

Economic Analysis of production of Methanol from Natural Gas

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Abstract—Methanol has been gaining importance in the market for a decade now so this paper aims to deal with economic analysis and design aspects of large scale production of methanol from natural gas. The composition of carbon monoxide and carbon dioxide in synthesis gas is controlled to optimize the production of methanol. Heat exchanger network design using MER analysis is done for efficient heat recovery and breakeven point is estimated empirically.

Index Terms—About four key words or phrases in alphabetical order, separated by commas.

I. INTRODUCTION

Methanol is used as a raw material for many products and has hence recorded the largest growth in production over the years. The production of methanol around the globe has increased from 15.9 million tons in 1983 to 22.1 million tons in 1991. It recorded a growth rate of 11% per annum during the period of 1990 to 1995. Methanol is a key raw material for the production of methyl tert-butyl ether (MTBE), which is one of the fastest growing chemicals in the world.

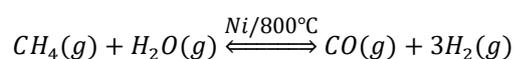
A. APPLICATIONS OF METHANOL

Methanol has the following applications:

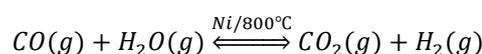
1. It is used as a reagent in several processes.
2. Methanol is used as a fuel in internal combustion engines in vehicles, aircrafts.
3. Methanol is used as a denaturing agent in synthetic ethanol.
4. Methanol is used in waste water treatment as a source of carbon to bacteria converting harmful nitrates to safer nitrogen, thus reducing the dangers of nitrification.
5. Methanol is used to produce biodiesel, in a reaction of trans esterification of lipids.
6. Methanol is used as a raw material in Direct-methanol fuel cells which is finding applications in many areas.

II. METHANOL PRODUCTION PROCESS

Synthesis gas is produced from natural gas from steam reforming. In steam reforming water and natural gas react with each other to form hydrogen and carbon monoxide in the presence of Nickel catalyst in a blast furnace at 800°C.^[6]

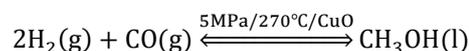


Simultaneously with steam reforming, the water gas shift reaction occurs to a certain extent. In the water gas shift reaction steam reacts with carbon monoxide to form carbon dioxide. It is very important to control the composition of carbon dioxide to carbon monoxide as only carbon monoxide reacts further with hydrogen to form methanol. The excess carbon dioxide formed in the water gas shift reaction has to be converted back to carbon monoxide by the reverse water gas shift reaction.



The synthesis gas coming after steam reforming contains traces of sulphur which have to be removed as it may lead to poisoning of the catalyst. Hence, the synthesis gas is reacted with a small amount of Hydrogen gas in the presence of cobalt-molybdenum catalyst to form hydrogen sulphide at 400°C which reacts with zinc oxide to form zinc sulphide.

The synthesis gas is then converted to methanol in a centrifugal compressor. The synthesis gas reacts in the presence of copper zinc catalyst to form methanol. This is a highly exothermic reaction where the excess heat is used to form steam for steam reforming used in the formation of synthesis gas.



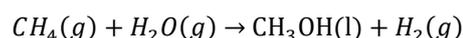
A three step distillation procedure is proposed which includes an extraction column, a refining column and a recovery column. Volatile impurities such as CO_2 , CO etc and dissolved gases are removed from the extraction column. Pure methanol is then extracted from the top of the refining column and then the recovery column is used for the separation of ethanol and methanol.

III. ECONOMIC POTENTIAL CALCULATION:

Table 1: International Values of Raw Materials and Final Products

Item	Price (\$/kg)
Methanol	0.395
Natural Gas	0.201
Hydrogen	1.8
Water	Negligible

All the above reactions sum into the final reaction as



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Assuming that the conversion in the reactor is X, the overall economic potential comes out to be a function of conversion.

$$EP = 32 * 0.395 * X + 2 * 1.8 * X - 16 * 0.201 * (1 - X)$$

$$EP = 19.456X - 3.216$$

Hence, for the process to be successful, the conversion has to be more than 16.56%. Further, we have used distillation column to separate water methanol mixture which is not a very difficult process as the relative volatility of a water methanol system is about 4.54^[7] at room temperature.

This process has been selected because it can be achieved as a continuous process and the catalysts required are cheaper than the other present methods. Further, natural gas is easier to transport than any solid product and is readily available in the market. The conversion rates can be as high as 90%^[10] which makes this process highly profitable which gives an overall economic potential of \$14.30/kg of methanol used.

IV. PROCESS FLOW DIAGRAM

Water and natural gas enter the initial mixer, which react in the reformer to form CO, CO₂ and H₂. Stream 5 coming out of the reactor is mixed with the recycle stream 14 which consist of unreacted gases. The product from the reactor (stream 9) is flashed using a flash drum to separate out the gases which are recycled back. Assuming complete separation only water and methanol are left which can be easily separated out using a distillation column as the relative volatility of water and methanol is about 4.54^[7]. It is important to understand the CO to CO₂ ratio formed in the reformer as that ratio determines the conversion rates in the final reactor.

A proposed process flow diagram has been drawn below taking into consideration the above mentioned reactions.

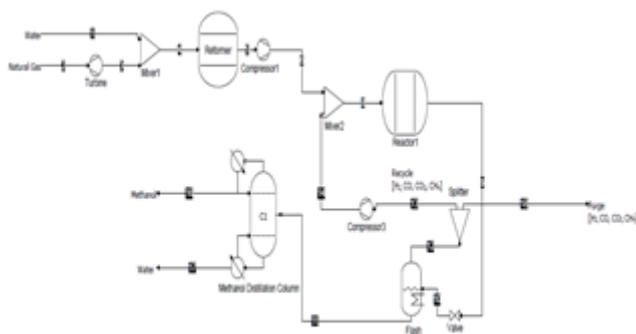


Figure 1: Process Flow Diagram for Methanol Production

V. DESIGN SPECIFICATION

The worldwide demand for methanol is roughly estimated to be about 65 million metric tons^[2]. For our process we wish to fix the amount of final production of methanol and we will like to cater to 1% of the overall demand. Thus, we will be making all mass balances taking 0.65 million metric tons per year of methanol produced as our basis.

In the first reactor where steam reforming takes place, We have assumed that the flash drum works with 100% efficiency as an initial guess so all the gases are completely separated from the product stream and it is then split into the

recycle and purge streams. Further, the distillation column works with 100% efficiency and completely separates the methanol water mixture to give us pure methanol as product. The fixed bed catalytic reactor is operated at 10-80 bar and 700° C in the presence of Ni catalyst for the methanol reaction and the water gas shift reaction. The non-ideal behaviour of the gases is predicted using Soave-Redlich-Kwong equation of state because the chemical equilibria can be described correctly by the thermodynamic data obtained from this equation as mentioned in the research paper. The natural gas fed is 95% methane, 3% ethane and rest higher hydrocarbons. Approximately 3:1 steam is to carbon ratio is fed to the mixer.^[1]

$$K_{P_1} = \left(\frac{y_{CH_3OH}}{y_{CO} y_{H_2}^2} \right)_{Eq} \frac{1}{P^2}$$

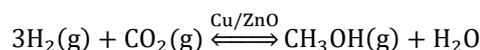
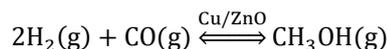
$$K_{P_1} = \left(\frac{y_{H_2O} y_{CO}}{y_{CO_2} y_{H_2}} \right)_{Eq}$$

For optimizing the production of methanol, we will have to adjust the K values in such a way that maximum amount of CO is formed which will be ensured by keeping the reaction rate of water gas shift reaction as low as possible. The selectivity of the process is given to be 60-70 % over a wide range of temperatures for the Ni catalyst.

VI. MATERIAL BALANCE

The basis for the material balance is taken to be the flow rate of methanol produced from the distillation column. The final production rate of methanol required is 0.65 million metric tons per year. We have assumed the conversion rate of CO to be around 64% and of CO₂ to be around 17% for the selectivity to be more than 60% as it was stated earlier and the economic potential to be positive^[13].

The two major reactions taking place in the reactor are



For an initial guess, at temperature 250°C it is shown that the optimum ratio of H₂: CO₂: CO entering the reactor is given by the following equation.^[11]

$$1.8 < \frac{x_{Hydrogen} - x_{CO_2}}{x_{CO} + x_{CO_2}} < 2.2$$

Let us assume that 100 moles per hour of H₂, CO₂ and CO enter the reactor according to the above relation and X moles of methane constitute the feed to the above reactor. Taking conversion of CO to be 64% and conversion of CO₂ to be 17%^[13] we get the output from the reactor as shown in the table below.

Applying Arrhenius equation for equilibrium constant as a function of temp, the temperature of the reactor is found to be 838.74°C.

VII. HEAT INTEGRATION

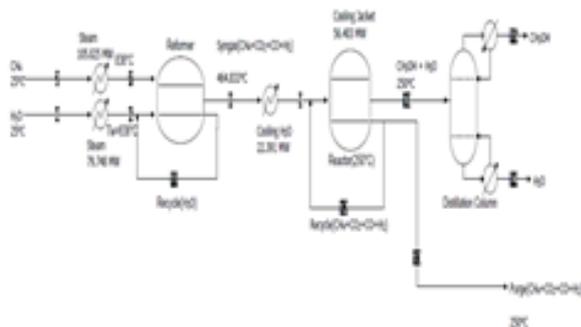


Figure 2: Proposed process flow diagram with heat integration

$$\text{Log}_{10}K_{eq} = -2.4198 + 0.0003855T + 2180.6/T \quad (T \text{ in K})^{[16]}$$

The single per pass conversion of methane is 85% and the equilibrium constant for the water gas shift reaction at this temperature is 1.05^[12]. Taking these factors into account the mole fractions of gas produced are:

Table 2: Mole Fractions of Initial Components

Component	Mole fraction
CO	0.24
CO ₂	0.06
H ₂	0.55
CH ₄	0.15

Thus, the flow rates are according to the final actual parameters:

Table 3: Flow rates of final components for the plant

Stream	Flow Rate (kmol/hr)
Process Inputs:	
CH ₄	8130.89
Water	9431.83
Process Outputs:	
Methanol	2318.78
Water (Product)	106.82
Purge:	1079.54
Hydrogen	509.52
CO	92.13
CO ₂	38.62
CH ₄	439.26
Recycle:	13797.94
Hydrogen	6370.79
CO	1151.98
CO ₂	482.90
CH ₄	5492.26
Synthesis Gas:	9565.75
Hydrogen	5261.16
CO	2295.78
CO ₂	573.94
CH ₄	1434.86

This is separated in distillation column whose designing is done using McCabe Thiele method. The distillation column calculation is done using MATLAB and no. of stages comes out to be 7.

The different streams with their respective enthalpy and Cp values are shown below. We have assumed the $\Delta T_{min} = 10$ °C. Also, we have assumed a loss of 1 °C of temperature in the reactor cooling jacket. We have used the heat of the isotropic reactor to heat the incoming streams which is represented as the 5th stream in the table shown below.

Using the Problem table algorithm we find the pinch point temperature as $T_{cold}^{pinch} = 240$ °C and $T_{hot}^{pinch} = 250$ °C. The minimum heat utilities required are $Q_c^{min} = 143.76$ MW and $Q_H^{min} = 9.36$ MW. The grand composite curve for the process is plotted below.

No loops are formed in the heat exchange network design as shown in the Process Flow Diagram so the Non Minimum Energy Requirement design is of no significance

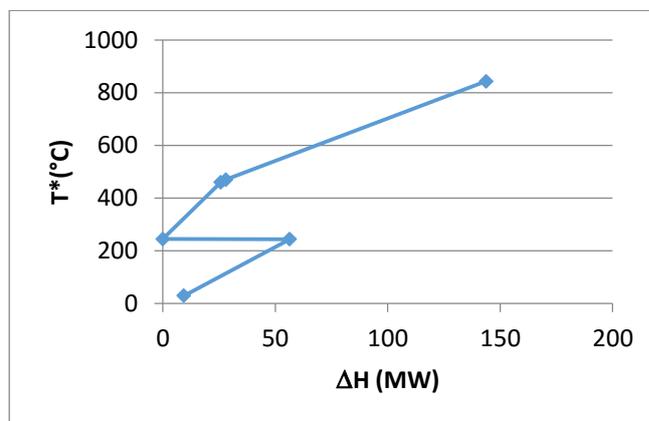


Figure 3: The Grand Composite Function

VIII. ECONOMIC ANALYSIS

A. Process Economics

1. Net Installation Cost = Summation of {Base Cost/ Purchase Cost^[20] x Multiplier^[19] (For that equipment)}

Table 4: Cost of Equipment

S. No	Name of Equipment	Purchase Cost (\$)	Multiplier	Net Installation Cost (\$)
1	2 Reactors	182,695.5	1.9	347,121.4
2	9 Heat Exchangers	295,200	1.9	560,880
3	Distillation Column	65,600	2.1	137,760

Total Installation Cost for all equipment = 1,045,761 \$

2. Total Onsite Cost/ Net Investment = 2,405,251 \$

3. Raw Materials Cost

Assuming cost of water as raw material is negligible.

Table 5: Raw Materials Cost

Raw Materials	Raw Materials Cost (\$)	Product	Revenue (\$/hr)	Net Revenue (\$/hr)	Total Operating Cost (\$/hr)
Methane	26,148.94	Methanol	103,309.38	1,046,43.7	104,595.8
		Hydrogen	1,334.272		

Total Operating Cost (Including Utilities) = 4 * Raw Materials Cost

Profit (\$/hr) = Revenue – Operating Cost = 47.883

Profit (\$/yr) = 419,455.08

Break Even Analysis

Interest rate = 10 %

Break- even Point = 2.69 years

Shell and tube heat exchanger

Let us consider heat exchanger 1

Overall heat transfer coefficient is: 30 W/(Km²)^[21]

The formula for area calculation is

$$A = \frac{Q}{U\Delta T_{LMTD}}$$

Q (MW)	22.95
T1(C)	25
T2(C)	201.53
T3(C)	250
T4(C)	249
ΔT_{LMTD} (C)	33.93

A = 22.54 m²

We are using a fixed type shell and tube heat exchanger as we require low temperature heat exchange with low temperature difference.

Purchase Costs - Shell-and-tube Heat Exchangers

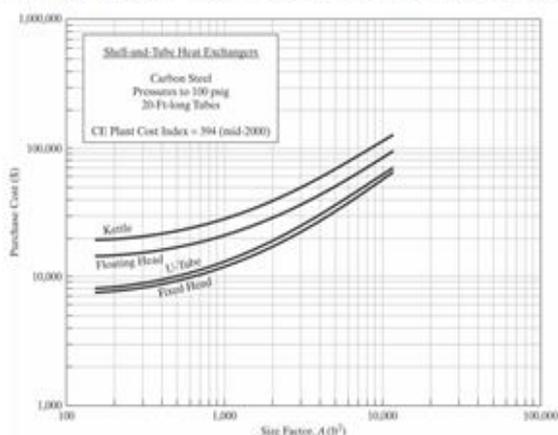


Figure 4: Purchase costs: Shell and tube heat exchangers

$$C_B = \exp\{11.0545 - 0.9228[\ln(A)] + 0.09861[\ln(A)]^2\}^{[22]}$$

Using the above graph or the correlation we get the cost of the shell and tube heat exchanger as: $C_B = \$20,289.48$

IX. CONCLUSION

The design can cater to almost 1% of the needs of the total worlds requirement. Total investment required for the plant was estimated empirically which includes all equipment costs and installations excluding in the land cost in the investment required as land is itself an asset whose value keeps on increasing with time. The breakeven point for the plant was calculated using these, which comes out to be about 2.69 years and is in accordance with real reported values of industry. It is shown that the current process is the most cost efficient with an added advantage of MER design of heat exchanger network.

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