

Annotation sheet

Name: Farid

Surname: Ismayilov

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Supervisor: Ing. Lukas Kratky, Ph D.

Submitter: Czech Technical University in Prague. Faculty of Mechanical Engineering, Department of Process Engineering

Annotation - Czech: Diplomová práce se zabývá technologií konverze CO₂ na methanol. V její první části jsou zmíněny technologické možnosti konverze odpadního CO₂ na cenné chemické látky. Důraz je kladen zejména na využití odpadního CO₂ k výrobě metanolu. V praktické části jsou pak tyto teoretické informace využity k vytvoření základní technicko-ekonomické studie technologie CO₂ to methanol.

Annotation – English: The diploma thesis deals with the technology of conversion of CO₂ to methanol. In the first part the technological possibilities of conversion of waste CO₂ to valuable chemical substances mentioned. Emphasis is placed in particular on the use of waste CO₂ for the production of methanol. In the practical part, this theoretical information is used to create the basic technical and economical study of CO₂ to methanol technology.

Keywords: Methanol, Methanol Synthesis, hydrogenation, CO₂ utilization

Utilization: Techno-Economical study

Declaration

I confirm that the diploma work was disposed by myself and independently, under leading of my thesis supervisor. I stated all sources of documents and literature

Prague.....

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1.Introduction

1.1.1 Global CO₂ emission and future

Carbon dioxide is the main anthropogenic greenhouse gas, and its emissions increased significantly during the last decades. At present, the carbon cycle, where CO₂ is the major factor, does not work in a balanced way. In 2015, this yielded a total amount in globally emitted CO₂ emitted of 36.2 billion tonnes – virtually the same level as in 2014, and keeping the current trends, they are likely to double by 2050. About 40 % of global anthropogenic CO₂ comes from thermoelectric plants fueled by natural gas and coal. [1]

Global CO₂ emissions per region from fossil-fuel use and cement production

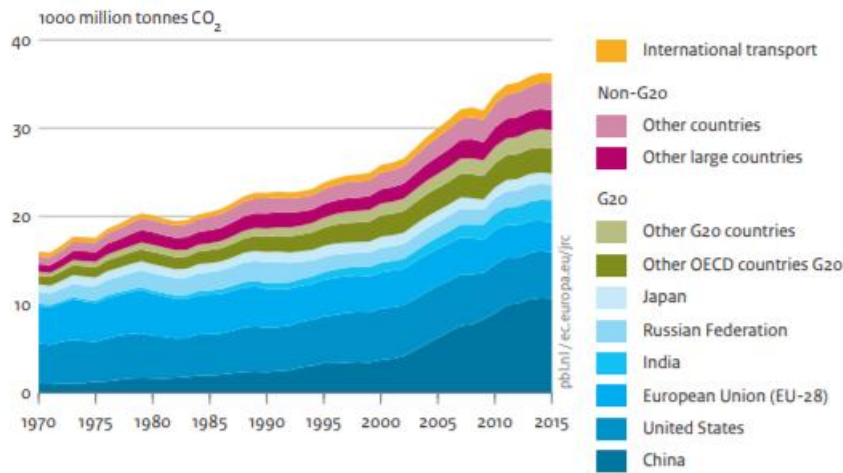


Figure 1. CO₂ Emission Globally[1]

The reduction of greenhouse gas emissions is an ever-increasing challenge for production units and power plants in view of global warming concerns. Carbon dioxide capturing from petrochemical process streams and flares has been recognized as one of the several strategies necessary for mitigating the emission of greenhouse gases into the atmosphere. To keep greenhouse gases at manageable level, large decrease in CO₂ emissions through separation and utilization will be required. As a result, carbon dioxide emission potential has become an important factor in technology since it was set to be valuable input parameters for further utilization. [2]

1.1.2 Carbon Capturing and Purification

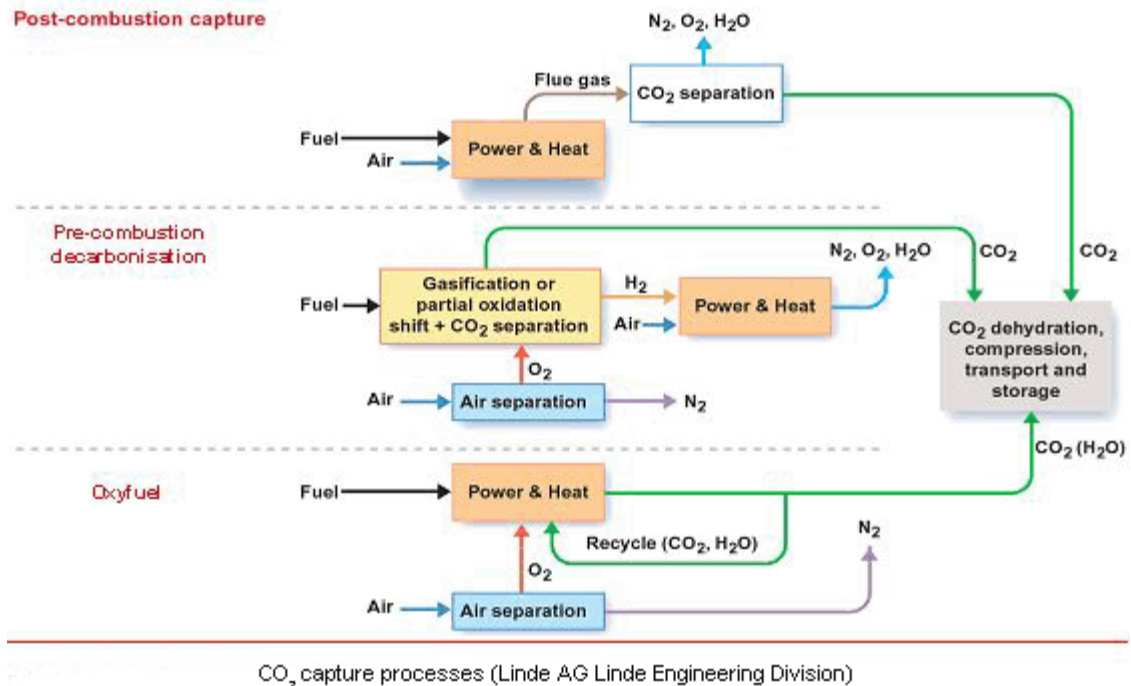
This chapter is taken as reference from an article [3]

Carbon dioxide is released by the burning of fossil fuels, and is a major contributor to global warming. Carbon capture and storage is the process of collecting waste carbon dioxide from fossil fuel power plants and storing it in a way that prevents it from entering the atmosphere. The process has been touted as a means of reducing fossil fuel's contribution to global warming.

Carbon capture and storage (CCS) is a range of technologies that hold the promise of trapping up to 90% of the carbon dioxide emissions from power stations and industrial sites. It involves collecting, transporting and then burying the CO₂ so that it does not escape into the atmosphere and contribute to climate change.

There are three main techniques: the post-combustion process involves scrubbing the power plant's exhaust gas using chemicals. Pre-combustion CCS takes place before the fuel is placed in the furnace by first converting coal into a clean-burning gas and stripping out the CO₂ released by the process. The third method, oxyfuel, burns the coal in an atmosphere with a higher concentration of pure oxygen, resulting in an exhaust gas that is almost pure CO₂.

Once the CO₂ has been trapped, it is liquefied, transported – sometimes for several hundred miles – and buried, either in suitable geological formations, deep underground saline aquifers or disused oil fields. The last method is often used in a process called "enhanced oil recovery", where CO₂ is pumped into an oil field to force out the remaining pockets of oil that would otherwise prove difficult



to extract.

Figure 2. Carbon Capture methods[26]

Post-combustion: In the post-combustion method, CO₂ is separated from the flue gas of the power station by bubbling the gas through an absorber column packed with liquid solvents (such as ammonia) that preferentially take out the CO₂. In the most commonly-used techniques, once the chemicals in the absorber column become saturated, a stream of superheated steam at around 120 C⁰ is passed through it. This releases the trapped CO₂, which can then be transported for storage elsewhere.

More experimental techniques to scrub CO₂ from flue gas without the two-step process include using seawater to absorb the gas and then returning the mixture back to the ocean for long-term storage. But, so far, these methods have proved less efficient and reliable.

Oxyfuel: When coal, oil or natural gas is burned in normal air, the amount of CO₂ produced is between 3-15% of the waste gases, depending on the conditions. Separating the greenhouse gas out after combustion requires energy so an alternative CCS method is to burn the fossil fuel in an atmosphere of pure oxygen. In this environment, virtually all the waste gas will be composed CO₂ and water vapor. The latter can be condensed out while the former can be piped or transported directly to a storage facility.

In the oxyfuel system, the air fed into the boiler has to be separated into liquid oxygen, gaseous nitrogen, argon and other trace gases and this process can use up to 15% of the power produced at the station.

Pre-combustion: This method is normally applied to coal-gasification combined cycle power plants. The coal is gasified to produce a synthetic gas made from carbon monoxide and hydrogen. The former is reacted with water to produce CO₂, which is captured, and more hydrogen. The hydrogen can be diverted to a turbine where it can be burned to produce electricity. Alternatively, some of this gas can be bled off to feed hydrogen fuel cells for cars.

One disadvantage of the pre-combustion method is that it cannot be retro-fitted to the older pulverised coal power plants that make up much of the world's installed base of fossil fuel power. It could perhaps be used in natural gas stations, where a synthetic gas is first produced by reacting the methane with steam to produce carbon dioxide and hydrogen. But the economic advantage of this method over post-combustion is yet to be proven.

A carbon dioxide gas stream is purified of contaminants by feeding it through a non-thermal plasma reactor. The contaminants are hydrocarbons and sulfur compounds which will be decomposed. The non-thermal plasma reactor may be part of an overall carbon dioxide purification process that uses a pre-purification step prior to further purification.

1.1.3 Utilization Methods of CO₂

Rather than burying CO₂ underground, companies are now exploiting organic chemistry and developing processes that use CO₂ emissions as chemical starting materials. Research efforts to investigate alternatives to sequestration options are already well advanced. Recently, Danish Government has proposed a move to zero reliance on fossil fuels by the year 2050. Carbon utilization emerges as a practical alternative to divert CO₂ from the transport and storage route and zero reliance on fossil fuels. Carbon utilization has been identified by the Engineering and Physical Sciences Research Council (EPSRC) in their Grand Challenges looking towards a sustainable chemical economy by 2050. ‘Carbon dioxide utilization’ (CU) is quite a different concept than storage technology. Storage technologies target reducing atmospheric carbon dioxide by trapping it into remote environments or by fixing it in long-living (hundred years or more) compounds. On the other hand, utilization technologies prevalently avoid CO₂-emissions and reduce fossil carbon extraction by recycling carbon. Quite obviously, most of the compounds into which CO₂ is converted, if used, will release CO₂ on a time scale from months to years. The only exception is polymeric materials that may last for decades (polycarbonates) or longer (polyurethanes as insulating materials). Nature utilizes CO₂ to produce myriad substances that are consumed by humans and animals. Some industrial processes aim to accelerate the utilization of CO₂. Technology of CO₂ utilization explores ways to change the basic characteristics of the CCS supply chain. There are essentially three pathways for utilizing CO₂ with: [4]

- (a) Use of CO₂ as a chemical feedstock.
- (b) As a fertilizer for algae production leading to further CO₂ emission reductions through the sustainable application of algae.
- (c) Mineral conversion of carbon dioxide.

The disposal or utilization of the captured CO₂ is another problem for adequate reduction of CO₂ emissions. A potential and attractive route to use the captured CO₂ is its fixation as valuable petrochemical commodities or fuels. Figure 3 presents some of the current and potential utilization routes for CO₂. Chemical fixation of carbon dioxide Carbon dioxide, a cheap and abundant C-containing raw material, is interesting as substrate, solvent, reactant, and extracting agent. CO₂ is a potential C₁ building block for C–C chains or as competitive source of C in chemical industry and appears very attractive, although the molecule is rather inert and its reactions are energetically highly unfavorable. There are several good recent review articles on CO₂ chemical fixation. [2]

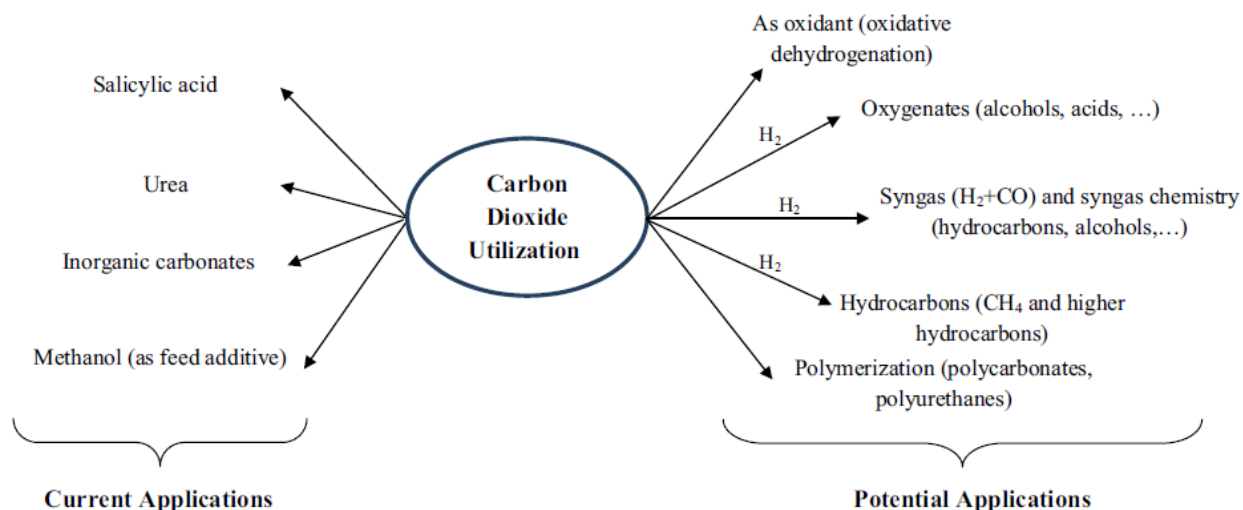


Figure 3. Utilization perspectives of Carbon Dioxide[2]

The total amount of carbon dioxide used in industry is approximately 200×10^6 metric tons per year. Its utilization as a technological fluid, where carbon dioxide is not chemically converted and thus can be recovered at the end, is estimated at 30×10^6 metric tons per year. The generation of energy used for CO₂ transformation, if based on hydrocarbon raw materials, still produces large amounts of CO₂. In addition, the resulting organic chemicals from CO₂ release carbon dioxide at the end of their use. However, despite the fact that, currently, the usage of CO₂ in the chemical industry cannot reduce significantly the global CO₂ levels, it is believed that the full potential of the fixation of CO₂ into value-added products has not yet been completely explored. The direct use of non-hydrocarbon based energy sources for reduction of CO₂ would change the above perspective and allow recycling of carbon dioxide via chemicals and liquid fuels. Thus, the further development of industrial processes, that are utilizing CO₂ for high demand products, is of importance. [2]

1.1.4 CO₂ utilization into Methanol

Methanol is a viable alternative energy source, offering a convenient solution for the efficient energy storage on a large scale, while playing an important role in economy and sustainability by converting the CO₂ waste from industry into a valuable product [5]. At industrial scale, methanol is produced from synthesis gas (CO/CO₂/H₂) using various catalysts based on CuO/ZnO/Al₂O₃ [6]. Complementary to carbon capture and sequestration (CCS), much effort is being put on the development of technologies for methanol production from carbon dioxide. Several review papers published during the past decade cover this topic very well.

Liu et al. [7] reviewed the progress in the catalyst innovation, optimization of the reaction conditions, reaction mechanism, and catalyst performance in CO and CO₂ hydrogenation to methanol, highlighting the key issues of catalyst improvement and areas of priority in R&D.

Centi and Perathoner [8] analyzed the possibilities of converting CO₂ to fuels, noting that the requisites for this objective are: minimization of the consumption of hydrogen (sources), production of fuels that can be easily stored and transported, and the use of renewable energy sources. Their review included CO₂ reverse water–gas shift (WGS) and hydrogenation to hydrocarbons, alcohols, dimethyl ether or formic acid, as well as the reaction to synthesis gas; photo- and electrochemical/catalytic conversion; and thermo-chemical conversion.

Saeidi et al. [9] focused on hydrocarbon and methanol synthesis as methods to convert CO₂ to value-added products. The reaction mechanisms as well as the effects of catalyst, reactor type and operating conditions on product efficiency enhancement of each process were reviewed. Also a brief overview on the reactor types and configurations was provided.

Currently, extensive attentions and efforts are made on conversion of CO₂ to methanol. Olah et al. [31] reported that CO₂ hydrogenation to methanol, a new concept of “methanol economy” which relies on combination of Carbon Capture and Storage (CCS) with chemical recycling. Whereas renewable feedstock such as CO₂ and water are abundantly available, the energy required for the synthetic carbon cycle can come from any source of alternative energy like wind, solar, nuclear, and geothermal energy. This alternative cycle offers a robust mechanism ensuring sustainable future for human beings when fossil fuels become deficient.

During past few years, many types of catalysts have been examined and analyzed for the synthesis of methanol from CO₂ hydrogenation. The majority of catalyst for hydrogenation of CO₂ contains Cu as the main component along with different promoters or modifiers (Zn, Zr, Si, Al, Ti, Cr, Ga, Ce, etc.) and literatures on catalytic CO₂ hydrogenation process containing Fe for methanol synthesis have been found a very few. [32]

According to the research conducted by Deerattrakul et al. [33], 10 wt% CuZn/rGO catalyst performed the highest activity for the CO₂ hydrogenation with a 26% CO₂ conversion, 51% CH₃OH selectivity, and $424 \pm 18 \text{mg}_{\text{MeOH}}$ at 250 °C and 15 bar after 5 h on stream of CO₂ and H₂. When the reaction was completed, the spent catalyst was reevaluated its structure using XRD in order to examine the stability of rGO. The obtained pattern of XRD indicated that the catalyst still had the same structure as that of the initially used catalyst. When the loading was increased beyond 10 wt%,

the conversion of CO₂ and space–time yield of methanol (STY_{MeOH}) decreased due to the agglomeration of active metals led to reduce copper oxides to metallic Cu⁰, which is a crucial active metal for synthesis of methanol [33].

In the Table we can see some experimental data from previous experiments for different catalysts under various temperature and pressure.

Type of catalyst	Type of reactor	Temperature(0C)	Pressure(bar)	Methanol Yield	Reference
CuO/ZnO/Al ₂ O ₃ -C-1	Fixed-bed	240	14.6	0.12	[34]
CuO/ZnO/Al ₂ O ₃ -O-1	Fixed-bed	240	12.1	0.1	[34]
Cu/ZnO/ZrO ₂ -0	Fixed-bed	270	22.5	N/A	[35]
Cu/ZnO/ZrO ₂ -5	Fixed-bed	270	23	N/A	[35]

Table 1. Catalyst types and yield

This article proposes an efficient production line of methanol synthesis using captured and purified carbon dioxide and wet hydrogen, with relevant mass balance, heat balance and economical evaluation of the plant.

1.2 Global Market

This chapter is taken as a reference from a finance article [10]

The global methanol market is expected to grow at a significant rate during the forecast period, driven mainly by the increasing use of methanol (in the form of fuel and antifreeze agent) in the automotive industry. The methanol industry has experienced an explosive growth, primarily in China and the United States, owing to significant developments in shale gas.

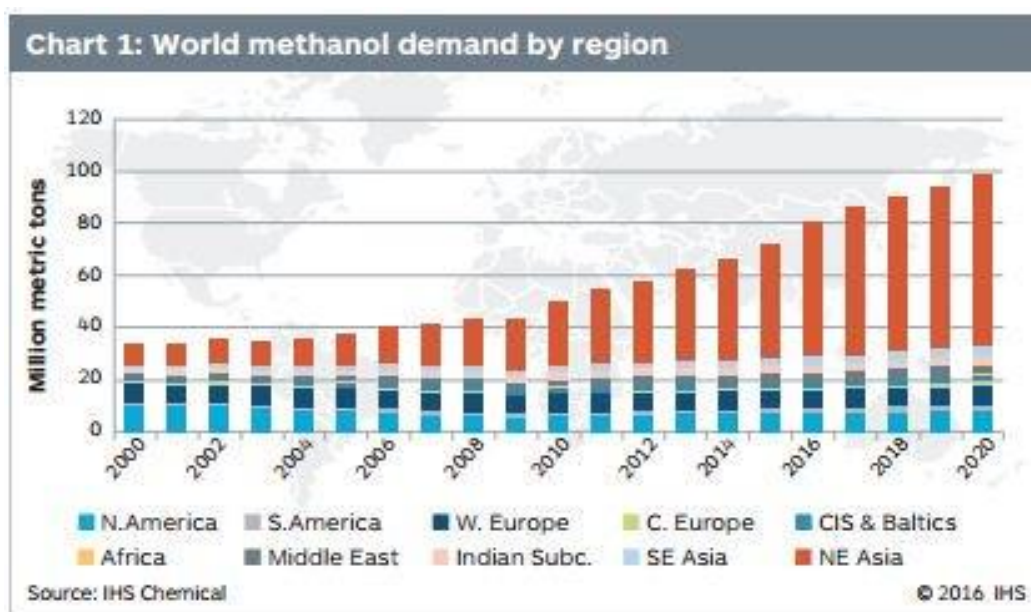


Figure 4. Methanol demand by regions[30]

Methanol is used directly as an affordable transportation fuel for automobile engines due to its efficient combustion, ease of distribution, and easy availability. It is also used as an antifreeze agent for automobile radiators. Moreover, it can be blended with gasoline to generate a fuel that is efficient and can boost octane number with lower emissions when compared to conventional gasoline. Methanol gasoline blends have widespread use in China and have been introduced in several countries outside of China as well.

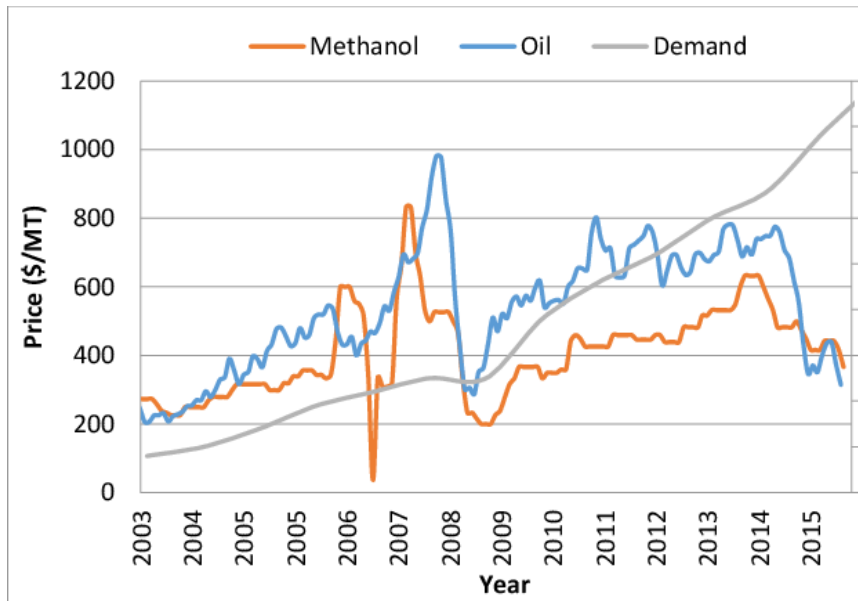


Figure 5. Methanol Price by year[27]

Acetic acid is the main feedstock to manufacture vinyl acetate monomer, which was at the forefront in terms of volumetric consumption of methanol in 2017. It is mainly driven by the growing demand for polyvinyl acetates and vinyl alcohols, which, in turn, are accelerating the demand for acetic acid. Acetic acid is a key building block to manufacturing various chemicals, such as vinyl acetate monomer (VAM), purified terephthalic acid (PTA), acetate esters, and acetic anhydride, which are further used by a wide range of end-user industries, such as synthetic fibers, textiles, inks, and pesticides. It is used in many applications, such as vinyl acetate monomer, purified terephthalic acid, acetate esters, acetic anhydride, and others. Vinyl acetate monomer (VAM) was the largest application segment for the market accounting for over 34% of the global acetic acid consumption in 2017. The acetate esters segment is expected to be the strongest growth segment of the market, primarily driven by the growing demand from the coatings industry.

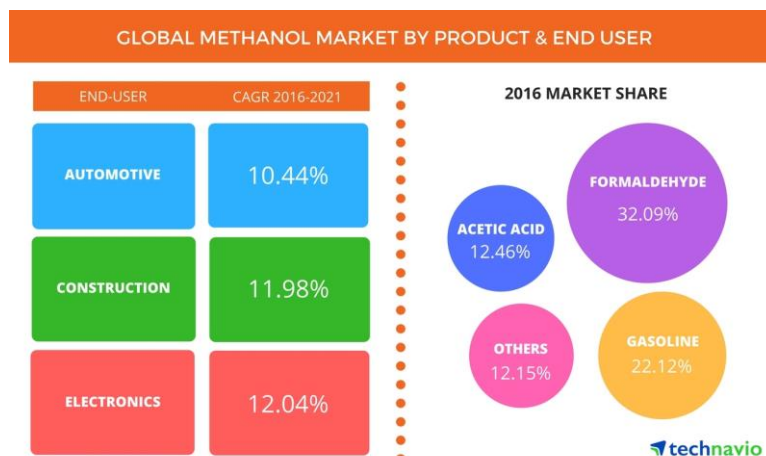


Figure 6. Main feedstock for methanol[29]

2. Methanol Production Technology and Parameters

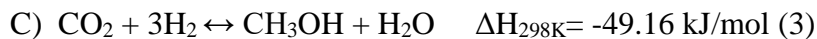
This technology is taken as reference from literature [15]

2.1 Property Model

By the author of this paper the complete process was simulated in Aspen Plus using the RK-Soave property model which is most suitable for these components (H₂, CO, CO₂, H₂O, and CH₃OH) and conditions (pressure up to 50 bar and temperature up to 250 °C). This model was compatible (NRTL) to the RK-Soave property model, for modeling the distillation section operating at low pressure and in which no hydrogen is present. This is in line with literature recommendations for such systems [11,12].

2.2 Chemical reactions

The reactions that refers to methanol formation from CO₂/CO and H₂ on a metallic Cu catalyst are given in Kondratenko et al. [13]. The chemistry of CO₂ hydrogenation involves three main equilibrium reactions (A, B and C) leading to methanol and water [14]:



In the reaction B The conversion of CO₂ to CO is endothermic. As a result, increase of temperature is favorable for the chemical equilibrium. On the other hand, Reaction A and C which represents the CO and CO₂ conversions to methanol are exothermic and the temperature increase affects the equilibrium negatively. Based on this summary, at lower temperatures and higher pressures higher methanol yields are obtained.

2.3 Chemical equilibrium

The values for the equilibrium constants (K_A , K_B and K_C) were evaluated by Lim et al. [16], using $R = 8.314 \text{ J/mol K}$ and K_i . And these values were obtained using the experimental data from Graaf et al. [8]. Based on this values the same data provided in an explicit model is used to provide consistent framework for process simulations in Aspen Plus by Anton A.Kiss[15].

The comparison between the data from literature [16] and the equilibrium constant values evaluated within Aspen Plus [15] using the equilibrium reactor showed an excellent agreement. In Aspen Plus, the equilibrium constants are evaluated based upon fugacity in [atm]. A conversion was made to [Pa] based correlations as those will be required to express the driving force term of the kinetic rate equations:

$$\begin{aligned} \ln K_A &= \frac{9.8438 \times 10^4}{RT} - 29.07 \rightarrow K_A = 2.3717 \times 10^{-13} \exp\left(\frac{9.8438 \times 10^4}{RT}\right) [\text{atm}^{-2}] \\ \ln K_A &= -52.096 + \frac{11840}{T} \quad \text{with } K_A [\text{Pa}^{-2}] \end{aligned} \quad (5)$$

$$\begin{aligned} \ln K_B &= \frac{-4.3939 \times 10^4}{RT} + 5.639 \rightarrow K_B = 2.8118 \times 10^2 \exp\left(\frac{-4.3939 \times 10^4}{RT}\right) [-] \\ \ln K_B &= 5.639 + \frac{-5285}{T} \quad \text{with } K_B [-] \end{aligned} \quad (6)$$

$$\begin{aligned} K_C &= K_A \times K_B \rightarrow K_C = 6.6688 \times 10^{-11} \exp\left(\frac{5.4499 \times 10^4}{RT}\right) [\text{atm}^{-2}] \\ \ln K_C &= -46.457 + \frac{6555}{T} \quad \text{with } K_C [\text{Pa}^{-2}] \end{aligned} \quad (7) \quad [15]$$

The model of Graaf et al. [18] is validated by the experimental data from An et al. [17] and it was obtained for a fibrous Cu/Zn/Al/Zr catalyst that was designed especially for the hydrogenation of CO_2 . According to Graaf et al. [18] the adsorption of methanol is assumed to be negligible, while H_2 is believed to adsorb dissociatively – hence the use of λ_H term. Nonetheless, it is rather straightforward to derive alternative kinetic rate expressions that are based on the molecular adsorption of H_2 . [18]:

The comparison between the experimental and simulated data from the author[15] shows a good agreement with less than 5% error around the operating process conditions, thus indicating a correct implementation of the kinetics. No model parameters were calculated and no changes were made to the kinetic data from An et al. [17] and the equilibrium data from Lim et al. [16] – based on the detailed model of Graaf et al. [19].

2.4 Reactor

The plug flow reactor model (PFR, sometimes called continuous tubular reactor, CTR, or piston flow reactors) is a model used to describe chemical reactions in continuous, flowing systems of cylindrical geometry. The PFR model is used to predict the behavior of chemical reactors of such design, so that key reactor variables, such as the dimensions of the reactor, can be estimated.

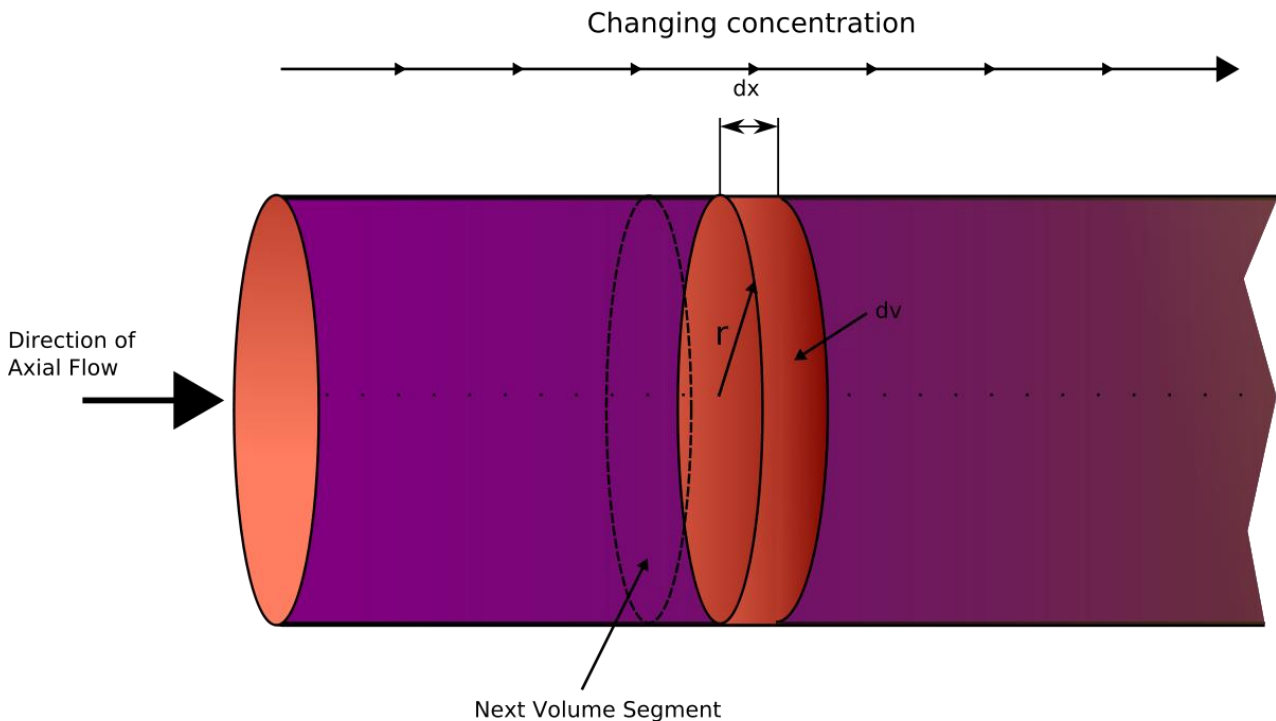


Figure 7. Plug Flow Reactor Model

Fluid going through a PFR may be modeled as flowing through the reactor as a series of infinitely thin coherent "plugs", each with a uniform composition, traveling in the axial direction of the reactor, with each plug having a different composition from the ones before and after it. The key assumption is that as a plug flows through a PFR, the fluid is perfectly mixed in the radial direction but not in the axial direction (forwards or backwards). Each plug of differential volume is considered as a separate entity, effectively an infinitesimally small continuous stirred tank reactor, limiting to zero volume. As it flows down the tubular PFR, the residence time (τ) of the plug is a function of its position in the reactor. In the ideal PFR, the residence time distribution is therefore a Dirac delta function with a value equal to τ .

In this Model PFR reactor with 810 tube and 12 m length will perform under the temperature of 250 °C and 50 bar with the flowrate of 122002 kg/h from the input stream based on experimental data from An et al. [17]

Reactor type	<i>PFR</i>
Operating pressure	<i>50 bar</i>
Operating temperature	<i>250 °C</i>
Number of Tubes	<i>810</i>
Tube length	<i>12m</i>
Tube diameter	<i>0.06m</i>

Table 2. Reactor parameters

3. Objectives

3.1 General Objective

- Design of Methanol Production Plant – Techno Economical analysis

3.2 Detailed Objectives

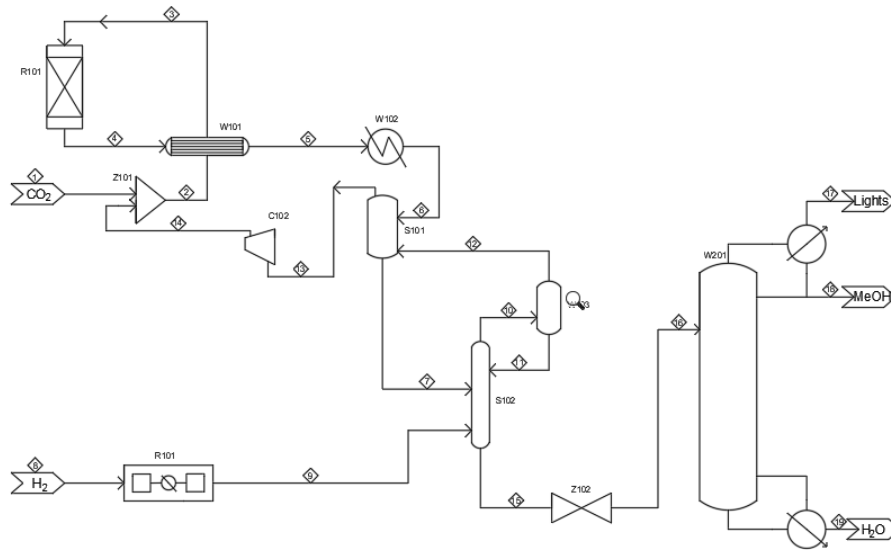
- ✓ To Create a flow sheet of methanol plant based on literature.
- ✓ To prepare detailed Process Flow Diagram of Process based on literature.
- ✓ To verify Mass Balance of technology taken as reference.
- ✓ To prepare Heat Balance of Process.
- ✓ To perform the economical calculations of total investment costs and operating costs.
- ✓ To perform economical evaluation of the plant with income and payback period.
- ✓ To analyze and discuss the results.
- ✓ To formulate visions necessary for the implementation of such a technology

4. Practical part

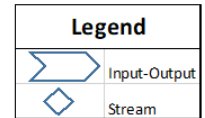
PFD of this technology was taken from literature[15] with slight changes.

4.1 Process Flow Diagram

Based on the objectives of technology, full PFD with details is Illustrated in Figure 8.



Equipment	Number
Static Mixer	Z101
SS Shell and Tube Heat Exchanger	W101
Cooler	W102
Reactor	R101
Separator	S101
Compressor 1	C101
Compressor 2	C102
Stripper	S102
Condenser	W103
Valve	Z102
Distillation Column	W201



Stream	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19
Flowrate kg/h	17209	122002.7	122002.7	122002.7	122002.7	122002.7	21104.86	2658.87	2658.87	3985.81	89.96	3895.87	104793.5	104793.5	19867.9	19867.9	12.5	12508.71	7346.68
Flowrate m ³ /h	22.05	4372.55	7644.01	7304.78	4878.2	3822.7	24.62	27734.24	992.69	735.89	0.11	695.46	4097.32	4608.29	25.79	31.68	26.7	16.12	8.05
Temperature Celsius	20	28.2	225	250	93.9	3.1	30	35	170	47	30	30	30	42.1	92.2	87.6	39	39	104.9
Pressure Bar	100	50	50	50	50	5.0	45	1.1	45	45	45	45	45	50	45.2	5.066	1.013	1.013	1.1

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Sheets	1 of 1	Methanol Production from CO2

Figure 8. Full PFD of Methanol Production Technology[15]

4.2. Process description

In this project, a plant capacity of 100 kTon/Year methanol is evaluated. Figure 9 presents the proposed process flowsheet. The CO₂ feed stream is mixed with the recycled gas stream coming from separator and sent to heat-exchanger without decompression and heating. Not mixing CO₂ before we compress the recycled gas results in lower gas flowrate to the recycle compressor (C102) and reduced requirements of electricity achieved.

Using classic process synthesis heuristics, alternative process configurations have been evaluated that will take advantage of having separate hydrogen and CO₂ feed streams. Nonetheless, feeding reactants mixed or as pure components doesn't have much improvement on effectiveness. The main reason is that the reactor outlet is in all cases close to the equilibrium hence implicitly limited. Therefore, feeding the reactants methods has no effect on a reactor achieving equilibrium conversion of 100%. The more optimal way was to feed the mixed reactants at lower end temperature to the reactor. Using feed hydrogen in order to strip out the dissolved CO₂ from the methanol is another improvement in this system to get higher efficiency of yield. Then stripped CO₂ will be mixed with the recycled gas and fresh CO₂. These optimizations lead to the highest methanol yield and the lowest energy requirements per ton product. This strategy is especially beneficial when wet fresh hydrogen is used, because when we use wet hydrogen it doesn't only strip out the dissolved CO and CO₂ from methanol, but also removes water from hydrogen that leads to further improvements in increasing CO₂ conversion per pass, resulting in energy reduction.

The wet hydrogen feed from the input stream is then pressurized to 45 bar in a primary multi-stage compressor (C101). The hydrogen compressor (C101) was optimized to take advantage of the compression curve, and hence to decrease the compression duty. The gas mixture from recycle stream and fresh CO₂ feed is then heated up in a heat-exchanger by the reactor outlet stream, and then fed to a multi-tubular plug-flow reactor (PFR) operated isothermally at 50 bar and 250 °C. The heat of reaction generated in the reactor can be used to generate high pressure steam. The multi-tubular plug flow catalytic reactor's characteristics is shown in Table 1.

Outlet stream from the reactor was first cooled down in Heat Exchanger and then fed to extra cooler in order to get the desired temperature in system to be sent to separator. After cooling the output until 31 °C, products were flashed in separator (S101) to split methanol and water (liquid) from the non-condensable gas components such as CO, CO₂ and H₂ that are recycled. The recycle stream is then and mixed with the fresh CO₂ feed stream and sent to the second compressor (C102). The liquid from the flash separator is further sent to a stripping tower (S102) where the compressed wet hydrogen stream from C101 is fed in counter-current mode. As it was mentioned before it has several advantages such as drying the hydrogen feed and removing water from the reactor feed, removing the lights (CO₂ but CO as well) which are completely recycled and resulting in sharp improvement of consumption figures. The bottom product of stripper that consist of mainly liquid is sent to a distillation column (W201) which separates water as bottom product and methanol as high purity top distillate. Additionally, by using stripping tower where we received bottom products(liquids) at high temperature, we diminished heat duty of reboiler as a result of using high temperature feed for distillation column. Methanol-water separation process

was carried out in a single distillation column with partial condenser that is able to deliver vapor distillate(lights), high purity liquid distillate methanol and bottom product of water. Therefore, only using one distillation column with reboiler and condenser, we managed to get high purity of Methanol product as a result.

4.3 Mass Balance calculation

Mass balance calculation was verified by using the conversion of input parameters in the reactor that was taken from the literature data[15]and approved to be correct.

Input of materials such as CO₂ and H₂ streams are decided by the amount of same components that was reacted in plug flow reactor and received as CH₃OH or H₂O in the output.

- Conversion rate of H₂ per pass in reactor is set to be 18.17% according to the thermal equilibrium for the given conditions (250 °C and 50 bar).
- Conversion rate of CO₂ per pass in reactor is set to be 17.2% according to the thermal equilibrium for the given conditions (250 °C and 50 bar).

Stream 1- CO₂ input:

Component	kg/h
CO ₂	17208.28
H ₂ O	0.86

Table 3. CO₂ feed

Stream 2- After mixing of stream 1(Input CO₂) and stream 14(recycled gas):

Component	kg/h
CO	7492.57
CO ₂	100018.93
H ₂	13011.73
H ₂ O	4.8
CH ₃ OH	1474.66

Table 4. Mixed feed

Stream 3- Heated product from heat exchanger (Input for reactor)

Stream 4- Reactor output:

Component	kg/h
CO	7492.57
CO ₂	82810.7331
H ₂	10647.0498
H ₂ O	7048.93
CH ₃ OH	14003.4

Table 5. Reactor output

Stream 5- Components cooled from heat exchanger

Stream 6- Additionally cooled components from cooler

Stream 7- Separator output for the stripping tower feed:

Component	kg/h
CO	2.11
CO ₂	1344.24
H ₂	1.3
H ₂ O	7045.4
CH ₃ OH	12711.83

Table 6. Separator feed to Stripping Tower

Stream 8- Wet Hydrogen Input going to Compressor:

Component	kg/h
H ₂	2366.14
H ₂ O	292.73

Table 7. Wet Hydrogen Input

Stream 9- Compressed Hydrogen feed for Stripping Tower:

Stream 10- Stripped gases

Component	kg/h
CO	2.11
CO ₂	1344.95
H ₂	2365.99
H ₂ O	28.07
CH ₃ OH	244.67

Table 8. Stripped gas from Tower

Stream 11- Condensed Liquid going back to Stripping Tower

Component	kg/h
CO	0
CO ₂	0.71
H ₂	0
H ₂ O	27.66
CH ₃ OH	61.58

Table 9. Condensed Liquid fed back to Stripping Tower

Stream 12- Condensed gas feed going back to Separator:

Component	kg/h
CO	2.11
CO ₂	1344.24
H ₂	2365.99
H ₂ O	0.41
CH ₃ OH	183.09

Table 10. Gas from Condenser

Stream 13- Recycled gas from Separator:

Component	kg/h
CO	7492.57
CO ₂	82810.65
H ₂	13011.73
H ₂ O	3.94
CH ₃ OH	1474.66

Table 11. Recycled gas

Stream 14- Compressed gas that will be mixed with input CO₂ and fed to Reactor:

Stream 15- Liquid separated in Stripping tower:

Component	kg/h
CO	0
CO ₂	0
H ₂	1.45
H ₂ O	7337.72
CH ₃ OH	12528.74

Table 12. Liquid from Stripping Tower

Stream 16- Pressure released feed for Distillation Column

Stream 17- Lights from DC(88.8%methanol):

Component	kg/h
CO	0
CO ₂	0
H ₂	1.4
H ₂ O	0
CH ₃ OH	11.12

Table 13. Light from Distillation column

Stream 18- Methanol from DC (100% methanol)

Component	kg/h
CO	0
CO ₂	0
H ₂	0.05
H ₂ O	1.2
CH ₃ OH	12507.46

Table 14. Methanol output from DC

Stream 19- Water from DC (99.9% water)

Component	kg/h
CO	0
CO ₂	0
H ₂	0
H ₂ O	7336.52
CH ₃ OH	10.16

Table 15. Water leaving DC

List of Streams with Temperature, Pressure, Mass/Volume flowrates:

Stream	Flowrate kg/h	Flowrate m ³ /h	Temperature Celsius	Pressure Bar
1	17209	22.05	20	100
2	122002.69	4572.55	28.2	50
3	122002.69	7644.01	225	50
4	122002.69	7304.78	250	50
5	122002.69	4878.2	93.9	50
6	122002.69	3822.7	31	50
7	21104.88	24.62	30	45
8	2658.87	27734.24	35	1.1
9	2658.87	992.69	170	45
10	3985.8	735.89	47	45
11	89.96	0.11	30	45
12	3895.87	695.46	30	45
13	104793.54	4097.32	30	45
14	104793.54	4608.29	42.1	50
15	19867.9	25.79	92.2	45.2
16	19867.9	31.68	87.6	5.066
17	12.5	26.7	39	1.013
18	12508.71	16.12	39	1.013
19	7346.68	8.05	104.9	1.1

Table 16. Stream Details [15]

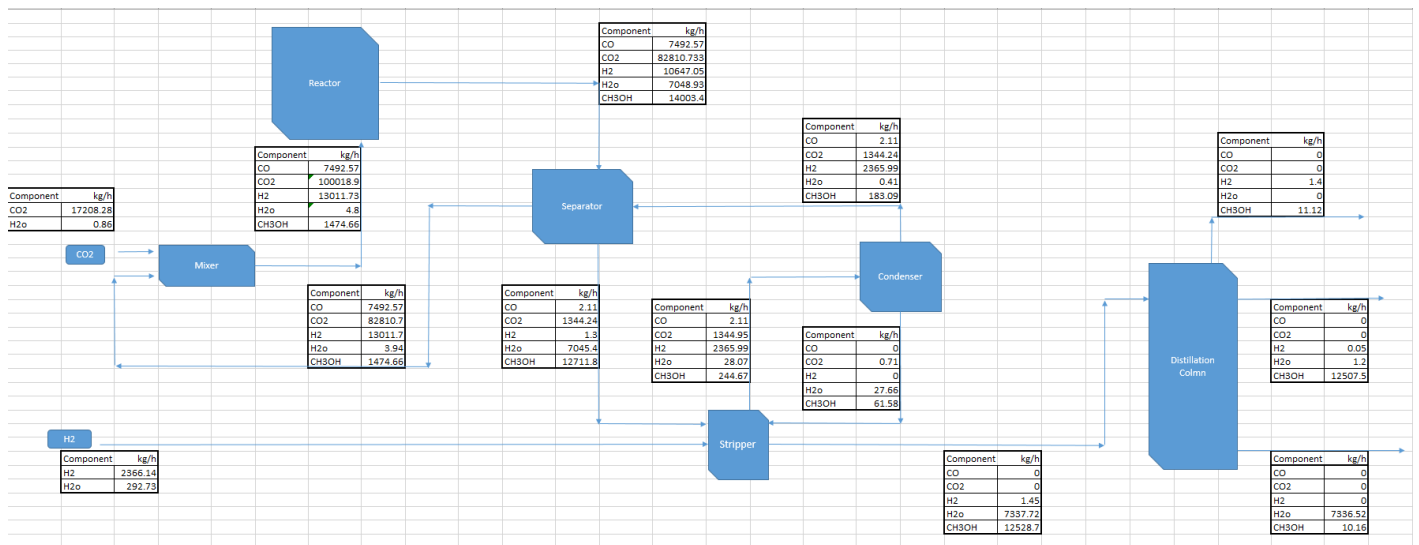


Figure 9. Full mass balance table

4.4 Heat Balance calculation

In this section heat balance calculations are done based on different parameters depending on equipment. In this section heat duties or power consumption of equipment will be calculated based on temperature or pressure. Heat losses in system neglected for simplicity.

W 101 Heat Exchanger

Heat Duty of HE is calculated based on temperature difference, average C_p values of each component with corresponding temperature and flowrate of streams.

We used:

$$Q_{HE} = C_p \text{ average} * \dot{m} * (T_{in} - T_{out})$$

In order to find amount of steam that is necessary for heat exchanger on the further stages we used evaporation energy of steam for relevant temperature by this formula:

$$Q_{HE} = m_{steam} * h_e$$

Heat exchanger W101							
Parameter	Value	Unit		Parameter	Value	Unit	
T2	225	Celcius		T2	93.9	Celcius	
T1	28.2	Celcius		T1	250	Celcius	
flowrate	122002.69	kg/h		flowrate	122002.69	kg/h	
Cp(water)	4.1812	KJ/kg*K		Cp(water)	4.77	KJ/kg*K	
Cp(co)	1.054	KJ/kg*K		Cp(co)	1.051	KJ/kg*K	
Cp(co2)	0.978	KJ/kg*K		Cp(co2)	0.956	KJ/kg*K	
Cp(methanol)	2.212	KJ/kg*K		Cp(methanol)	2.715	KJ/kg*K	
Cp(Hydrogen)	14.312	KJ/kg*K		Cp(Hydrogen)	14.51	KJ/kg*K	
Cp average	2.4972333	KJ/kg*K		Cp average	3.1483578	KJ/kg*K	
Q	16655.249	kW		Q	16655.3549	kW	

Table 17. Heat balance table of Heat Exchanger

W 102 Cooler

Using the same method as heat exchanger we also calculated heat required for cooler

Cooler W102			
Parameter		Value	Unit
T2		31	Celcius
T1		93.9	Celcius
Cp average		3.148358	KJ/kg*K
flowrate		122002.7	kg/h
Q		6711.222	kW

Table 18. Heat balance of Cooler

W103 Condenser

To calculate heat duty of condenser, specific enthalpy of water and methanol was found from the table for the corresponding temperature and we used:

$$Q = h_w * m_w + h_{meoh} * m_{meoh}$$

Condenser W103			
Parameter		Value	Unit
Specific Enthalpy of water		2257	KJ/kg
Specific Enthalpy of Methanol		1104	KJ/kg
Flowrate of water		27.66	kg/h
Flowrate of Methanol		61.58	kg/h
Q		36.22582	kW

Table 19. Heat balance of Condenser

W 201 Distillation Column

Heat duty of condenser and reboiler on Distillation Column is calculated based on Heat of vaporization/condensing of water and methanol

Distillation Column W203		
Parameter	Value	Unit
heat of vap of water	40.66	KJ/mol
heat of con of methanol	38.3	KJ/mol
molar flow rate of water	407.56	Kmol/h
molar flow rate of methanol	390	Kmol/h
Heat duty of reboiler	4603.164	kW
Heat duty of condenser	-4149.17	kW
No of stages	30	N/A

Table 20. Heat balance of Distillation Column

R101 Reactor

Reactor heat is calculated based on amount of methanol produced (by moles) and heat of reaction

Reactor R101		
Parameter	Value	Unit
dH(MeOH)	49.16	KJ/mol
MeOH	390.79	Mol/h
T1	225	Celcius
T2	250	Celcius
Pressure	50	bar
Q	5.336454556	kW

Table 21. Heat balance of Reactor

C101-102 Compressors

First Compressor is a 5 stage compressor and power value is calculated using online simulator [20]

Compressor (5 stages) C101			
Parameter		Value	Unit
T1		35	Celcius
T2		170	Celcius
P1		1.1	bar
P2		45	bar
Flowrate		27734.24	m3/h
Accentric factor		-0.22	N/A
Polytropic Efficiency		75	%
P(Power)		4455.15	kW

Table 22. Power consumption of first Compressor

Second compressor is one stage compressing unit and its power value is calculated using the same simulator [20]

Compressor C102			
Parameter		Value	Unit
T2		42.1	Celcius
T1		30	Celcius
P2		50	bar
P1		45	bar
flowrate		4907	m3/h
Efficiency		0.72	N/A
P(Power)		911.96	kW

Table 23. Power consumption of second Compressor

5. Economy

This part of the project will focus on evaluation of economic aspect of the project considering capital costs, raw materials and operational costs.

5.1 Capital cost

In order to find the individual prices of equipment, online sources and online price calculation method were used. In the example below we can see an online simulator which gives us the price for the equipment for the given data from: <http://matche.com/equipcost/Exchanger.html>

Matches provides conceptual process, cost and optimization engineering services to the chemical and metallurgical industry. This educational content should assist you in the evaluation of process alternatives. We hope you will comment (below).

Heat Exchanger Cost Estimate - An interactive JavaScript equipment capital cost estimating aid (order-of-magnitude). These costs are helpful during a project's early development and budgeting. The actual cost of a piece of equipment depend upon many factors. You should exercise caution in use of this educational content.

Exchanger Type:

Area should be between 1500 and 6000 ft²

Area : ft²

Material:

Internal Pressure:

Cost 2014 US \$: **620400**

F.O.B. Gulf Coast U.S.A.

Cost Information Exchange

Have you recently purchased process equipment? If you would like to share process equipment cost, just follow the link below. When we update the cost pages we will consider placing the information you and others provide on Matches' website. Click here to go to [Shared Equipment Cost](#) form.

Equipment Type

- [Agglomerator](#)
- [Agitator](#)
- [Bin](#)
- [Blender](#)
- [Blower](#)
- [Boiler](#)
- [Centrifuge](#)
- [Classifier](#)
- [Compressor](#)
- [Conveyor](#)
- [Cooling](#)
- [Crystallizer](#)
- [Dryers](#)
- [Dust Collector](#)
- [Ejector](#)
- [Elevator](#)
- [Exchanger, Heat](#)
- [Fan](#)
- [Filter](#)
- [Fired Heater](#)
- [Incinerator](#)
- [Material Handling](#)
- [Pump - Centrifugal](#)
- [Pump - Positive Displacement](#)
- [Pump - Vacuum](#)
- [Reactor](#)
- [Screen](#)
- [Scrubber](#)
- [Separator](#)
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Figure 10. Online price simulator

Capital cost is calculated based on real values of equipment found from online sources or simulator and +40% of total equipment cost for construction and engineering costs.
 [21][22][23][24][25]

Equipment	Number	Quantity	Cost
Static Mixer	Z101	1	\$3,000.00
SS Shell and Tube Heat Exchanger	W101	1	\$620,400.00
Cooler	W102	1	\$202,300.00
Reactor	R101	1	\$200,000.00
Separator	S101	1	\$83,000.00
Compressor 1	C101	1	\$3,866,900.00
Compressor 2	C102	1	\$584,000.00
Stripper	S102	1	\$200,000.00
Condenser	W103	1	\$40,600.00
Valve	Z102	1	\$700.00
Distillation Column	W201	1	\$100,000.00
		Total	\$5,900,900.00
Grand Total=Equipments+Construction(20%)+Engineering(20%)		Grand Total	\$8,261,260.00

Table 24. Equipment prices with construction and engineering costs

Grand Total Capital Cost: 8.26mln USD

5.2 Operating costs and Investment return

Operating costs cover direct operating costs(raw materials, personal costs, maintenance etc.) indirect operating costs(Insurance and corporate directions) and distributional costs(transport).

Maintenance costs (% of capital investment)	%	5.0
Material costs for maintenance (% of maintenance cost)	%	50
Personal maintenance costs (% of maintenance cost)	%	50
Number of employees for operation	piece	12
Number of shifts in operation	piece	2
The average brutto wage in industry	USD	1,000
Cost of supervision (%of personal costs)	%	8
The cost of consumables (% of capital investments)	%	2
The cost of laboratory (% of personal costs)	%	3
Reserve (% of direct operation costs)	%	3
Corporate direction (of personal and supervision costs and 50 % of maintenance cost)	%	16
Insurance (% of fix capital investments)	%	2.0
Cost of transport (% of price)	%	3
Construction time	Year	1
The percentage of capital investments made in the first year	%	90
Life of the unit (= operating time)	Year	10
Bank credit (bank loan)	USD	8,261,260
The period of interest rate	Year	5
Interest rate of the bank credit	%	11
Average time of the asset depreciation	Year	10
Depreciation for the first year	%	6.0
Depreciation on other years	%	10.0
Income tax	%	19

Table 25. Input data for operating cost calculation

Values in table 25 were calculated Based on operation expenditures shown in table 24.

Parameter	Unit	Variant A
Proceeds from the sale of Orange Juice (revenues from sales)	USD/Year	48,528,945
Operating costs excluding depreciation and interest payments	USD/Year	34,630,798
Direct operating costs	USD/Year	34,158,812
Raw materials and Energy consumption	USD/Year	32,124,191
Personal costs of employees of the operation	USD/Year	388,800
Supervision	USD/Year	31,104
Maintenance costs	USD/Year	413,063
Consumables	USD/Year	165,225
Laboratory	USD/Year	11,664
Reserve	USD/Year	1,024,764
Indirect operating costs	USD/Year	265,455
Insurance	USD/Year	165,225
Corporate directions	USD/Year	100,230
Distributional costs	USD/Year	206,532
Transport	USD/Year	206,532
Taxable income	USD/Year	13,898,147

Table 26. Revenue and Operating costs

Detailed information of economical calculation can be found in Appendix

Raw materials and Methanol price in this project are set to be:

Price of Hydrogen = 1200 USD/ton

Price of Carbon dioxide = 12 USD/Ton

Price of Electricity = 0.08 USD/kWh

Price of Steam = 30 USD/ton

Price of Methanol = 485 USD/ton

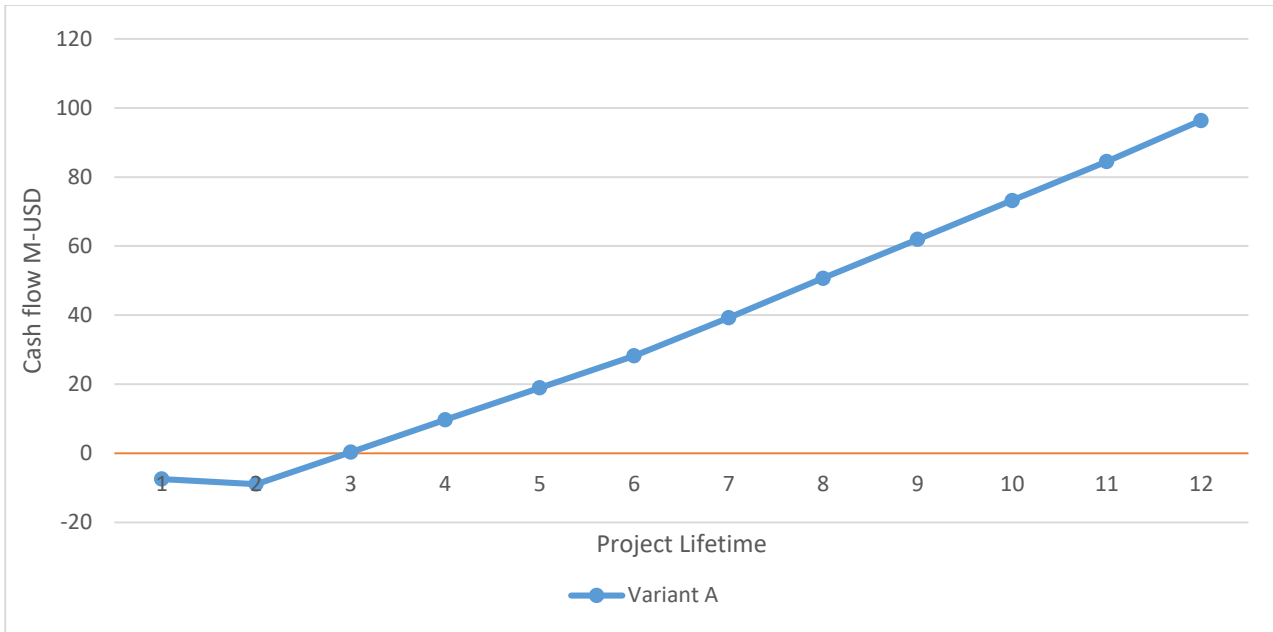


Figure 11. Cash flow by years

Based on chart above we can see that payback time of investment is roughly around 3 years and there is steady increase of 10+ million USD cash flow per year without discounted price.

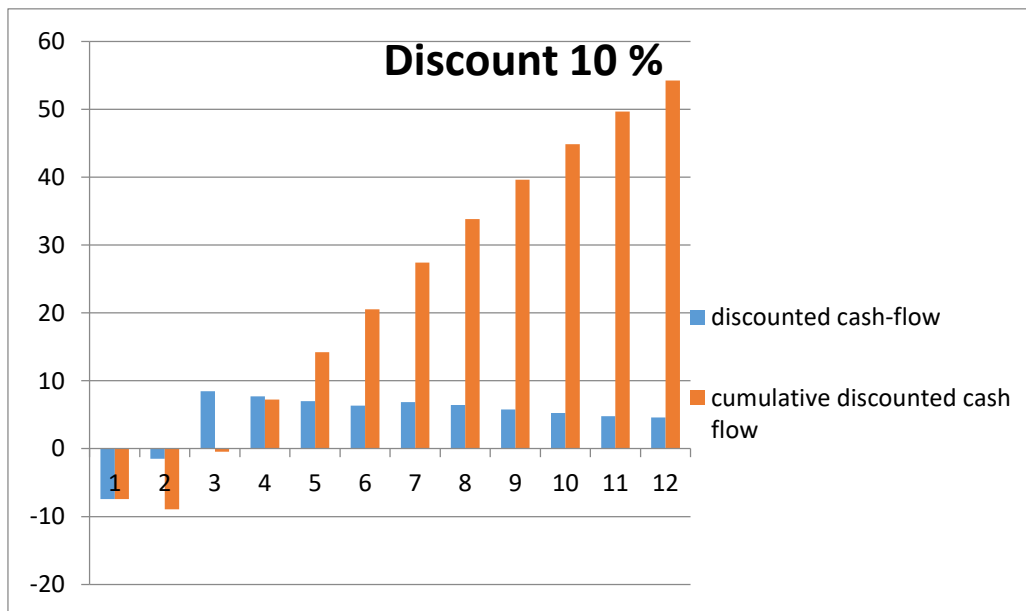


Figure 12. Discounted cash flow

In Figure 11 we can see 10% discounted cash flow of Project with cumulative discounted cash flow.

6. Discussion

6.1 General observations

This chapter discuss the calculation outcomes of the project alongside what could be developed and improved in order to increase efficiency or to decrease the costs from operations or investment.

As we can notice in the project, more than 50% of the investment cost is coming from the Compression units together. However, power consumption of compressors has already been decreased by several methods at the beginning such as using less units, avoiding input stream to be compressed before feeding to the heat exchanger and using multistage compressor for hydrogen in order to decrease the compression duty. Real plant might demand more sophisticated methods with advanced technologies that can affect the capital cost of this project.

Energy cost of plant were decreased by using steam(hot and cold) instead of electricity for heating and cooling in most of equipment's (besides compressors) which saved majority of operational cost and resulted in feasible outcomes.

Energy consumption Table			
Amount of energy provided by steam		10434.24913	kW
Evoporation Energy of Steam		2085	kJ/kg
Steam needed		5.004436036	kg/s
Amount of Steam per MeOH		1.440355751	ton/ton
Electricity Consumption		5367.11	kWh
Electricity Consumption per ton of MeOH		429.0941797	kWh/ton

Table 27. Energy consumption

The methanol synthesis by carbon dioxide hydrogenation is feasible in the new efficient process proposed here. A key feature of this novel process is the use of a stripping unit where the wet hydrogen (saturated with water) flows in counter-current with the condensed mixture methanol–water resulting from the flash separation after reaction. This operation has a double positive effect, as it removes CO_x from the methanol–water mixture thus allowing a complete recycle of CO₂, while also removing the water from the wet hydrogen (initially saturated with water) thus avoiding the negative impact on the reaction equilibrium conversion. [15]

6.2 Future projects

For the future we can concentrate on price of raw materials in this project:

Majority of the operational costs are based on raw materials and mainly hydrogen. For the future development of this project, people can concentrate on producing hydrogen for the plant. This can be done by few methods and most trending methods are producing syngas and using electrolysis.

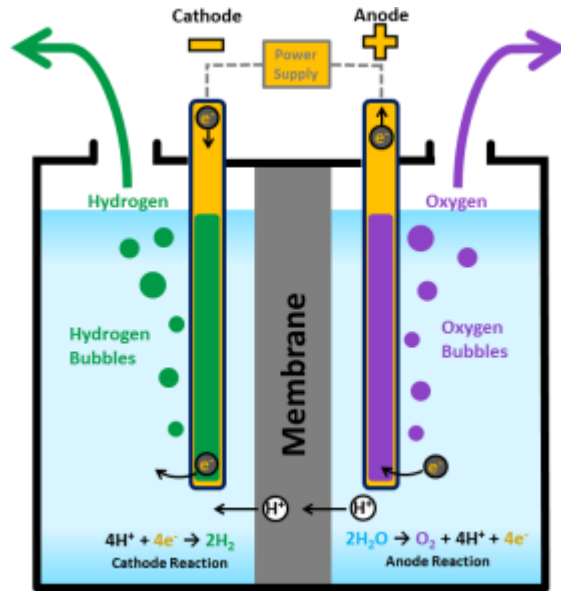


Figure 13. Water Electrolysis[28]

Producing hydrogen and using internal sources can be a key for reducing costs for the plant, decreasing the payback time and increasing efficiency of the plant.

7. Conclusion

This article includes following analysis and results:

- Extensive research on literature and recalculation of Methanol production plant from CO₂ show that it is a viable technology to utilize waste Carbon dioxide and produce clean fuel from it.
- Detailed Flow sheet of chosen technology from literature were prepared. PFD of project were created Using AUTOCAD software.
- Mass balance of all the streams were verified using Microsoft Excel software for chosen technology in order to approve the values taken from reference.
- Heat balance of all the necessary equipment were done using relevant calculations by the help of Microsoft Excel software.
- Description of streams and equipment are explained in detail for clear understanding of Process.
- Economic analysis of the plant was calculated based on real prices. Results show that Compression units take more that 50% of the investment cost. Additionally, 65% of Operating cost is the raw material “Hydrogen”
- Payback time for this project is approximated to be 3 years.
- Further researches needed to increase efficiency of plant by decreasing operating costs with advanced methods and new technologies.

SYMBOLS

Basic quantities

C	Capital cost	\$
\dot{m}	Mass flow rate	$kg \cdot s^{-1}$
Q	Power	kW
ΔT	Temperature difference	$^{\circ}C$
C_p	Specific heat capacity	$kJ \cdot (kg \ K)^{-1}$
P	Pressure	Pa
V	Volume	m^3
T	Temperature	$^{\circ}C$
ρ	Density	kg/m^3
η	Efficiency	%
h_e	Evaporation energy of water	$kJ \cdot K^{-1} \cdot mol^{-1}$
h_w	Specific enthalpy of water	kJ/kg

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LIST OF APPENDIX

- Appendix A. Mass balance
- Appendix B. Heat balance
- Appendix C. Equipment price
- Appendix D. Economical part