

Energy and Conversion Investigations of Different Process Configurations for Hydrogenation of CO₂ into Methanol from Industrial Flue Gases

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Utilization of CO₂ into sustainable energy carriers results into achievement towards near zero emissions level. Complementary with its environmental benefits, methanol becomes a virtuous candidate to make a profitable business by CO₂ hydrogenation process. This study illustrates various process configurations: water removal and carbon capture by MEA absorption from industrial flue gases with evaluation of its effects on the methanol total conversion and energy consumptions. Our source of CO₂ is from 349 t/h flue gases released from power plant using natural gas as burning source for producing electricity with a capacity of 122 MW while CO₂ represents (15 %) of the total stream. Unconventional cheap source of hydrogen comes from chlor-alkali process as a by-product is proposed for hydrogenation. Modeling of this process is conducted with Aspen HYSYS® v8.6 simulation software (Advanced System for Process Engineering) which helps significantly to analyze the results. Sensitivity analysis is carried out to evaluate different parameters effect on the reactions and total productivity.

1. Introduction

Global temperature increase is one of the major consequences of Greenhouse Gas (GHG) emissions concentration growth through the last decade. Minimizing carbon dioxide (CO₂) concentration as a GHG, in the atmosphere has become a significant challenge among researchers and scientists. Besides its natural occurring, more CO₂ emissions occurred by burning fossil fuels, biomass and combustion of fuels which is equivalent to 7 Gt every year of anthropogenic CO₂ (Aresta, 2010). With that high rise of CO₂ emission, Carbon capture either chemically (Rivera-Tinoco and Bouallou, 2010) or by underground storage in geological reservoirs (Câmara et al., 2013) is decisive. By 2050, 19 % reduction of emissions shall be achieved to accomplish the 2 °C target of COP 21 agreement (Yu et al., 2012).

CO₂ conversion to fuels through hydrogenation to alcohols, hydrocarbons and DME (Dimethylether) or formic acid is a hot research topic with minimization of hydrogen (Kondratenko et al., 2013). CO₂ sources are plenty but featured processes of hydrogen are like steam methane reforming, partial oxidation of light residues, dry reforming, water electrolysis or coal gasification (Jadhav et al., 2014). This study proposes cheap source of hydrogen, which is available as by-product from chlor-alkali production. However, the direct use of water saturated hydrogen stream has a drawback on the chemical equilibrium, which should be separated first. (Kiss et al., 2016)

In this study, we investigated solutions for CO₂ emissions from industrial power plant flue gases to produce methanol through CO₂ hydrogenation by unconventional wet hydrogen from chlor-alkali process. Two different processes configurations are proposed with comparing the advances of capturing CO₂ to enhance productivity and conversion of liquid methanol as a major petrochemicals source. Aspen HYSYS® simulation software is used to perform and assess the two process flowsheets with sensitivity analysis of reactor modelling to choose the best conditions for the reactions. Data input for this study originally reported by (Abdelaziz et al., 2017).

2. Processes description

Flue gas is fed at 91.3 kPa, 95 °C and hydrogen at 100 kPa, at 40 °C. Flue gas is compressed to 75 bar in a series of compressors with intercooling to 40 °C. Hydrogen is compressed to 75 bar in four consecutive stages. The two gases are mixed (MIX-100). The stream is then heated (E-100) to 250 °C and injected into the fixed bed adiabatic reactor. The gases leaving the reactor are cooled (E-104) to 40.4 °C. Afterwards it heads to two flash separators (V-100) and in between the isenthalpic valve to decrease the pressure and releases light ends hydrogenation of CO₂ into methanol from industrial flue gases, Chemical Engineering Transactions, 70, 1345-1350

(unreacted CO₂ and Nitrogen). After the heater (E-105) the stream enters 10 stages distillation column (T-100) at 80 °C and 120 kPa. The methanol exits at the top and 99 % of the water as residue from the bottom. Water removal process configuration has the same operating conditions however; it includes three flash separators before each compressor stage (V-103, V-104, and V-105) to separate water from the remainder of the flue gases. This approach decreases the compressors heat load and compression ratio also the heat load of intercooling processes. Table 1 shows streams data input.

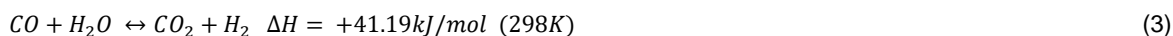
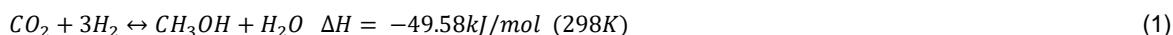
Table 1: Data of the flue gases and hydrogen streams

Parameter	Flue gas	Hydrogen gas
Flowrate (kg/h)	3.49 x 10 ⁵	9.33 x 10 ³
Pressure (kPa)	91.3	100
Temperature (°C)	95.2	45
Molar Composition (%)		
CO ₂	15	-
H ₂ O	6.5	-
N ₂	74.69	-
O ₂	3.75	-
H ₂	0	100

2.1 Carbon dioxide hydrogenation into methanol

Primarily, Gibbs equilibrium reactor has been modeled in terms to converge other process equipment in the process flowsheet and to define different operating conditions on the methanol conversion then a plug flow reactor was simulated with heterogeneous catalysis type that is based on specific kinetic model.

The kinetic model was adopted using commercial Cu/ZnO/Al₂O₃ catalyst with original kinetic employment from (Vanden Bussche and Froment, 1996) with further rearrangements by (Van-Dal and Bouallou, 2013). Further details on the reactor modelling illustrated at section 3.1.



2.2 Chlor-Alkali Process

Hydrogen produced as a by-product from Chlor-alkali electrolysis process, which has three main different technology approaches mercury cell technique, which is obsolete, diaphragm technique and membrane cell technique (Brinkmann et al., 2014). Figure 1 illustrates the block flow diagram for the process of producing chlorine mainly and sodium hydroxide when hydrogen produced as a by-product thus; its valorization is an efficient option for introducing hydrogen for hydrogenation of carbon dioxide at no cost (Kiss et al., 2016). Comparing with other researchers that suggested H₂ sources from fossil fuels or electrolysis of water and the amount required for hydrogenation process is much less than available from the local facility generation.

3. Process Simulation and results

In terms of identifying process and energy streams, install process equipment for the flowsheet, conduct different case studies, describe simulation basis, define reaction sets, evaluate variables and different scenarios, steady state simulation is used.

Firstly, two different fluid packages were opted for the simulation work. Due to its accurate dealing with aqueous real systems containing methanol and accurate prediction for hydrocarbon phase behaviour, Peng–Robinson–Stryjek–Vera equations of state (PRSV EOS) is chosen as a fluid package for methanol synthesis. (Acid Gases EOS) fluid package is chosen because it has shown to predict experimental results accurately of treating liquid hydrocarbons with amine solvents.

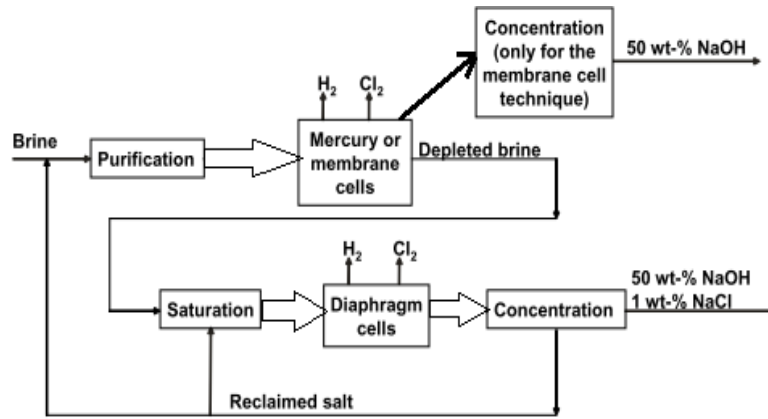


Figure 1: Block Flow diagram of the integration of the membrane or mercury and the diaphragm cell techniques

3.1 Reactor modeling and sensitivity analysis results

To successfully model the reaction a sensitivity study should have been conducted to select a specific pressure and temperature for the reaction. (Vanhove and Matos, 2015) has reported high CO₂ conversion and methanol selectivity with very high operating pressures. The rate equations for carbon hydrogenation into methanol represented by equations (4-8) in which pressures are expressed in bar and temperatures in K with rate constants mentioned in Table 2. However, it cannot be implemented directly in Aspen HYSYS[®] simulation without further adjustments. The new constants have been calculated using hand calculations and entered inside Hysys with respect to the units of pressure and reaction rates in mol/kg_{cat}/s (Vanden Bussche and Froment, 1996). The reaction basis is partial pressure and base component is CO₂ for the three reactions combined in two main reactions inside Aspen HYSYS[®] with respect to stoichiometry. Figure 2 and Figure 3 illustrate the conversion for the 2 reactions (Methanol synthesis as 1st reaction and RWGS as 2nd reaction) with Temperature and pressure respectively. The CO₂ conversion into methanol uses the plug flow reactor PFR-100-2 which is for the carbon capture case. The case specs described at Table 3.

Methanol synthesis

$$r_{CH_3OH} = \frac{k_1 P_{CO_2} P_{H_2} \left(1 - \frac{1}{K_{eq1}} \frac{P_{H_2O} P_{CH_3OH}}{P_{H_2}^3 P_{CO_2}} \right)}{\left(1 + k_2 \frac{P_{H_2O}}{P_{H_2}} + k_3 P_{H_2}^{0.5} + k_4 P_{H_2O} \right)^3} \left[\frac{mol}{kg_{cat} \cdot s} \right] \quad (4)$$

Reverse water gas shift reaction

$$r_{RWGS} = k_5 P_{CO_2} \left(1 - \frac{K_{eq2} P_{H_2O} P_{CO}}{P_{CO_2} P_{H_2}} \right) \left[\frac{mol}{kg_{cat} \cdot s} \right] \quad (5)$$

$$k_i = A_i \exp\left(\frac{B_i}{RT}\right) \quad (6)$$

$$\log_{10} K_{eq1} = \frac{3066}{T} - 10.592 \quad (7)$$

$$\log_{10} \frac{1}{K_{eq2}} = -\frac{2073}{T} + 2.029 \quad (8)$$

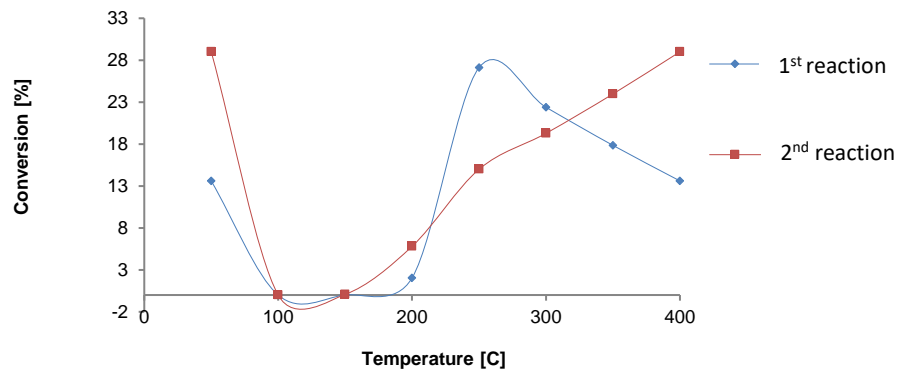
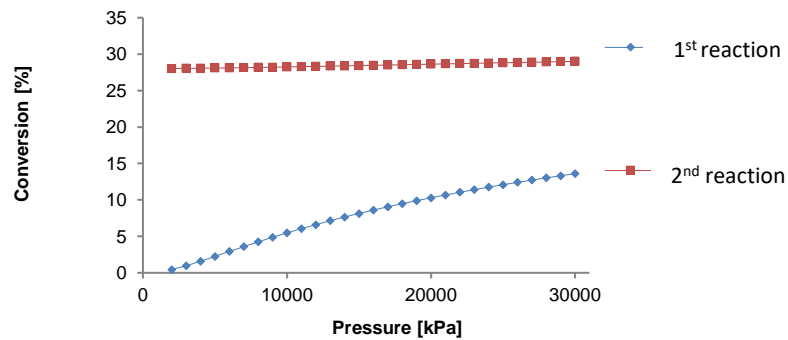
k_i , P_i , K_{eq} represent respectively kinetic model constant, partial pressure and thermodynamic equilibrium constant.

Table 2: Parameters for kinetic model kinetic model [B_i given in J/mol].

k_1	A_1	1.07
	B_1	40,000
k_2	A_2	3,453.38
	B_2	—
k_3	A_3	0.499
	B_3	17,197
k_4	A_4	6.62×10^{-11}
	B_4	124,119
k_5	A_5	1.22×10^{10}
	B_5	-98,084

Table 3: Reactor and catalyst specs

Parameter	Value
Tube inside Diameter (mm)	21.2
Tube Length (m)	10
Number of tubes	11,643
Particle Diameter (m)	0.00574
Solid Catalyst Density (kg/m ³)	1,775

Figure 2: Temperature effect on limited reactant CO₂ conversion into methanol for combined reactionsFigure 3: Pressure effect on limited reactant CO₂ conversion into methanol for combined reactions

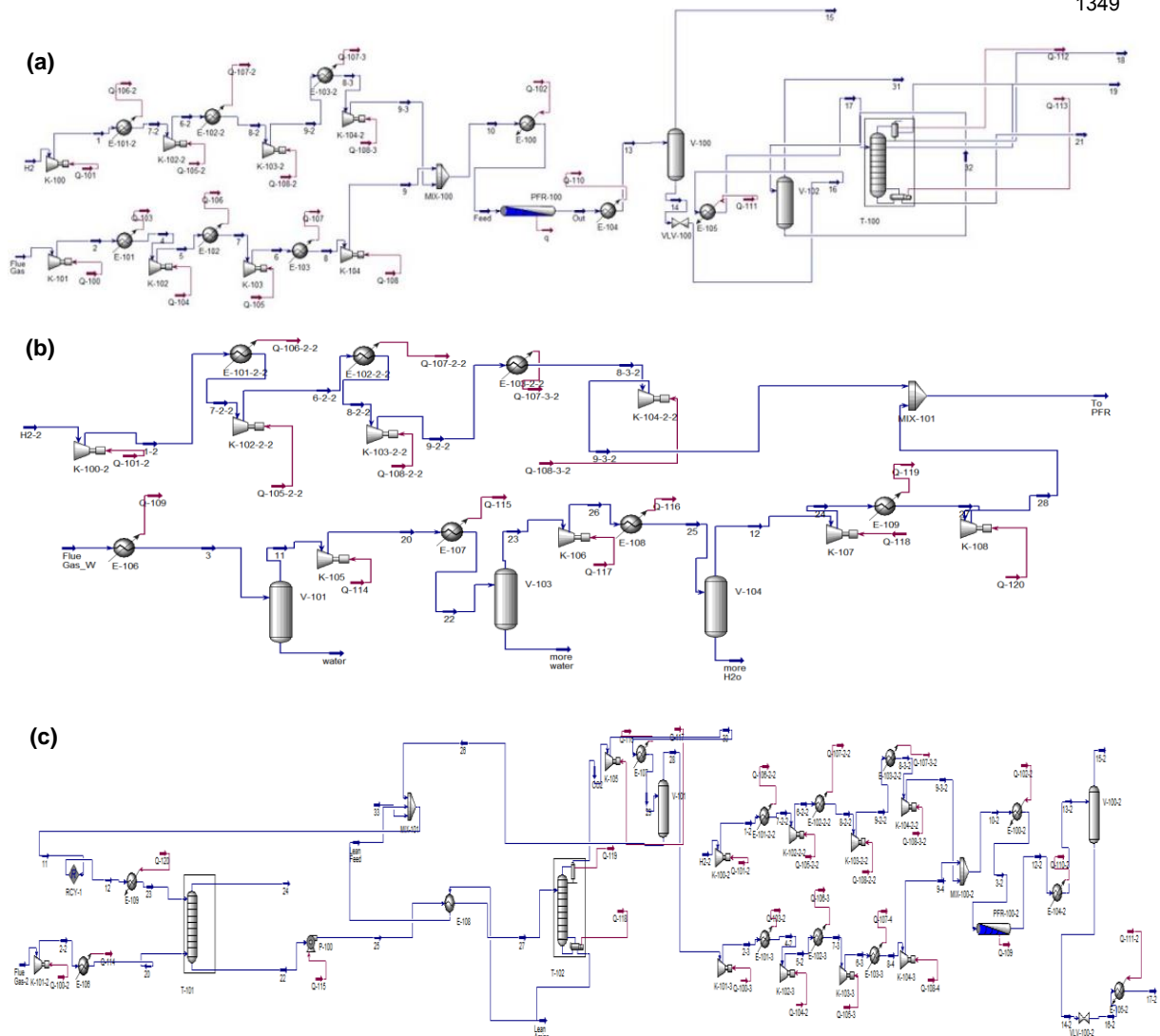


Figure 4: (a) Process Flowsheet of Base Case study. (b) Process Flowsheet of Water Removal Case study. (c) Process Flowsheet of Carbon Capture case study

3.2 Carbon capture results

As aforementioned, an effective configuration for the base case process has been introduced as a second case study for carbon capturing from flue gases to increase product quantity and reaction conversion. In our case, the Monoethanolamine (MEA) absorption has 88 % recovery. However, it has drawbacks like solvent loss, degradation and significant energy expenditure (Perevertaylenko et al., 2014). More investigation into energy analysis and minimization for optimizing energy consumption for the unit could have been conducted furtherly. Moreover, more developments in this aspect are conducted and reported into achievements by systematic and process modifications for improving energy efficiency (Ferrara et al., 2017). In another way of differentiating from the base case, CO₂ is captured by the absorber column T-101 (Figure 4) with 1,677 t/h feed (stream 22) which contains (43.72 % mole fraction) diluted MEA at 40 °C and 101 kPa with 2 t/h fresh amine. The flue gases are compressed to atmospheric pressure and 40 °C to meet the conditions inside the column, which is 10 stages tower operated at 101 kPa.

The rich amine exits the column with 83 % of CO₂ in the flue gases (stream 22) at 59 °C to be pumped to 200 kPa and heated to 90 °C to enter the distillation column T-102. T-102 is 10 stages distillation column to separate the lean amine stream (recycled stream) from CO₂ stream, which continues to a compressor, and flash vessel. To be separated from water and compressed then mixed with hydrogen to the reactor PFR-100-2 as the same base case of the flue gases. Results obtained shown in Table 4 with comparison with (Abdelaziz et al., 2017) which the data inputs were based on.

Table 4: Comparison between results obtained from this study and (Abdelaziz et al., 2017)

Parameter	Base Case	Water removal	CO ₂ Capture
Conversion (%)	25.03	38.96	63.12
(B)	65.4	67.6	99.74
Electricity (MW)	97.2	69.4	46.5
(B)	86.3	72.1	38.7
Q _c (MW)	162	314.9	235
(B)	180.28	151.9	99.4
Q _h (MW)	107	113	197
(B)	51.6	52.5	99.72

(B) Results obtained by (Abdelaziz et al., 2017)

4. Conclusions

Inspired by environmental challenges, investigations of methanol production from industrial flue gases were carried out in this work through process simulation. Different process configurations have been assessed in this study towards enhancements of CO₂ utilization. Detailed economic and environmental outlooks could be furtherly investigated to choose the most environmental and efficient process configuration. Meanwhile, Carbon capture has the highest conversion 63 % and thus the highest productivity but it has a significant high-energy usage Q_h 197 MW that is equivalent to higher CO₂ emissions. Therefore, it would not be the best solution for environmental point of view. Moreover, with further energy integration and economic analyses (water removal) configuration could be the best choice for both economic and environmental perspectives.

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