Simulation of Methanol Synthesis in Packed Bed Reactor for Utilization of CO_2 from Acid Gas Removal Unit

Bayu Sari Adji[1,*], *Yuswan* Muharam[1] and *Sutrasno* Kartohardjono[1]

[1]University of Indonesia, Chemical Engineering Department, 16424 Depok, Indonesia

Abstract. There are many oil and gas fields in Indonesia which contain high CO_2 that need to be treated. The Acid Gas Removal Unit (AGRU) is installed to remove the CO_2. The AGRU will release the CO_2 gas from the regeneration column. It still contains a high concentration of CO_2 (higher than 80%). The accumulation of CO_2 emission to the atmosphere will impact the environment. To promote environment-friendly technology, the process can be improved with conversion of CO_2 into methanol. It will provide a relatively closed loop of the carbon cycle and as a renewable energy alternative. This study aims to provide packed bed reactor design which can be implemented in the small-scale methanol production plant utilizing high CO_2 feed gas. The reactor temperature was varied from 200°C to 250°C and pressure were operated in the range of 40 Bar up to 75 Bar. These variations were used to analyze the effects of methanol production. The simulation results showed that peak methanol production rate was achieved at the temperature around 230°C. As the conclusion, the reactor showed better performance at the higher pressure and higher temperature although the reaction is exothermic including the recycling process can reduce the cost of hydrogen.

Keywords: methanol synthesis, packed bed reactor, renewable energy, production rate.

1 Introduction

In oil and gas industry, the well fluid is processed to remove unnecessary impurities such as CO_2[1] from the natural gas prior to deliver the sales gas to the gas buyer to meet the quality as required by the gas sales specification.

The sour gas which contains high CO_2 component is mostly removed from the gas stream utilizing acid gas removal unit (AGRU). The membrane-based gas liquid contactor recently also studied as the alternative technology for removing CO_2 from natural gas[2]. AGRU also used in coal gasification process to capture CO_2[3]. The regeneration columns in AGRU will release a high concentration of CO_2 that removed from the feed gas stream including water and some non-condensables to the atmosphere. The current increasing CO_2 in the atmosphere is believed to impact the environment as greenhouse gas emission affecting the global climate change[4].

The CO_2 can be converted into other compounds through chemical processes which one of them is by hydrogenation process into methanol[5]. The released CO_2 can be captured and convert into methanol utilizing $Cu.ZnO.Al_2O_3$ as the catalyst in the hydrogenation process. The produced methanol can be converted further into DME which also beneficial chemical intermediate as well as energy resource[6]. The process will involve the following chemical reactions in the catalytic reactor of CO_2 hydrogenation process to produce methanol.

$$CO_2 + 3H_2 \leftrightarrow CH_3OH + H_2O \quad \Delta H^o_{rxn} = -49 \text{ kJ/mole} \quad (1)$$

$$CO + 2H_2 \leftrightarrow CH_3OH \quad \Delta H^o_{rxn} = -90 \text{ kJ/mole} \quad (2)$$

$$CO_2 + H_2 \leftrightarrow CO + H_2O \quad \Delta H^o_{rxn} = 41 \text{ kJ/mole} \quad (3)$$

Referring to the previous study by Sutrasno and Bayu [7], a typical feed gas composition which contains more than 80% CO_2 and operating condition coming from the AGRU unit can be presented in Table 1 and Table 2 which were used as the basis of this study.

The CO_2 stream sourced from AGRU is considered free substance. However, the hydrogenation process will also need H_2 feed stream. Currently, the H_2 stream in the petrochemical industry is generated from the steam reforming process of the natural gas. The other alternative process uses water electrolysis[8] which requires electric power to generate. This study assumed the hydrogen were sourced from steam reforming of the fuel gas as the natural gas fuel is available normally in AGRU utilities. As steam reforming of natural gas is required significant investment, this study attempts to use minimum case for the hydrogen consumption.

* Corresponding author: bayusa93@gmail.com

Table 1. Feed gas composition.

Composition	Mol %
CO_2	86.5923
H_2O	11.3495
CH_4	2.0523
C_2H_6	0.0057
C_3H_8	0.0002

Table 2. Feed gas operating condition.

Parameter	Value
Reactor inlet pressure (Bar)	50
Temperature (^oC)	232
Flow of CO_2 stream (MMSCFD)	5
Flow of H_2 stream (MMSCFD)	10

This study aims to propose a packed bed reactor design for the small-scale methanol production plant utilizing high CO_2 acid gas released from typical AGRU in oil or gas industries.

This study uses UniSim software to perform process simulation for the process of converting the CO_2 content in the gas stream into methanol. The gas composition in the previous Table 1 is used as the feed gas stream in the simulation. The steady-state reactor inlet stream data come from the UniSim process simulation are later taken as the feed gas into the packed bed reactor which was modeled in COMSOL. The COMSOL reactor simulation is used to study the predicted performance of the designed reactor to produce the desired methanol which will be reported in the next section.

2 Reaction kinetics

The reactions of methanol synthesis (1),(2) and reverse water gas shift reaction (3) occur in the methanol synthesis reactor. In the current petrochemical industry, methanol is produced by hydrogenation of CO or CO_2 over a Cu-based catalyst in a multi-tubular reactor or quenched bed reactor. The packed bed experiment has been developed also in 1996 by Froment et.al[9].

The followings are the kinetic model proposed by Froment et.al[9].

$$r_{CH_3OH} = \frac{k'_{5a}K'_2 \; K_3K_4K_{H_2}p_{CO_2}p_{H_2}\left[1-\frac{1}{K}*\left(\frac{p_{H_2O}\;p_{CH_3OH}}{P^3_{H_2}p_{CO_2}}\right)\right]}{\left(1+\left(\frac{K_{H_2O}}{K_8K_9K_{H_2}}\right)\left(\frac{p_{H_2O}}{p_{H_2}}\right)+\sqrt{K_{H_2}}\sqrt{p_{H_2}}+K_{H_2O}\;\;p_{H_2O}\right)^3} \quad (4)$$

$$r_{RWGS} = \frac{k'_1p_{CO_2}[1-K^*_3)\left(\frac{p_{H_2O}\;\;p_{CO}}{p_{H_2}p_{CO_2}}\right)}{\left(1+\left(\frac{K_{H_2O}}{K_8K_9K_{H_2}}\right)\left(\frac{p_{H_2O}}{p_{H_2}}\right)+\sqrt{K_{H_2}}\sqrt{p_{H_2}}+K_{H_2O}\;\;p_{H_2O}\right)} \quad (5)$$

3 Methods

The process simulation study was performed using UniSim Design R390.1. The flow of the CO_2 feed gas with the operating parameter as shown in Table 2 is mixed with the hydrogen stream under several stoichiometric ratios from 0.5 to 3, prior to entering the single pass fixed bed catalytic reactor.

The kinetic parameters developed by Froment et.al.[9] were used for the kinetic parameter of UniSim reactor design module. The simulation cases with or without the recycle stream of unconverted hydrogen were studied. The selected case was used as the basis of COMSOL reactor design which was performed using COMSOL Multiphysics 5.3 to represent a real reactor. COMSOL has been widely used nowadays to rigorously model the mass, momentum and heat transfer in the 3D modeling environment. The scale-up modeling from the lab-scale experiment into the plant scale can also be performed using COMSOL with using similarity of governing dimensionless number such as Reynolds and others in the design[10].

The process simulation study uses Peng-Robinson-Stryjek-Vera (PRSV) as the equation of state. The UniSim model of methanol synthesis process with a packed bed reactor is shown in Figure 1.

4 Result and discussion

The results of process simulation using UniSim are presented in Table 3 which summarized the main inlet stream data of the methanol synthesis reactor to be used as basic data for COMSOL input parameter.

The methanol production from the simulation study presented in Table 3 for the ideal stoichiometric ratio of H_2 feed stream with the CO_2 feed stream of 15 MMSCFD to 5 MMSCFD (the ratio of 3), for the case without recycling mode, it can be surpassed by the ratio of only 1 with recycling mode. Therefore the further COMSOL simulation study uses the UniSim simulation result with the flow of 5 MMSCFD for both feed stream with recycling mode as the basis for the reactor modeling.

Table 3. Methanol production with variation of H_2 feed stream flowrate at 50 Bar and 232 ^oC.

	Unit	Flow of H_2 feed stream (MMSCFD)			
		15	10	5	2.5
H_2	%mol	76.9	61.8	37.08	21.61
CO_2	%mol	16.65	30.12	54.35	70.42
CO	%mol	4.40	5.38	5.25	4.33
Methanol rate (without Recycle)	Kgmol /hr	37.60	26.84	13.77	6.08
Methanol rate (with Recycle)	Kgmol /hr	170.83	126.59	70.79	35.84

The methanol production profile as the effect of the variation of pressure from 40, 50 to 75 Bar and also the temperature of 200 ^oC, 232 ^oC, and 250 ^oC were presented in Figure 2.

The methanol production profile increases if the pressure to the reactor is increased. However, the production of methanol decreases when the increased temperature exceeding 232 ^oC. This phenomenon caused by the exothermic nature of the reaction. The catalyst will be more active with the increase of the temperature. However, to a certain limit of temperature, the exothermic reaction will then provide no further increase in the conversion and instead will decrease the production. This aligned with the result of the previous study by A Kiss et.al[11] and Sutrasno et al[7].

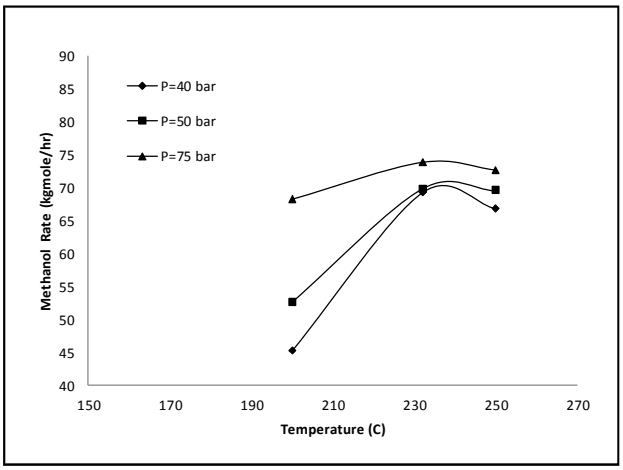

Fig. 2. Methanol production (Kgmol/hr)

For the COMSOL reactor modeling the operating conditions as mentioned in Table 2 were used with the H_2 feed stream rate of 5 MMSCFD. The gas composition of CO_2, H_2, and CO at the inlet stream to the reactor was taken from the UniSim simulation result as tabulated in Table 3.

COMSOL 2D axisymmetric geometry was used to model the cylindrical packed bed reactor. The following design parameter as mentioned in Table 4 was also set for the model. The molar flow of 2484 Kgmol/hr was the total flow entering the reactor as calculated by UniSim. The volumetric flow rate corresponds to this molar flow rate is 0.579 m^3/s. The condition of pressure and temperature used the same basis as in the previous Table 2.

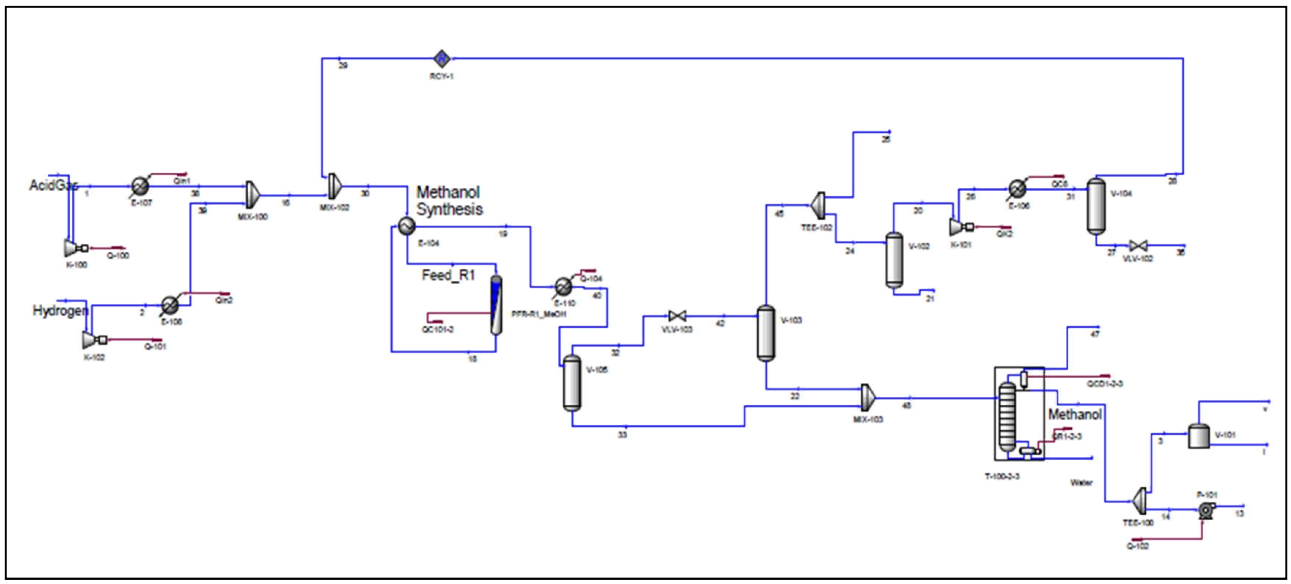

Fig. 1. Process flowsheet of methanol synthesis in UniSim with recycle process

Table 4. Design parameter

Parameter	Value
Molar flow (Kgmol/hr)	2484
Volumetric feed rate (m^3/s)	0.579
Temperature (^oC)	232
Pressure (Bar)	50
Diameter (m)	1
Height (m)	25

COMSOL can calculate and present the methanol concentration profile inside the reactor as can be seen in Figure 3 and 4. The concentration of methanol gradually increased as feed gas flow from the bottom of the reactor through the catalyst bed. The produced methanol concentration can be multiplied by the volumetric rate of the fluid to obtain the molar flow rate of methanol.

The result of methanol production coming from the packed bed reactor is 70.9 Kgmol/hr which is very close to the rate calculated by UniSim of 70.79 Kgmol/hr. The reactor sized with a diameter of 1 meter and height of 25 meters can achieve the desired conversion. However, since the reactor will be relatively tall therefore it is recommended to install 2 reactors in series with its height of 12.5 meters each. The configuration of 2 reactors with a diameter of 1 meter and height of 12.5 meters in series will be better constructibility compared with a single reactor with 25 meters height. Therefore it is the selected design size for the packed bed reactor dimension in order to achieve the desired conversion and production of the methanol in this study condition.

In the future study, the length can be further optimized by performing several process intensification efforts. As for the current process simulation study the reactor design only considers a single pass conversion of catalyst in the packed bed, therefore the methanol production can still be further improved in the future study by increasing the passes as well as provide multibed configuration of the catalytic reactor.

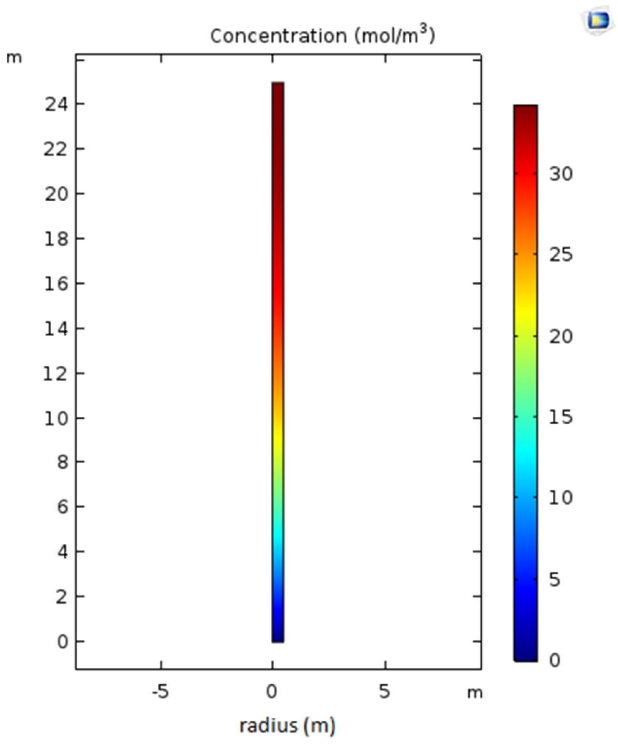

Fig. 3. Methanol concentration profile in the reactor (mol/m^3)

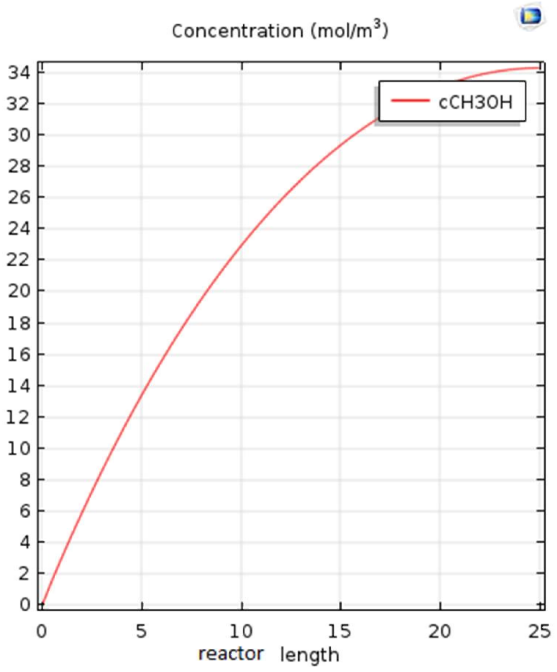

Fig. 4. Methanol concentration profile in the reactor (mol/m^3)

5 Conclusion

The process simulation result shows the peak production of methanol was obtained at the reactor temperature of around 232 ^{o}C at 50 Bar. The increase in pressure will also increase the methanol production. The H_2 feed flow rate can be reduced by utilizing the recycling process in the design flowsheet. The use of minimum hydrogen will save some investment for the utilization of released CO_2 from AGRU for the methanol production.

The authors acknowledge financial support for this work from the Universitas Indonesia through Hibah PITTA 2018 No. 2572/UN2.R3.1/HKP.05.00/2018.

References

[1] S. Dara and A. S. Berrouk, *"Computer-based optimization of acid gas removal unit using modified CO2 absorption kinetic models*," International Journal of Greenhouse Gas Control, vol. **59**, pp. 172-183, (2017).

[2] S. Kartohardjono, A. Paramitha, A. A. Putri, and R. Andriant, *"Effects of Absorbent Flow Rate on CO2 Absorption through a Super Hydrophobic Hollow Fiber Membrane Contactor*," International Journal of Technology, vol. Volume **8**(8), pp. 1429-1435, (2017).

[3] X. Liu, S. Yang, Z. Hu, and Y. Qian, *"Simulation and assessment of an integrated acid gas removal process with higher CO2 capture rate*," *Computers & Chemical Engineering,* vol. **83**, pp. 48-57, 2015/12/05/ (2015).

[4] E. L. Fornero, D. L. Chiavassa, A. L. Bonivardi, and M. A. Baltanás, *"CO2 capture via catalytic hydrogenation to methanol: Thermodynamic limit vs. 'kinetic limit'*," *Catalysis Today,* vol. **172**, pp. 158-165, 2011/08/25/ (2011).

[5] X. An, Y. Zuo, Q. Zhang, and J. Wang, *"Methanol Synthesis from CO2 Hydrogenation with a Cu/Zn/Al/Zr Fibrous Catalyst,"* Chinese Journal of Chemical Engineering, vol. **17**, pp. 88-94, 2009/02/01/ (2009).

[6] G. Bonura, C. Cannilla, L. Frusteri, A. Mezzapica, and F. Frusteri, *"DME production by CO2 hydrogenation: Key factors affecting the behaviour of CuZnZr/ferrierite catalysts*," *Catalysis Today,* vol. **281**, Part 2, pp. 337-344, (2017).

[7] B. S. Adji and S. Kartohardjono, "Process Simulation of CO2 Utilization from Acid Gas Removal Unit for Dimethyl Ether Production," Journal of Environmental Science and Technology, vol. **10**, pp. 220-229, (2017).

[8] D. Symes, B. Al-Duri, A. Dhir, W. Bujalski, B. Green, A. Shields, *et al.*, *"Design for On-Site Hydrogen Production for Hydrogen Fuel Cell Vehicle Refueling Station at University of Birmingham, U.K*," *Energy Procedia,* vol. **29**, pp. 606-615, 2012/01/01 (2012).

[9] G. H. Graaf and A. A. C. M. Beenackers, *"Comparison of two-phase and three-phase methanol synthesis processes,"* *Chemical Engineering and Processing: Process Intensification,* vol. **35**, pp. 413-427, (1996).

[10] Y. Muharam and A. Kurniawan, *"Computational Fluid Dynamic Application in Scale-up of a Stirred-batch Reactor for Degumming Crude Palm Oil,"* International Journal of Technology, vol. Volume **7**, pp. 1344-1351, (2016).

[11] A. A. Kiss, J. J. Pragt, H. J. Vos, G. Bargeman, and M. T. de Groot, *"Novel efficient process for methanol synthesis by CO2 hydrogenation*," Chemical Engineering Journal, vol. **284**, pp. 260-269, 1/15/ 2016, (2016).