf{\dfrac{F_{O_2}}{F_{CH_4}}}$","fontsize",4)
ylabel("$\mathsf{X_1}$","fontsize",4)
zlabel("$\mathsf{Q_{turbine}}$","fontsize",4)
gca.rotation_angles = angle
drawnow()

//Plot Qexpander
scf(12)
drawlater()
clf
gcf.figure_size=[500 500]
gcf.color_map = rainbowcolormap(64);
gca.margins = [0.2,0.2,0.1,0.2]
surf(Ratio,X1,Qexpander)
gce.color_mode=-1
gce.color_flag=3
xlabel("$\mathsf{\dfrac{F_{O_2}}{F_{CH_4}}}$","fontsize",4)
ylabel("$\mathsf{X_1}$","fontsize",4)
zlabel("$\mathsf{Q_{expander}}$","fontsize",4)
gca.rotation_angles = angle
drawnow()

//plot sumQ
scf(13)
drawlater()
clf()  //to plot multiple layers, turn this off by using //
gcf.figure_size=[500 500]
gcf.color_map = rainbowcolormap(64);
gca.margins = [0.22,0.22,0.1,0.2]
surf(Ratio,X1,sumQ)
gce.color_mode=-1
gce.color_flag=3
xlabel("$\mathsf{\dfrac{F_{O_2}}{F_{CH_4}}}$","fontsize",4)
ylabel("$\mathsf{X_1}$","fontsize",4)
zlabel("$\mathsf{\sum_i Q_i}$","fontsize",3)
gca.rotation_angles = angle
//colorbar
//gce().title.text="Energy(kW)"
//gce().title.font_size = 3
drawnow()

//plot obj
scf(14)
drawlater()
clf()  //to plot multiple layers, turn this off by using //
gcf.figure_size=[500 500]
gcf.color_map = rainbowcolormap(64);
gca.margins = [0.22,0.22,0.1,0.2]
surf(Ratio,X1,obj)
gce.color_mode=-1
gce.color_flag=3
xlabel("$\mathsf{\dfrac{F_{O_2}}{F_{CH_4}}}$","fontsize",4)
ylabel("$\mathsf{X_1}$","fontsize",4)
zlabel("$\mathsf{obj}$","fontsize",3)
gca.rotation_angles = angle
//colorbar
//gce().title.text="Energy(kW)"
//gce().title.font_size = 3
drawnow()

//xs2svg(1,"fig1.svg")
//xs2svg(2,"fig2.svg")
//xs2svg(3,"fig3.svg")
```

```
//xs2svg(4,"fig4.svg")
//xs2svg(5,"fig5.svg")
//xs2svg(6,"fig6.svg")
//xs2svg(7,"fig7.svg")
//xs2svg(8,"fig8.svg")
//xs2svg(9,"fig9.svg")
//xs2svg(10,"fig10.svg")
//xs2svg(11,"fig11.svg")
//xs2svg(12,"fig12.svg")
//xs2svg(13,"fig13.svg")
//xs2svg(14,"fig14.svg")
//xs2svg(15,"fig15.svg")
//xs2svg(16,"fig16.svg")
//xs2svg(17,"fig17.svg")
```

Appendix 7: Results of Simulation in Scilab (Direct route)

```
purge ratio = 0.909500

conditions and outputs at maximum Xoverall
Ratio(max)=0.150000
X1(max)=0.950000
S1(max)=0.909500
Xch4(max)=0.288756
Fmeoh(max)=1218.607718
Smeoh(max)=0.986996
Xoverall(max)=0.795665
Soverall(max)=0.932229
Fo2(max)=679.049296
Q1(max)=-5803.790470
Q2(max)=-5012.163196
Q3(max)=4543.008157
Q4(max)=-2622.975046
Q5(max)=2683.508834
Q6(max)=-2862.601850
Q7(max)=-405.881589
Q8(max)=-76555.363623
Q9(max)=133441.922477
Qrctr10(max)=179756.928854
Qc11(max)=101640.365268
Qb12(max)=-151654.190785
Qf13(max)=0.000000
Qf14(max)=47964.423730
Qturbine(max)=199.660490
Qexpander(max)=1319.562549
sumQ(max)=226632.413802

conditions and outputs which minimise the objective function
obj(min)=-1.923107
Ratio(min)=0.080000
X1(min)=0.950000
S1(min)=0.909500
Xch4(min)=0.154000
Fmeoh(min)=997.540803
Smeoh(min)=0.987012
```

```
Xoverall(min)=0.653183
Soverall(min)=0.929576
Fo2(min)=557.458444
Q1(min)=-5803.790470
Q2(min)=-4114.683147
Q3(min)=3729.535207
Q4(min)=-2153.304031
Q5(min)=2202.998614
Q6(min)=-2350.023159
Q7(min)=-743.750787
Q8(min)=-117942.861047
Q9(min)=166121.344364
Qrctr10(min)=147439.465196
Qc11(min)=82752.142026
Qb12(min)=-123542.088922
Qf13(min)=0.000000
Qf14(min)=39259.465430
Qturbine(min)=162.529163
Qexpander(min)=2417.147270
SumQ(min)=187434.125707

--> exec('C:\Users\HP\Downloads\Leila(CH42MEOH)km_parametric_v1-6.sce', -1)

purge ratio = 0.919000

conditions and outputs at maximum Xoverall
Ratio(max)=0.150000
X1(max)=0.950000
S1(max)=0.919000
Xch4(max)=0.288750
Fmeoh(max)=1241.491802
Smeoh(max)=0.987008
Xoverall(max)=0.810519
Soverall(max)=0.932329
Fo2(max)=691.738251
Q1(max)=-5803.790470
Q2(max)=-5105.822246
Q3(max)=4627.900411
Q4(max)=-2671.988883
Q5(max)=2733.653827
Q6(max)=-2916.093438
Q7(max)=-418.224133
Q8(max)=-78194.801909
Q9(max)=136052.458272
Qrctr10(max)=183115.559982
Qc11(max)=103624.836321
Qb12(max)=-154603.219498
Qf13(max)=0.000000
Qf14(max)=48865.733880
Qturbine(max)=203.563583
Qexpander(max)=1204.437817
sumQ(max)=230714.203515
```

```
conditions and outputs which minimise the objective function
obj(min)=-2.079586
Ratio(min)=0.080000
X1(min)=0.950000
S1(min)=0.919000
Xch4(min)=0.153998
Fmeoh(min)=1033.192713
Smeoh(min)=0.986995
Xoverall(min)=0.676062
Soverall(min)=0.930215
Fo2(min)=576.987351
Q1(min)=-5803.790470
Q2(min)=-4258.828898
Q3(min)=3860.188439
Q4(min)=-2228.738668
Q5(min)=2280.174153
Q6(min)=-2432.349268
Q7(min)=-778.627865
Q8(min)=-122451.994420
Q9(min)=172140.287790
Qrctr10(min)=152601.965968
Qc11(min)=85770.945871
Qb12(min)=-128039.321042
Qf13(min)=0.000000
Qf14(min)=40663.131340
Qturbine(min)=168.461861
Qexpander(min)=2241.548854
SumQ(min)=193733.053646

--> exec('C:\Users\HP\Downloads\Leila(CH42MEOH)km_parametric_v1-6.sce', -1)

purge ratio = 0.928500

conditions and outputs at maximum Xoverall
Ratio(max)=0.150000
X1(max)=0.950000
S1(max)=0.928500
Xch4(max)=0.288750
Fmeoh(max)=1265.192415
Smeoh(max)=0.987008
Xoverall(max)=0.825946
Soverall(max)=0.932382
Fo2(max)=704.904164
Q1(max)=-5803.790470
Q2(max)=-5203.001800
Q3(max)=4715.983637
Q4(max)=-2722.845077
Q5(max)=2785.683695
Q6(max)=-2971.595695
Q7(max)=-431.077953
Q8(max)=-79902.759147
Q9(max)=138768.481027
Qrctr10(max)=186601.338378
```

```
Qc11(max)=105688.193433
Qb12(max)=-157668.233344
Qf13(max)=0.000000
Qf14(max)=49799.256350
Qturbine(max)=207.622357
Qexpander(max)=1084.698193
sumQ(max)=234947.953585

conditions and outputs which minimise the objective function
obj(min)=-2.262502
Ratio(min)=0.080000
X1(min)=0.950000
S1(min)=0.928500
Xch4(min)=0.154000
Fmeoh(min)=1071.390812
Smeoh(min)=0.986986
Xoverall(min)=0.700608
Soverall(min)=0.930812
Fo2(min)=597.921146
Q1(min)=-5803.790470
Q2(min)=-4413.344329
Q3(min)=4000.240715
Q4(min)=-2309.599985
Q5(min)=2362.901612
Q6(min)=-2520.597823
Q7(min)=-816.161307
Q8(min)=-127306.543875
Q9(min)=178615.830894
Qrctr10(min)=158141.808096
Qc11(min)=89014.964980
Qb12(min)=-132870.571136
Qf13(min)=0.000000
Qf14(min)=42167.117400
Qturbine(min)=174.837803
Qexpander(min)=2052.917196
SumQ(min)=200490.009771

-->

--> exec('C:\Users\HP\Downloads\Leila(CH42MEOH)km_parametric_v1-6.sce', -1)

purge ratio = 0.938000

conditions and outputs at maximum Xoverall
Ratio(max)=0.150000
X1(max)=0.950000
S1(max)=0.938000
Xch4(max)=0.288747
Fmeoh(max)=1289.754934
Smeoh(max)=0.987008
Xoverall(max)=0.841971
Soverall(max)=0.932393
Fo2(max)=718.591181
```

```
Q1(max)=-5803.790470
Q2(max)=-5304.027694
Q3(max)=4807.553174
Q4(max)=-2775.714146
Q5(max)=2839.772892
Q6(max)=-3029.294717
Q7(max)=-444.500587
Q8(max)=-81686.961057
Q9(max)=141600.351230
Qrctr10(max)=190222.341765
Qc11(max)=107835.967522
Qb12(max)=-160857.203074
Qf13(max)=0.000000
Qf14(max)=50766.787170
Qturbine(max)=211.847794
Qexpander(max)=960.098531
sumQ(max)=239343.228334

conditions and outputs which minimise the objective function
obj(min)=-2.479925
Ratio(min)=0.080000
X1(min)=0.950000
S1(min)=0.938000
Xch4(min)=0.154000
Fmeoh(min)=1112.410283
Smeoh(min)=0.987011
Xoverall(min)=0.726994
Soverall(min)=0.931371
Fo2(min)=620.451534
Q1(min)=-5803.790470
Q2(min)=-4579.644458
Q3(min)=4150.974603
Q4(min)=-2396.628494
Q5(min)=2451.938590
Q6(min)=-2615.576984
Q7(min)=-856.670001
Q8(min)=-132557.394283
Q9(min)=185612.521989
Qrctr10(min)=164102.640013
Qc11(min)=92511.747006
Qb12(min)=-138076.214806
Qf13(min)=0.000000
Qf14(min)=43782.288310
Qturbine(min)=181.711408
Qexpander(min)=1849.843325
SumQ(min)=207757.745749


--> exec('C:\Users\HP\Downloads\Leila(CH42MEOH)km_parametric_v1-6.sce', -1)

purge ratio = 0.947500

conditions and outputs at maximum Xoverall
```

```
Ratio(max)=0.150000
X1(max)=0.950000
S1(max)=0.947500
Xch4(max)=0.288747
Fmeoh(max)=1315.225373
Smeoh(max)=0.987008
Xoverall(max)=0.858633
Soverall(max)=0.932355
Fo2(max)=732.813190
Q1(max)=-5803.790470
Q2(max)=-5409.002439
Q3(max)=4902.701936
Q4(max)=-2830.649734
Q5(max)=2895.976300
Q6(max)=-3089.249049
Q7(max)=-458.526312
Q8(max)=-83552.077835
Q9(max)=144555.483640
Qrctr10(max)=193987.300011
Qc11(max)=110074.323632
Qb12(max)=-164178.950746
Qf13(max)=0.000000
Qf14(max)=51770.150650
Qturbine(max)=216.252163
Qexpander(max)=830.285567
sumQ(max)=243910.227314

conditions and outputs which minimise the objective function
obj(min)=-2.744853
Ratio(min)=0.080000
X1(min)=0.950000
S1(min)=0.947500
Xch4(min)=0.154000
Fmeoh(min)=1156.512608
Smeoh(min)=0.987005
Xoverall(min)=0.755453
Soverall(min)=0.931819
Fo2(min)=644.740194
Q1(min)=-5803.790470
Q2(min)=-4758.922643
Q3(min)=4313.471757
Q4(min)=-2490.448704
Q5(min)=2547.924011
Q6(min)=-2717.968316
Q7(min)=-900.712545
Q8(min)=-138251.966831
Q9(min)=193188.721771
Qrctr10(min)=170526.532529
Qc11(min)=96288.024796
Qb12(min)=-143695.353199
Qf13(min)=0.000000
Qf14(min)=45518.969030
Qturbine(min)=189.135521
```

```
Qexpander(min)=1630.419868
SumQ(min)=215584.036575

-->

--> exec('C:\Users\HP\Downloads\Leila(CH42MEOH)km_parametric_v1-6.sce', -1)

purge ratio = 0.957000

conditions and outputs at maximum Xoverall
Ratio(max)=0.150000
X1(max)=0.950000
S1(max)=0.957000
Xch4(max)=0.288750
Fmeoh(max)=1341.646491
Smeoh(max)=0.987008
Xoverall(max)=0.875971
Soverall(max)=0.932260
Fo2(max)=747.597859
Q1(max)=-5803.790470
Q2(max)=-5518.130269
Q3(max)=5001.615040
Q4(max)=-2887.758724
Q5(max)=2954.403268
Q6(max)=-3151.575337
Q7(max)=-473.202558
Q8(max)=-85504.593712
Q9(max)=147643.079164
Qrctr10(max)=197904.974239
Qc11(max)=112409.711410
Qb12(max)=-167642.632218
Qf13(max)=0.000000
Qf14(max)=52811.045560
Qturbine(max)=220.848327
Qexpander(max)=694.894180
sumQ(max)=248658.887900

conditions and outputs which minimise the objective function
obj(min)=-3.077470
Ratio(min)=0.080000
X1(min)=0.950000
S1(min)=0.957000
Xch4(min)=0.154000
Fmeoh(min)=1204.077654
Smeoh(min)=0.987006
Xoverall(min)=0.786233
Soverall(min)=0.932164
Fo2(min)=671.008547
Q1(min)=-5803.790470
Q2(min)=-4952.813241
Q3(min)=4489.213555
Q4(min)=-2591.915912
Q5(min)=2651.732908
```

```
Q6(min)=-2828.705250
Q7(min)=-948.609959
Q8(min)=-144458.238374
Q9(min)=201432.113847
Qrctr10(min)=177475.453752
Qc11(min)=100383.707129
Qb12(min)=-149786.220178
Qf13(min)=0.000000
Qf14(min)=47392.166150
Qturbine(min)=197.189088
Qexpander(min)=1392.567112
SumQ(min)=224043.850157

--> exec('C:\Users\HP\Downloads\Leila(CH42MEOH)km_parametric_v1-6.sce', -1)

purge ratio = 0.957000

conditions and outputs at maximum Xoverall
Ratio(max)=0.150000
X1(max)=0.950000
S1(max)=0.957000
Xch4(max)=0.288750
Fmeoh(max)=1341.646491
Smeoh(max)=0.987008
Xoverall(max)=0.875971
Soverall(max)=0.932260
Fo2(max)=747.597859
Q1(max)=-5803.790470
Q2(max)=-5518.130269
Q3(max)=5001.615040
Q4(max)=-2887.758724
Q5(max)=2954.403268
Q6(max)=-3151.575337
Q7(max)=-473.202558
Q8(max)=-85504.593712
Q9(max)=147643.079164
Qrctr10(max)=197904.974239
Qc11(max)=112409.711410
Qb12(max)=-167642.632218
Qf13(max)=0.000000
Qf14(max)=52811.045560
Qturbine(max)=220.848327
Qexpander(max)=694.894180
sumQ(max)=248658.887900

conditions and outputs which minimise the objective function
obj(min)=-3.077470
Ratio(min)=0.080000
X1(min)=0.950000
S1(min)=0.957000
Xch4(min)=0.154000
Fmeoh(min)=1204.077654
Smeoh(min)=0.987006
```

```
Xoverall(min)=0.786233
Soverall(min)=0.932164
Fo2(min)=671.008547
Q1(min)=-5803.790470
Q2(min)=-4952.813241
Q3(min)=4489.213555
Q4(min)=-2591.915912
Q5(min)=2651.732908
Q6(min)=-2828.705250
Q7(min)=-948.609959
Q8(min)=-144458.238374
Q9(min)=201432.113847
Qrctr10(min)=177475.453752
Qc11(min)=100383.707129
Qb12(min)=-149786.220178
Qf13(min)=0.000000
Qf14(min)=47392.166150
Qturbine(min)=197.189088
Qexpander(min)=1392.567112
SumQ(min)=224043.850157

-->

-->

--> exec('C:\Users\HP\Downloads\Leila(CH42MEOH)km_parametric_v1-6.sce', -1)

purge ratio = 0.966500

conditions and outputs at maximum Xoverall
Ratio(max)=0.150000
X1(max)=0.950000
S1(max)=0.966500
Xch4(max)=0.288750
Fmeoh(max)=1369.058840
Smeoh(max)=0.987008
Xoverall(max)=0.894025
Soverall(max)=0.932098
Fo2(max)=763.005123
Q1(max)=-5803.790470
Q2(max)=-5631.853558
Q3(max)=5104.693454
Q4(max)=-2947.272618
Q5(max)=3015.290641
Q6(max)=-3216.526235
Q7(max)=-488.603146
Q8(max)=-87554.608438
Q9(max)=150875.968096
Qrctr10(max)=201984.461415
Qc11(max)=114849.131040
Qb12(max)=-171258.104503
Qf13(max)=0.000000
Qf14(max)=53891.087050
```

```
Qturbine(max)=225.650283
Qexpander(max)=553.541610
sumQ(max)=253599.064621

conditions and outputs which minimise the objective function
obj(min)=-3.514388
Ratio(min)=0.080000
X1(min)=0.950000
S1(min)=0.966500
Xch4(min)=0.154000
Fmeoh(min)=1255.500291
Smeoh(min)=0.987012
Xoverall(min)=0.819630
Soverall(min)=0.932369
Fo2(min)=699.516097
Q1(min)=-5803.790470
Q2(min)=-5163.231677
Q3(min)=4679.936129
Q4(min)=-2702.032499
Q5(min)=2764.390798
Q6(min)=-2948.881744
Q7(min)=-1001.042347
Q8(min)=-151258.208860
Q9(min)=210444.923275
Qrctr10(min)=185016.521381
Qc11(min)=104843.227869
Qb12(min)=-156413.269375
Qf13(min)=0.000000
Qf14(min)=49417.494180
Qturbine(min)=205.960168
Qexpander(min)=1133.743090
SumQ(min)=233215.739918

--> exec('C:\Users\HP\Downloads\Leila(CH42MEOH)km_parametric_v1-6.sce', -1)

purge ratio = 0.976000

conditions and outputs at maximum Xoverall
Ratio(max)=0.150000
X1(max)=0.950000
S1(max)=0.976000
Xch4(max)=0.288750
Fmeoh(max)=1397.505282
Smeoh(max)=0.987008
Xoverall(max)=0.912841
Soverall(max)=0.931853
Fo2(max)=779.063319
Q1(max)=-5803.790470
Q2(max)=-5750.381476
Q3(max)=5212.126767
Q4(max)=-3009.300880
Q5(max)=3078.750409
Q6(max)=-3284.221205
```

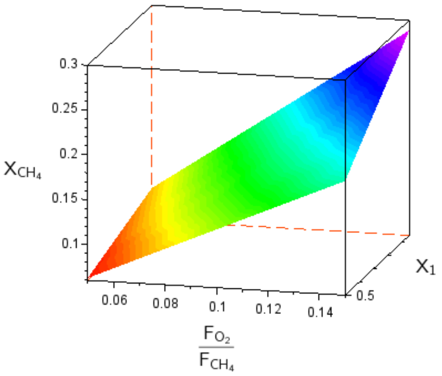
```
Q7(max)=-504.792596
Q8(max)=-89710.698881
Q9(max)=154266.030972
Qrctr10(max)=206236.174709
Qc11(max)=117400.835071
Qb12(max)=-175036.918494
Qf13(max)=0.000000
Qf14(max)=55011.985890
Qturbine(max)=230.674560
Qexpander(max)=405.755593
sumQ(max)=258742.229970

conditions and outputs which minimise the objective function
obj(min)=-4.130399
Ratio(min)=0.080000
X1(min)=0.950000
S1(min)=0.976000
Xch4(min)=0.153999
Fmeoh(min)=1311.193106
Smeoh(min)=0.987003
Xoverall(min)=0.855997
Soverall(min)=0.932359
Fo2(min)=730.557819
Q1(min)=-5803.790470
Q2(min)=-5392.355212
Q3(min)=4887.612944
Q4(min)=-2821.937875
Q5(min)=2887.063386
Q6(min)=-3079.741301
Q7(min)=-1058.791334
Q8(min)=-158756.475339
Q9(min)=220354.582340
Qrctr10(min)=193225.563755
Qc11(min)=109719.230705
Qb12(min)=-163652.113958
Qf13(min)=0.000000
Qf14(min)=51611.302280
Qturbine(min)=215.553401
Qexpander(min)=850.844676
SumQ(min)=243186.547998

--> exec('C:\Users\HP\Downloads\Leila(CH42MEOH)km_parametric_v1-6.sce', -1)

purge ratio = 0.985500

conditions and outputs at maximum Xoverall
Ratio(max)=0.150000
X1(max)=0.950000
S1(max)=0.985500
Xch4(max)=0.288750
Fmeoh(max)=1427.025899
Smeoh(max)=0.987007
Xoverall(max)=0.932469
```

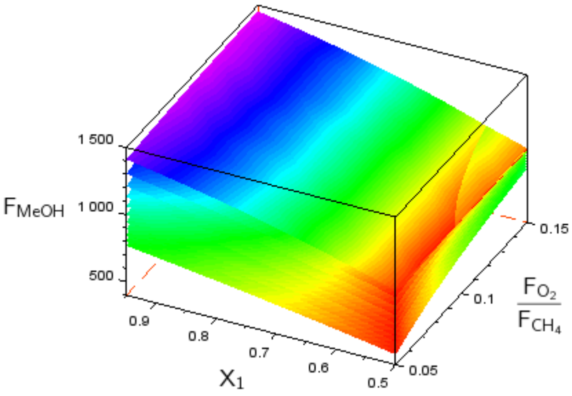
```
Soverall(max)=0.931507
Fo2(max)=795.815207
Q1(max)=-5803.790470
Q2(max)=-5874.029639
Q3(max)=5324.201053
Q4(max)=-3074.008678
Q5(max)=3144.951553
Q6(max)=-3354.840506
Q7(max)=-521.836783
Q8(max)=-91984.265988
Q9(max)=157828.224671
Qrctr10(max)=210671.383198
Qc11(max)=120074.229571
Qb12(max)=-178992.118298
Qf13(max)=0.000000
Qf14(max)=56175.348940
Qturbine(max)=235.940047
Qexpander(max)=251.011291
sumQ(max)=264100.399963

conditions and outputs which minimise the objective function
obj(min)=-5.116889
Ratio(min)=0.080000
X1(min)=0.950000
S1(min)=0.985500
Xch4(min)=0.154000
Fmeoh(min)=1371.665716
Smeoh(min)=0.987003
Xoverall(min)=0.895750
Soverall(min)=0.932074
Fo2(min)=764.472855
Q1(min)=-5803.790470
Q2(min)=-5642.687108
Q3(min)=5114.512947
Q4(min)=-2952.942052
Q5(min)=3021.090916
Q6(min)=-3222.713611
Q7(min)=-1122.885407
Q8(min)=-167091.497005
Q9(min)=231330.739482
Qrctr10(min)=202201.034344
Qc11(min)=115082.138634
Qb12(min)=-171603.308820
Qf13(min)=0.000000
Qf14(min)=53993.803620
Qturbine(min)=226.109012
Qexpander(min)=540.009568
SumQ(min)=254069.614051

--> exec('C:\Users\HP\Downloads\Leila(CH42MEOH)km_parametric_v1-6.sce', -1)

purge ratio = 0.985500
```

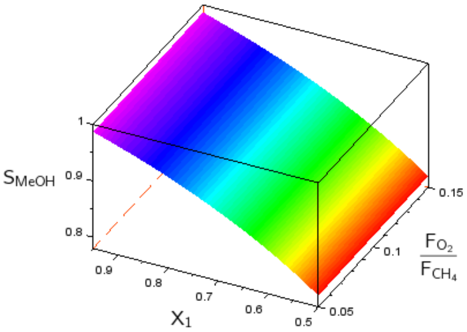
```
conditions and outputs at maximum Xoverall
Ratio(max)=0.150000
X1(max)=0.950000
S1(max)=0.985500
Xch4(max)=0.288750
Fmeoh(max)=1427.025899
Smeoh(max)=0.987007
Xoverall(max)=0.932469
Soverall(max)=0.931507
Fo2(max)=795.815207
Q1(max)=-5803.790470
Q2(max)=-5874.029639
Q3(max)=5324.201053
Q4(max)=-3074.008678
Q5(max)=3144.951553
Q6(max)=-3354.840506
Q7(max)=-521.836783
Q8(max)=-91984.265988
Q9(max)=157828.224671
Qrctr10(max)=210671.383198
Qc11(max)=120074.229571
Qb12(max)=-178992.118298
Qf13(max)=0.000000
Qf14(max)=56175.348940
Qturbine(max)=235.940047
Qexpander(max)=251.011291
sumQ(max)=264100.399963

conditions and outputs which minimise the objective function
obj(min)=-5.116889
Ratio(min)=0.080000
X1(min)=0.950000
S1(min)=0.985500
Xch4(min)=0.154000
Fmeoh(min)=1371.665716
Smeoh(min)=0.987003
Xoverall(min)=0.895750
Soverall(min)=0.932074
Fo2(min)=764.472855
Q1(min)=-5803.790470
Q2(min)=-5642.687108
Q3(min)=5114.512947
Q4(min)=-2952.942052
Q5(min)=3021.090916
Q6(min)=-3222.713611
Q7(min)=-1122.885407
Q8(min)=-167091.497005
Q9(min)=231330.739482
Qrctr10(min)=202201.034344
Qc11(min)=115082.138634
Qb12(min)=-171603.308820
Qf13(min)=0.000000
Qf14(min)=53993.803620
```

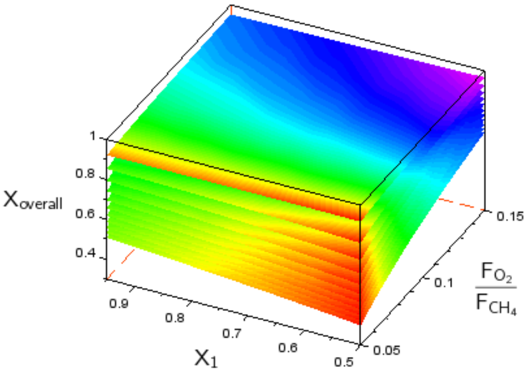
```
Qturbine(min)=226.109012
Qexpander(min)=540.009568
SumQ(min)=254069.614051

--> exec('C:\Users\HP\Downloads\Leila(CH42MEOH)km_parametric_v1-6.sce', -1)

purge ratio = 0.995000

conditions and outputs at maximum Xoverall
Ratio(max)=0.150000
X1(max)=0.500000
S1(max)=0.995000
Xch4(max)=0.187499
Fmeoh(max)=937.334778
Smeoh(max)=0.799976
Xoverall(max)=0.966249
Soverall(max)=0.590465
Fo2(max)=1269.926078
Q1(max)=-5803.790470
Q2(max)=-9373.512038
Q3(max)=8496.120335
Q4(max)=-4905.364651
Q5(max)=5018.572097
Q6(max)=-5353.503437
Q7(max)=-2057.719912
Q8(max)=-312929.202301
Q9(max)=398740.326957
Qrctr10(max)=418467.913517
Qc11(max)=119435.075717
Qb12(max)=-172184.255088
Qf13(max)=0.000000
Qf14(max)=36757.156060
Qturbine(max)=276.073744
Qexpander(max)=350.884510
sumQ(max)=474934.775040

conditions and outputs which minimise the objective function
obj(min)=-7.131546
Ratio(min)=0.070000
X1(min)=0.950000
S1(min)=0.995000
Xch4(min)=0.134750
Fmeoh(min)=1431.281885
Smeoh(min)=0.987012
Xoverall(min)=0.935311
Soverall(min)=0.931446
Fo2(min)=798.245099
Q1(min)=-5803.790470
Q2(min)=-5891.965027
Q3(min)=5340.457630
Q4(min)=-3083.394661
Q5(min)=3154.554148
Q6(min)=-3365.083962
```

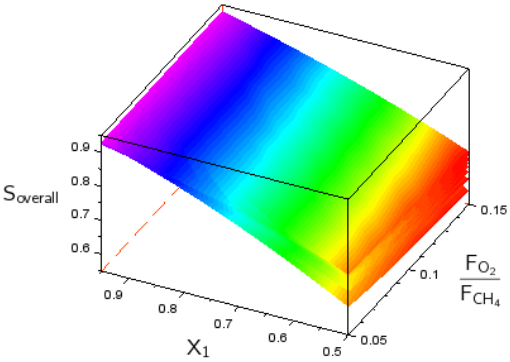
```
Q7(min)=-1391.143521
Q8(min)=-201068.940404
Q9(min)=268171.635435
Qrctr10(min)=211110.286558
Qc11(min)=120463.307771
Qb12(min)=-179567.335276
Qf13(min)=0.000000
Qf14(min)=56343.094820
Qturbine(min)=236.706543
Qexpander(min)=228.550502
SumQ(min)=264876.940087
```

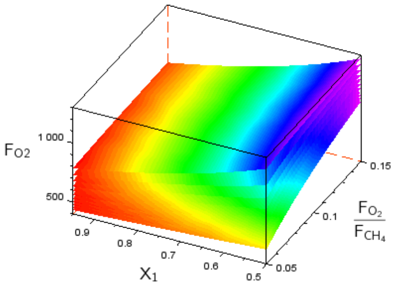


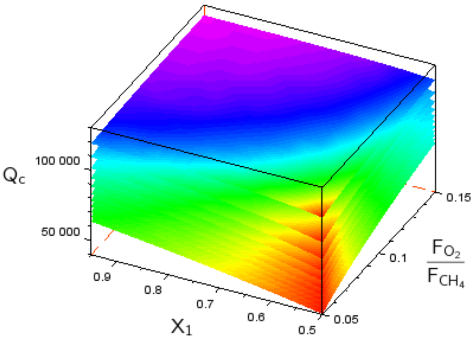


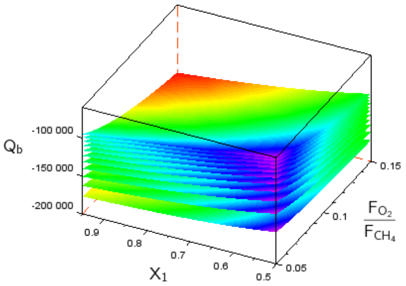


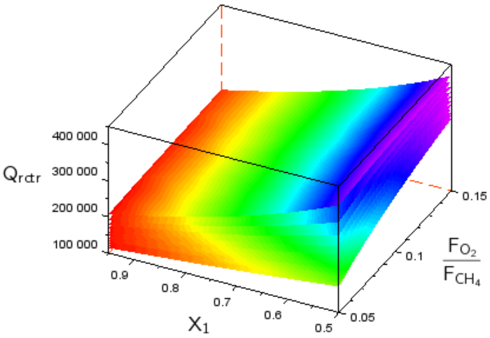


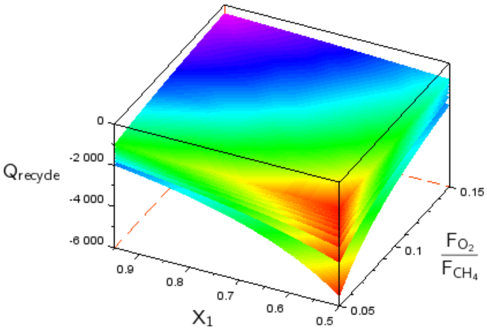

$S_{overall}$
0.9
0.8
0.7
0.6
0.9
0.8
0.7
0.6
0.5
X_1
0.15
0.1
0.05
$\frac{F_{O_2}}{F_{CH_4}}$

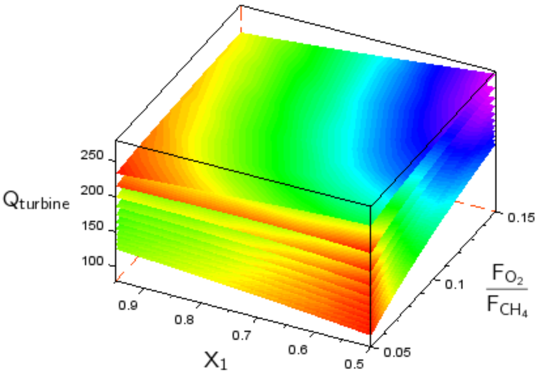

F_{O2}
1 000
500
0.9
0.8
0.7
0.6
0.5
X_1
0.15
0.1
0.05
$\frac{F_{O_2}}{F_{CH_4}}$

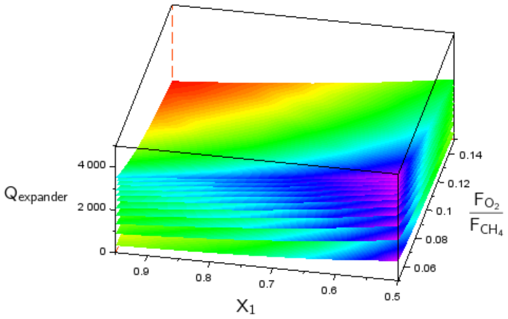

Q_c
100 000
50 000
0.9
0.8
0.7
0.6
0.5
X_1
0.15
0.1
0.05
$\frac{F_{O_2}}{F_{CH_4}}$

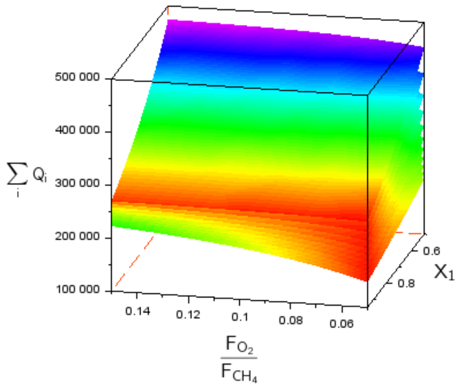

Q_b
-100 000
-150 000
-200 000
0.9
0.8
0.7
0.6
0.5
X_1
0.15
0.1
0.05
$\frac{F_{O_2}}{F_{CH_4}}$


Q_{rctr}
400 000
300 000
200 000
100 000
0.9
0.8
0.7
0.6
0.5
X_1
0.15
0.1
0.05
$\frac{F_{O_2}}{F_{CH_4}}$


$Q_{recycle}$
0
-2 000
-4 000
-6 000
0.9
0.8
0.7
0.6
0.5
X_1
0.15
0.1
0.05
$\frac{F_{O_2}}{F_{CH_4}}$


$Q_{turbine}$
250
200
150
100
0.9
0.8
0.7
0.6
0.5
X_1
0.15
0.1
0.05
$\frac{F_{O_2}}{F_{CH_4}}$


$Q_{expander}$
4 000
2 000
0
0.9
0.8
0.7
0.6
0.5
X_1
0.14
0.12
0.1
0.08
0.06
$\frac{F_{O_2}}{F_{CH_4}}$



Appendix 8: Calculation of Carbon efficiencies

- **Syngas route:**

$$C_E=\frac{\text{molar flow of } CH_3OH}{\text{molar flow of carbon contents in natural gas for the plant}}$$

$$C_E=\frac{1360.21}{1642.9}= 0.827932*100 = 82,7\%$$

- **Direct route:**

$$C_E=\frac{\text{molar flow of } CH_3OH}{\text{molar flow of carbon contents in natural gas for the plant}}$$

$$C_E=\frac{1302.84 \text{ mol/s}}{1642.9 \text{ mol/s}} = 0.793012*100= 79,3\%$$

Appendix 9: Calculation of energy requirement

- **Syngas route**

Stream	**Q12**	**DH**	**Q13**	**Q14**	**Qreactor15**	**Qreactor16**	**Q18**	**Unit**
DH		25832.3						
TemperatureHigh	79.85			200	250.268	250.268	226.516	°C
TemperatureLow	60			57.3892	200	200	90	°C
Work	-608.63	25832.3	-369.942	-125647	0	100802	136579	kW
Stream	**Q6**	**Q7**	**Q8**	**Q9**	**Q10ATR**	**QF11**	**Q5**	**Unit**
DH								
TemperatureHigh		400		600	1002.79	60		°C
TemperatureLow		25.4159		264.471	1002.79	60		°C
Work	-274.171	-131628	-5803.79	-73575.2	0	320503	-3872.33	kW
Stream	**Qf17**	**Q17**	**Qturbine**	**QF18**	**QB20**	**QC19**	**QF21**	**Unit**
DH								
TemperatureHigh	50			40	109.93	72.13	40	°C
TemperatureLow	50			40	109.93	72.13	40	°C
Work	73446.8	-3770.9	223.401	1519.23	-165049	106390	55033.7	kW
Stream	**Qexpander2**	**Qexpander1**	**Q1**	**Q2**	**Q3**	**Q4**		**Unit**
DH								
TemperatureHigh				178.892		211.321		°C
TemperatureLow				25		25		°C
Work	1939.23	262.76	-4046.38	4069.59	-4913.73	5013.48		kW
Qtotal (Kw)	312055.4 kW							
Qtotal (kJ/mol)	=312055.4(kJ/s) /1360.21 (mol/s) = 229.4171kJ/mol							

- **Direct route**

The best results that minimse the objective fucntion

	1	2	3	4	5	
Ratio	0.07	0.08	0.08	0.08	0.08	
X1	0.95	0.95	0.95	0.95	0.95	
S1	0.9	0.9095	0.919	0.9285	0.938	
X_{ch4}	0.13475	0.154	0.153998	0.154	0.154	
S_{CH3OH}	0.986983	0.987012	0.986995	0.700608	0.987011	
$X_{overall}$	0.596846	0.653183	0.676062	0.700608	0.726994	
$S_{overall}$	0.927514	0.929576	0.930215	0.930812	0.931371	
SumQ	171900.4895	187434.1	193733.0536	200490	207757.7	
	6	7	8	9	10	11
Ratio	0.08	0.08	0.08	0.08	0.08	0.07
X1	0.95	0.95	0.95	0.95	0.95	0.95
S1	0.9475	0.957	0.9665	0.976	0.9855	0.995
X_{ch4}	0.154	0.154	0.154	0.153999	0.154	0.13475
S_{CH3OH}	0.987005	0.987006	0.987012	0.987003	0.987003	0.987012
$X_{overall}$	0.755453	0.786233	0.81963	0.855997	0.89575	0.935311
$S_{overall}$	0.931819	0.932164	0.932369	0.932359	0.932074	0.931446
SumQ	215584.0366	224043.9	233215.7399	243186.5	254069.6	264876.9

Qmin= 171900.4895 Kw

Qmin (Kj/mol)= 171900.4895(kJ/mol)/1302.84 mol/s= 131.9429013 mol/s

Appendix 10: Simulation results

- **Syngas route**

Stream	Water(out)	MeOH(out)	purge(out)2	purge(out)3
Pressure (atm)	1	1	1	2
Temperature (°C)	101.373	40	40	40
Flow rate (mol/s)	290.216	1360.21	4.75102	40.1451
Mole frac Methane	0	4.58E-05	0.0557237	0.201511
Mole frac Carbon monoxide	0	1.35E-07	0.000677224	0.00916467
Mole frac Carbon dioxide	0	0.00429505	0.601263	0.524387
Mole frac Hydrogen	3.36E-20	6.89E-07	0.00575621	0.114537
Mole frac Oxygen	0	0	0	0
Mole frac Water	1	0.000213493	2.35E-05	0.00901327
Mole frac Methanol	6.66E-08	0.995445	0.336557	0.141386

Stream	Purge(out)	5	1	2
Pressure (atm)	47.5975	50	4	4
Temperature (°C)	50	173.704	178.892	25
Flow rate (mol/s)	438.093	878.951	878.951	878.951
Mole frac Methane	0.215179	0	0	0
Mole frac Carbon monoxide	0.0369508	0	0	0
Mole frac Carbon dioxide	0.0941377	0	0	0
Mole frac Hydrogen	0.639433	0	0	0
Mole frac Oxygen	0	1	1	1
Mole frac Water	0.000860948	0	0	0
Mole frac Methanol	0.0134382	0	0	0
Stream	**3**	**4**	**33**	**31**
Pressure (atm)	16	16	50	47.5975
Temperature (°C)	211.321	25	55.6261	50
Flow rate (mol/s)	878.951	878.951	21466.5	438.093
Mole frac Methane	0	0	0.215179	0.215179
Mole frac Carbon monoxide	0	0	0.0369508	0.0369508
Mole frac Carbon dioxide	0	0	0.0941377	0.0941377
Mole frac Hydrogen	0	0	0.639433	0.639433
Mole frac Oxygen	1	1	0	0
Mole frac Water	0	0	0.000860948	0.000860948
Mole frac Methanol	0	0	0.0134382	0.0134382
Stream	**34**	**35**	**36**	**MeOH(dist)**
Pressure (atm)	47.5975	2	2	1
Temperature (°C)	50	48.5519	40	64.4763
Flow rate (mol/s)	1695.32	1695.32	1655.17	1364.96
Mole frac Methane	0.00496469	0.00496469	0.000197596	0.000239608
Mole frac Carbon monoxide	0.000219025	0.000219025	2.05E-06	2.49E-06
Mole frac Carbon dioxide	0.0175485	0.0175485	0.0052555	0.00637292
Mole frac Hydrogen	0.00272893	0.00272893	1.71E-05	2.07E-05
Mole frac Oxygen	0	0	0	0
Mole frac Water	0.171572	0.171572	0.175514	0.000212832
Mole frac Methanol	0.802967	0.802967	0.819013	0.993151
Stream	**MeOH**	**35**	**36**	**MeOH(dist)**
Pressure (atm)	1	2	2	1
Temperature (°C)	40	48.5519	40	64.4763
Flow rate (mol/s)	1360.21	1695.32	1655.17	1364.96
Mole frac Methane	4.58E-05	0.00496469	0.000197596	0.000239608
Mole frac Carbon monoxide	1.35E-07	0.000219025	2.05E-06	2.49E-06

Mole frac Carbon dioxide	0.00429505	0.0175485	0.0052555	0.00637292
Mole frac Hydrogen	6.89E-07	0.00272893	1.71E-05	2.07E-05
Mole frac Oxygen	0	0	0	0
Mole frac Water	0.000213493	0.171572	0.175514	0.000212832
Mole frac Methanol	0.995445	0.802967	0.819013	0.993151
Stream	Water	24	syngas	25
Pressure (atm)	1	49	49	50
Temperature (^{o}C)	101.373	63.5546	63.5546	66.0968
Flow rate (mol/s)	290.216	4867.78	4867.78	4867.78
Mole frac Methane	0	0.0210949	0.0210949	0.0210949
Mole frac Carbon monoxide	0	0.229174	0.229174	0.229174
Mole frac Carbon dioxide	0	0.0696748	0.0696748	0.0696748
Mole frac Hydrogen	3.36E-20	0.675315	0.675315	0.675315
Mole frac Oxygen	0	0	0	0
Mole frac Water	1	0.00474134	0.00474134	0.00474134
Mole frac Methanol	6.66E-08	0	0	0
Stream	26	27	28	29
Pressure (atm)	50	50	47.5975	47.5975
Temperature (^{o}C)	57.3891	200	226.516	90
Flow rate (mol/s)	26334.3	26334.3	23600	23600
Mole frac Methane	0.179304	0.179304	0.200078	0.200078
Mole frac Carbon monoxide	0.0724824	0.0724824	0.0343122	0.0343122
Mole frac Carbon dioxide	0.0896158	0.0896158	0.0886359	0.0886359
Mole frac Hydrogen	0.646066	0.646066	0.593695	0.593695
Mole frac Oxygen	0	0	0	0
Mole frac Water	0.00157822	0.00157822	0.0131241	0.0131241
Mole frac Methanol	0.0109542	0.0109542	0.0701546	0.0701546
Stream	30	32	12	13
Pressure (atm)	47.5975	47.5975	50	50
Temperature (^{o}C)	50	50	264.471	600
Flow rate (mol/s)	21904.6	21466.5	4821.91	4821.91
Mole frac Methane	0.215179	0.215179	0.340716	0.340716
Mole frac Carbon monoxide	0.0369508	0.0369508	0	0
Mole frac Carbon dioxide	0.0941377	0.0941377	0	0
Mole frac Hydrogen	0.639433	0.639433	0	0
Mole frac Oxygen	0	0	0.182283	0.182283
Mole frac Water	0.000860948	0.000860948	0.477002	0.477002
Mole frac Methanol	0.0134382	0.0134382	0	0
Stream	14	15	16	18
Pressure (atm)	50	49	49	49
Temperature (^{o}C)	1002.79	60	60	60

Flow rate (mol/s)	7023.38	4952.57	2070.81	990.514
Mole frac Methane	0.0146212	0.0207337	2.49E-06	0.0207337
Mole frac Carbon monoxide	0.158838	0.22525	4.44E-06	0.22525
Mole frac Carbon dioxide	0.0604599	0.0856024	0.000328518	0.0856024
Mole frac Hydrogen	0.468059	0.663753	3.44E-05	0.663753
Mole frac Oxygen	0	0	0	0
Mole frac Water	0.298022	0.00466017	0.99963	0.00466017
Mole frac Methanol	0	0	0	0
Stream	20	20'	19	21
Pressure (atm)	49	49	49	49
Temperature (^{o}C)	79.85	79.85	60	79.85
Flow rate (mol/s)	990.514	990.514	3962.06	905.724
Mole frac Methane	0.0207337	0.0207337	0.0207337	0.0226747
Mole frac Carbon monoxide	0.22525	0.22525	0.22525	0.246337
Mole frac Carbon dioxide	0.0856024	0.0856024	0.0856024	0
Mole frac Hydrogen	0.663753	0.663753	0.663753	0.725892
Mole frac Oxygen	0	0	0	0
Mole frac Water	0.00466017	0.00466017	0.00466017	0.00509643
Mole frac Methanol	0	0	0	0
Stream	22	23	H2O	CH4
Pressure (atm)	49	49	1	20
Temperature (^{o}C)	63.5546	63.5546	25	50
Flow rate (mol/s)	4867.78	4867.78	2300.06	1642.9
Mole frac Methane	0.0210949	0.0210949	0	1
Mole frac Carbon monoxide	0.229174	0.229174	0	0
Mole frac Carbon dioxide	0.0696748	0.0696748	0	0
Mole frac Hydrogen	0.675315	0.675315	0	0
Mole frac Oxygen	0	0	0	0
Mole frac Water	0.00474134	0.00474134	1	0
Mole frac Methanol	0	0	0	0
Stream	O2	6	9	10
Pressure (atm)	1.23365	50.3331	50	50
Temperature (^{o}C)	25	25.4159	144.773	144.773
Flow rate (mol/s)	878.951	2300.06	1642.9	1642.9
Mole frac Methane	0	0	1	1
Mole frac Carbon monoxide	0	0	0	0
Mole frac Carbon dioxide	0	0	0	0
Mole frac Hydrogen	0	0	0	0
Mole frac Oxygen	1	0	0	0
Mole frac Water	0	1	0	0
Mole frac Methanol	0	0	0	0

Stream	7	11
Pressure (atm)	50.3331	50
Temperature (^{o}C)	400	281.027
Flow rate (mol/s)	2300.06	3942.96
Mole frac Methane	0	0.416667
Mole frac Carbon monoxide	0	0
Mole frac Carbon dioxide	0	0
Mole frac Hydrogen	0	0
Mole frac Oxygen	0	0
Mole frac Water	1	0.583333
Mole frac Methanol	0	0

- **Direct route**

Stream	**CH4**	**9**	**8**	**13**	**14**
Pressure (atm)	20	50	50	50	50
Temperature (^{o}C)	50	66.4907	62.0979	400	400
Flow rate (mol/s)	1642.9	18875.9	17976.7	18156.5	18156.5
Mole frac Methane	1	0.79393	0.833642	0.741196	0.741196
Mole frac Carbon monoxide	0	0	0	0	0
Mole frac Carbon dioxide	0	0.141359	0.14843	0.151912	0.151912
Mole frac Hydrogen	0	0	0	0	0
Mole frac Oxygen	0	0.0476358	0	1.57E-18	1.57E-18
Mole frac Water	0	0.00136086	0.00142893	0.0113194	0.0113194
Mole frac Methanol	0	0.0157137	0.0164997	9.56E-02	9.56E-02
Stream	10	11	O2feed	3.1	4.1
Pressure (atm)	50	50	1.23365	7	7
Temperature (^{o}C)	66.4907	66.4907	25	268.411	50
Flow rate (mol/s)	18875.9	18875.9	899.167	899.167	899.167
Mole frac Methane	0.79393	0.79393	0	0	0
Mole frac Carbon monoxide	0	0	0	0	0
Mole frac Carbon dioxide	0.14136	0.141359	0	0	0
Mole frac Hydrogen	0	0	0	0	0
Mole frac Oxygen	0.04764	0.0476358	1	1	1
Mole frac Water	0.00136	0.00136086	0	0	0

Mole frac Methanol	0.01571	0.0157137	0	0	0
Stream	15	16	18	RECYCLE	24
Pressure (atm)	48	48	48	48	50
Temperature (^{o}C)	399.803	50	50	50	54.0081
Flow rate (mol/s)	18156.5	18156.5	16415.9	16333.8	16333.8
Mole frac Methane	0.741196	0.741196	0.816909	0.816909	0.816909
Mole frac Carbon monoxide	0	0	0	0	0
Mole frac Carbon dioxide	0.151912	0.151912	0.163359	0.163359	0.163359
Mole frac Hydrogen	0	0	0	0	0
Mole frac Oxygen	1.57E-18	1.57E-18	0	0	0
Mole frac Water	0.0113194	0.0113194	0.001573	0.001573	0.001573
Mole frac Methanol	9.56E-02	9.56E-02	0.018159	0.018159	0.018159
Stream	10	11	O2feed	3.1	4.1
Pressure (atm)	50	50	1.2337	7	7
Temperature (^{o}C)	66.4907	66.4907	25	268.411	50
Flow rate (mol/s)	18875.9	18875.9	899.17	899.167	899.167
Mole frac Methane	0.79393	0.79393	0	0	0
Mole frac Carbon monoxide	0	0	0	0	0
Mole frac Carbon dioxide	0.14136	0.141359	0	0	0
Mole frac Hydrogen	0	0	0	0	0
Mole frac Oxygen	0.04764	0.0476358	1	1	1
Mole frac Water	0.00136	0.00136086	0	0	0
Mole frac Methanol	0.01571	0.0157137	0	0	0
Stream	6.1	PURGE	22	17	19
Pressure (atm)	18	48	2	48	2
Temperature (^{o}C)	50	50	-73.221	50	42.0131
Flow rate (mol/s)	899.167	82.0794	82.079	1740.65	1740.65
Mole frac Methane	0	0.816909	0.8169	0.027153	0.027153
Mole frac Carbon monoxide	0	0	0	0	0
Mole frac Carbon dioxide	0	0.163359	0.1634	0.043954	0.043954
Mole frac Hydrogen	0	0	0	0	0
Mole frac Oxygen	1	0	0	1.63E-17	1.63E-17
Mole frac Water	0	0.00157265	0.0016	0.10324	0.10324
Mole frac Methanol	0	0.0181592	0.0182	0.825654	8.26E-01
Stream	MeOH	FMeoh	O2feed(in)	water	21
Pressure (atm)	1	1	50	1	1
Temperature (^{o}C)	62.583	50	191.118	101.373	50
Flow rate (mol/s)	1561.13	1302.84	899.167	179.525	1302.84
Mole frac Methane	0.030275	0.00044619	0	0	0.000446

Mole frac Carbon monoxide	0	0	0	0	0
Mole frac Carbon dioxide	0.049008	0.0028246	0	0	0.002825
Mole frac Hydrogen	0	0	0	0	0
Mole frac Oxygen	1.82E-17	1.41E-19	1	0	1.41E-19
Mole frac Water	0.0001151	0.0001333	0	1	0.000133
Mole frac Methanol	9.21E-01	9.97E-01	0.00E+00	7.01E-08	0.996596

Stream	20	23
Pressure (atm)	1	2
Temperature (^{o}C)	50	-73.221
Flow rate (mol/s)	258.284	82.0794
Mole frac Methane	0.180738	0.816909
Mole frac Carbon monoxide	0	0
Mole frac Carbon dioxide	0.281968	0.163359
Mole frac Hydrogen	0	0
Mole frac Oxygen	1.09E-16	0
Mole frac Water	2.33E-05	0.00157265
Mole frac Methanol	5.37E-01	1.82E-02