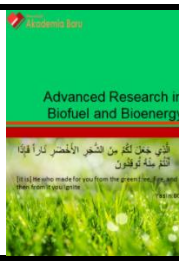
Penerbit Akademia Baru

Journal of Advanced Research in Biofuel and Bioenergy

Journal homepage: www.akademiabaru.com/arbb.html
ISSN: 2600-8459



Optimization of Methanol Production using Aspen Plus

Norul Suhada[1], Nurfatin Azma[1], Maizirwan Mel[1,*], Sarina Sulaiman[1]

[1] Dept. of Biotechnology Engineering, Kulliyyah of Engineering, International Islamic University Malaysia

ABSTRACT

Methanol has wide application include to be use as fuel, biodiesel and solvent. The purpose of this research was to convert biogas to methanol using Aspen Plus simulation and to optimize methanol production through Design Expert (DOE) software. The optimization was done by varying two parameters, pressure and temperature. The simulation consists of three-unit operations include water scrubber, pressure swing adsorption (PSA) and methanol reactor. First and foremost, biogas entered water scrubber and it would discard acid gases. The remaining gas include methane and carbon dioxide was moved into PSA with alumina as adsorbent. The purpose of PSA was to adsorb carbon dioxide from the stream. After that, carbon dioxide would react with hydrogen to produce methanol under specific temperature and pressure. The simulation was repeated with different value of pressure and temperature of methanol. The methanol production was recorded. Lastly, optimization of methanol was done by Design Expert (DOE) software. Based on the result of DOE, the relationship between pressure and temperature has been observes. For methanol production, it has been observed that carbon dioxide hydrogenation favor at high pressure and low temperature. At 170 ℃ in temperature and 80 bar of pressure, 24 kg of methanol was recorded in which it was the highest mass of methanol produced.

Keywords:
Methanol; pressure; and temperature;
Aspen Plus

Received: 2 May 2020 **Revised: 1 June 2020** **Accepted: 25 June 2020** **Published: 28 June 2020**

1. Introduction

Nowadays, people depend on the fossil fuel solely for fuel of vehicle whereas it is currently depleting day by day. As a result, many researches have been done to replace fossil fuel with renewable energy. One of possible sources that can replace fossil fuel is methanol [1]. Methanol is known as wood alcohol and methyl alcohol in which it has been used as fuel, biodiesel and solvent [2]. Pure methanol can be used as a fuel in vehicles and aircraft by directly combusted in the engine while methanol that undergo reaction of transesterification of lipids can be used as biodiesel [3]. This shows that the production of methanol is an important step in enhancing of renewable energy field.

There are many applications of methanol such as an antifreeze in pipelines and windshield washer fluid [4]. Also, a small amount of methanol is added in some wastewater treatment plants. The purpose of the methanol addition is to supply a food source of carbon for the denitrifying bacteria, which convert nitrates to nitrogen to reduce the denitrification of sensitive aquifers [5].

* *Corresponding author.*
E-mail address: maizirwan@iium.edu.my

Besides, methanol is also a common laboratory solvent due to its low UV cut off, thus it is useful for HPLC and UV/VIS spectroscopy [6].

A proposed raw material for methanol production was biogas. Biogas can be obtained after organic waste decomposition through anaerobic digestion [7]. In Malaysia, there are abundance of biogas include biogas released from palm oil industry. According to Malaysian Palm Oil Board (MPOB), there are 453 mills in 2016. Nevertheless, only half of the biogas produced is utilized for energy production of the plant whereas another opts to flare the gas. They choose to flare the gas because it is relatively less of a hassle and inexpensive [8]. However, if biogas is released to the environment, it can create environmental problem including global warming. Moreover, biogas has high calorific value in which can be harnessed as a fuel [9]. It is a waste to be released to the environment without using it as a source of renewable energy.

In International Journal of Hydrogen, method of methanol production from biogas is discussed in detail [10]. The production plant consists of several main equipment which are renewable system, H_2 production system, Biogas inlet, gas cleaning section, gas mixer and methanol production system as shown in Figure 1.

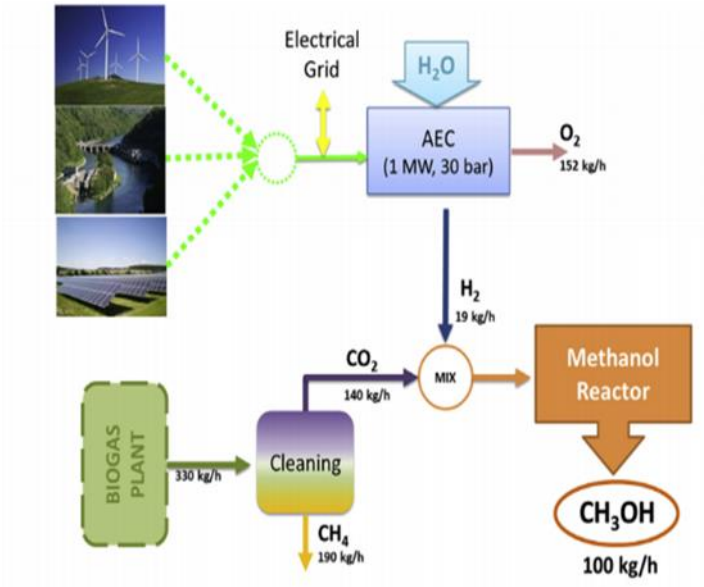


Fig. 1. Process of methanol production

Methanol production through direct carbon dioxide hydrogenation attract many parties due to several reasons. First and foremost, methanol is a starting feedstock for numerous important chemicals include formaldehyde, acetic acid, Methyl tert-butyl ether (MTBE) and light hydrocarbons (ethylene and propylene) [11]. Secondly, methanol is a medium for the storage and transportation for hydrogen and potential clear fuel for fuel additive [12]. Thirdly, methanol synthesis from direct carbon dioxide hydrogenation is high in terms of economical and energetic efficiency than the indirect synthesis of methanol [13]. Lastly, direct carbon dioxide hydrogenation produces high purity of methanol compared to methanol synthesis from syngas [14].

2. Methodology

2.1 Flow Chart of Methodology

Figure 2 below shows a flow chart of the simulation. First and foremost, biogas and water entered water scrubber and separation of acid gases occured inside. Then, carbon dioxide and methane

exited as in gas phase. The second unit operation was PSA where carbon dioxide has been adsorb by alumina and it was used for generation of methanol in reactor. The methanol production was recorded before the experiment was repeated with different temperatures and pressures in the reactor. Based on the literature review, the range of temperature and pressure that would be implemented were 170-260 ℃ and 1-80 bar [10].

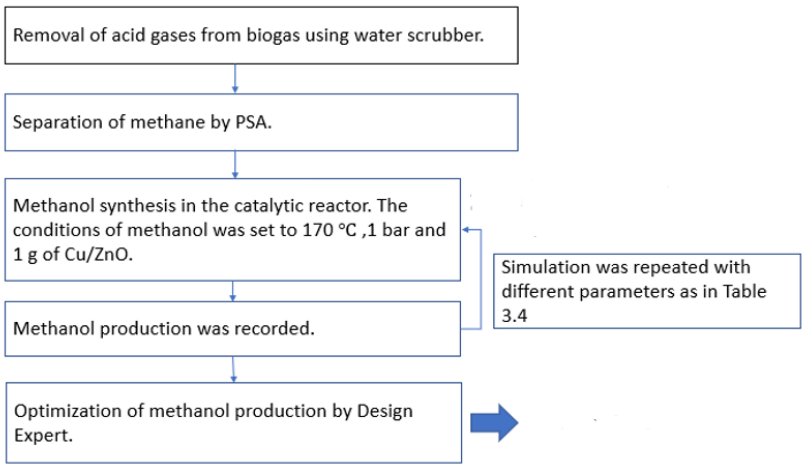


Fig. 2. Flow chart of methanol production by Aspen Plus simulation.

2.2 Aspen Plus Simulation

The physical controller in the steady state system will not show up during the simulation but the system is being fixed or manipulated in the design specification option. With design specification, the user is able to define the value of calculated flow sheet quantity to a certain value. This is to ensure that the objective is accomplished by changing the specified input variable. The steps of using design specifications are measured variables are identified, the target was specified, and the range of manipulated variable was specified. The flow sheet of the simulation was shown in Figure 2.

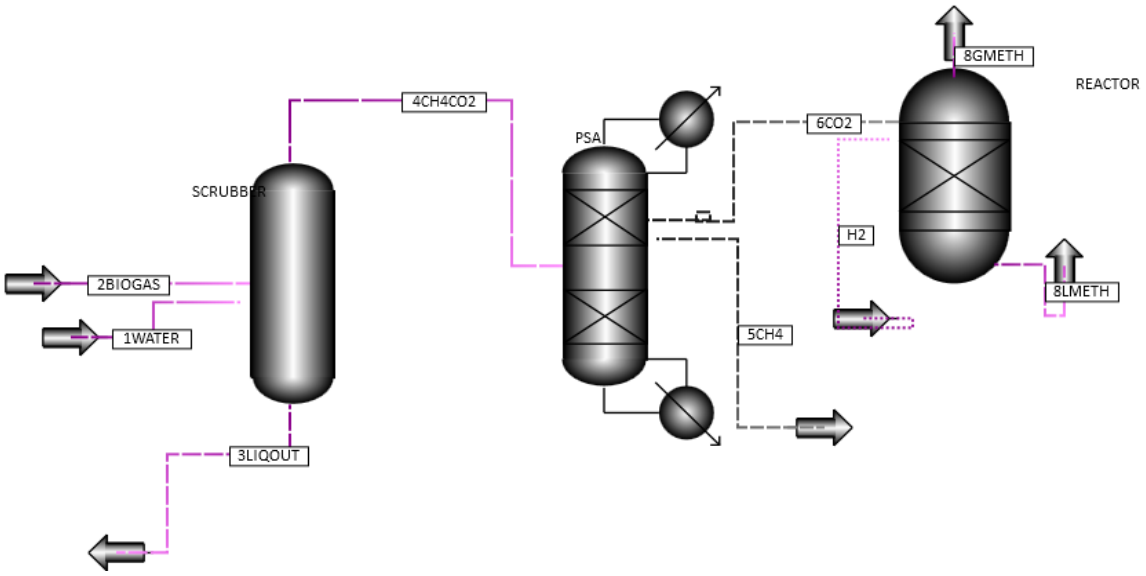


Fig. 2. Flow sheet of the simulation

2.3 Design of Experiment (DOE)

Design Expert version 6 was used to design the experiment for optimization of methanol production. Central composite design (CCD) method was choose in varying those two parameters. Table 3 below show the parameters that was generated by (Design Expert Version 6.5) software.

Table 3
Table of parameters by DOE software

RUN	Temperature (℃)	Pressure (bar)	Mass of methanol (kg)
1	170	80	
2	215	40	
3	260	1	
4	215	40	
5	215	1	
6	170	1	
7	260	41	
8	215	80	
9	215	41	
10	260	80	
11	215	41	
12	170	41	
13.	215	41	

Table 4
Parameters and level used in Central Composite (CCD)

Factor	**Parameter**	**Unit**	**Level**		
			Low (-)	Centre (0)	High (1)
A	Temperature	℃	170	215	260
B	Pressure	Bar	1	40	80

3. Results

3.1 Theoretical and Simulation Value

3.1.1 Mass balance

Table 5 show a stream summary of methanol production in which the value was compared between theoretical value and simulation value. For stream 1 and stream 2, the theoretical value and simulation value was exactly same. However, for stream 3 and stream 4 there was slightly different in term of the composition of the streams. Theoretically, stream 3 does not contain carbon dioxide in which assumption has been made that 100 percent of carbon dioxide was absorbed. But, for simulation value 0.66 kg of carbon dioxide was present in the stream. In stream 4, there was 0.036 kg of ammonia present in which contradict to assumption that has been made. It was assumed that 100 percent of ammonia was solute into water. Also, stream 5 and stream 6 from show insignificant difference. For stream 8, there was addition components like carbon dioxide, hydrogen and carbon monoxide. There was assumption that has been made where all the reactants were fully react. However, simulation value showed 25. 85 kg of carbon dioxide exit through stream 8 which means that carbon dioxide was not fully converted at first temperature and pressure. In addition, carbon dioxide, hydrogen and carbon monoxide.

Table 5
Stream summary of methanol production based on theoretical and simulation value

Stream		1	2	3	4	5	6	7	8
Components	Mass flow rate (kg/h)								
NH_3	Theoretical	3	-	3	-		-	-	-
	Simulation	3	-	2.96	0.036		0.04	-	-
H_2S	Theoretical	2	-	1.98	0.02	0.02	-	-	-
	Simulation	2	-	1.36	0.643	0.64	-	-	-
CO_2	Theoretical	35	-	-	35		35	-	-
	Simulation	35	-	0.66	34.32	0	34.32	-	25.85
CH_4	Theoretical	60	-	-	60	60	-	-	-
	Simulation	60	-	-	60	60	-	-	-
H_2O	Theoretical	-	10	10	-			-	14.32
	Simulation	-	10	10	-			-	3.875
H_2	Theoretical							4.77	-
	Simulation							4.77	3.58
CH_3OH	Theoretical								25.45
	Simulation								6.039
CO	Theoretical								-
	Simulation								0.75

3.1.1 Energy balance

Table 6 below show an energy balance for all streams. Theoretical value for energy balance was calculated as below (m = mass, C_P = specific heat capacity, ΔT = difference of temperature):

$$\mathrm{Q} = mC_P\Delta T \quad (1)$$

Based on the theoretical and simulation value, most of the value showed big differences. For instance, at stream 1, the theoretical value of energy balance was 783.56 kJ/mol, but simulation value was -628 kJ/h.

Table 6
Energy balance for all unit operation

Stream	Enthalpy (kJ/h)	
	Theoretical value	Simulation value
1	783.56	-628
2	1113.00	-
3	2954.13	-624
4	-1057.57	-606806
5	805.5	-296414
6	7843.5	-324721
7	-9369	1022.98
8	-21265	-297428

3.2 Statistical Analysis

The software that was used to model the experiment was Design Expert software (Version 6.5). The experimental design for methanol production consists of 13 runs in which Central Composite Design (CCD) was implemented. The methanol production that was obtained from optimization is illustrated on Table 7.

Table 7
Experimental design for optimization of methanol production

Type of Experiment: 2 Factor Interaction (2FI)			Mass of methanol (kg)	
Run number	Temperature (°C)	Pressure (bar)	Experimental value	Predicted Value
1	170.00	80.00	24.86	21.27
2	215.00	40.50	6.04	6.60
3	260.00	1.00	0.003	1.35
4	215.00	40.50	2.90	6.60
5	215.00	1.00	6.04	0.94
6	170.00	1.00	0.12	0.53
7	260.00	40.50	2.90	2.31
8	215.00	80.00	9.37	12.27
9	215.00	40.50	5.98	6.60
10	260.00	80.00	5.92	3.27
11	215.00	40.50	6.04	6.60
12	170.00	40.50	9.65	10.90
13	215.00	40.50	6.04	6.60

The software's numerical and graphical optimization tools was used to analyze variance (ANOVA) and response surfaces. The sum of squares from two functional interaction (2FI) was selected where the additional terms were significant. Table 8 presented the ANOVA of 2FI model in which proved the validity of the model with the F-value to be 16.05, which was significant.

Table 8
Analysis of variance (ANOVA)

	Sum of Squares	Degree of Freedom	F-value	p-value	
Model	392.01	3	16.05	0.0006	Significant
A	110.86	1	13.62	0.0050	Significant
B	192.59	1	23.66	0.0009	Significant
AB	88.56	1	10.88	0.0093	Significant
Lack of fit	65.47	5	6.73	0.0443	Significant
Pure error	7.78	4	1.95		
Total (correlation)	465.26	12			

There was only 0.06% probability that large model F-value to occur due to noise. It can be observed that the models, A, B and AB were significant. The final equation in terms of coded factors was shown in Equation 2 as,

$$\text{Mass flow rate of methanol} = +6.60 - 4.30\text{A} + 5.67\text{B} - 4.71\text{AB} \quad (2)$$

where A and B represent temperature and pressure. The predicted R^2 value of 0.4183 was not as close to the adjacent R^2 which may indicate a large block effect or a possible error with the model and data. To overcome this issue, a model reduction, response transformation and outliers can be considered to improve the model. The signal to noise ratio is measured adequate precision, and a ratio greater than 4 is desirable. From the analysis, it is showed that the adequate precision ratio of

13.016 which implied an adequate signal. Therefore, this model can be used to navigate the design space.

Figure 9 showed a correlation of prediction versus actual of methanol production. The linear relationship between actual and predicted of methanol production was observed. Thus, it can be concluded that all the experimental values were in good agreement with predicted values with an R_2 0.8425.

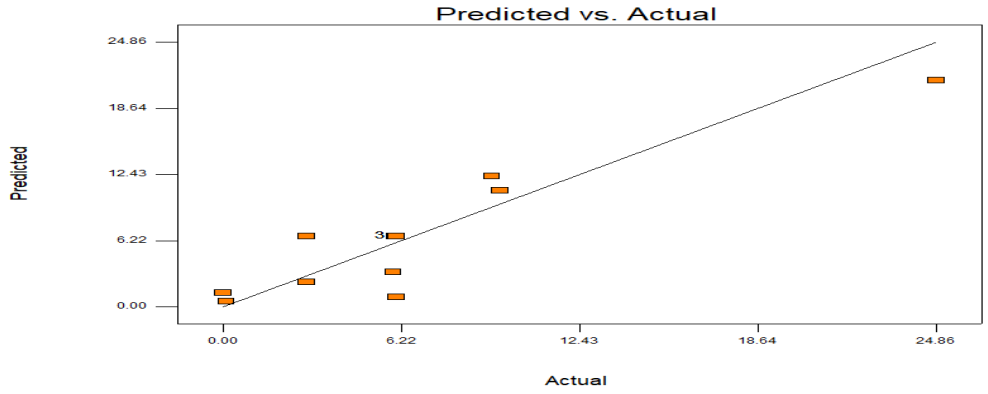


Fig.9. Correlation of prediction vs actual methanol production

3.2.3 Interaction of parameters and the effect on response

The interactions between the parameters on mass of methanol produced were evaluated using Design-Expert three-dimensional plot surface. It can be observed that the combined effects of temperature and pressure were influencing the methanol production significantly. From Figure 10 it was observed that increasing pressure will result in increasing of mass of methanol.

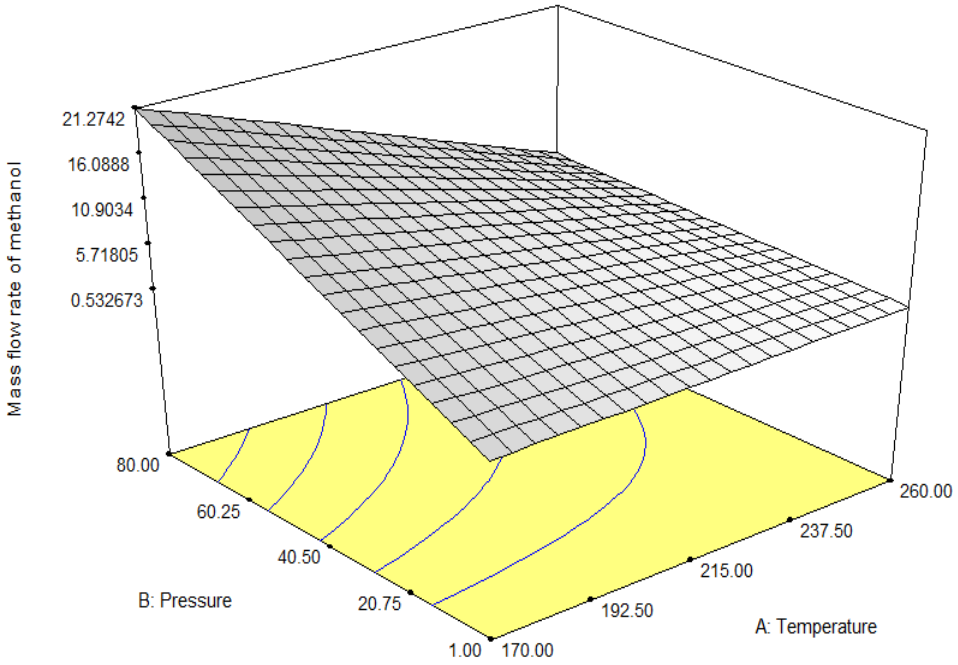


Fig. 10. Effect of pressure and temperature on mass of methanol

Meanwhile, increasing in temperature lead to decreasing of production of methanol. This is because methanol production is an exothermic reaction. The reaction is favor to lower temperature.

Lenzio *et al*., said when temperature is decreasing while pressure is increasing, equilibrium conversion of carbon dioxide to methanol will increase significantly [15]. Figure 4.6 below illustrate result of analysis of ANOVA from the previous article. The article consists of 4 factors which are temperature, pressure, CO_2/H_2O ratio and recycle produced stream and 2 response which are methanol production and reactor volume. First factor, temperature show a negative effect for reactor volume and methanol production. This negative effect shows that when temperature is increasing both reactor volume and methanol production will be decreased. Figure 11 only show significant factors. However, pressure factor is not available on the graph, which mean that the factor is not significant with the effects. The research also considers other factors apart from pressure and temperature. In term of recycle of produced stream affect, the reactor volume and methanol production have a positive effect value.

A = reaction temperature in K

B = reaction pressure in bars

C = H_2/CO_2 ratio

D= recycle of produced stream

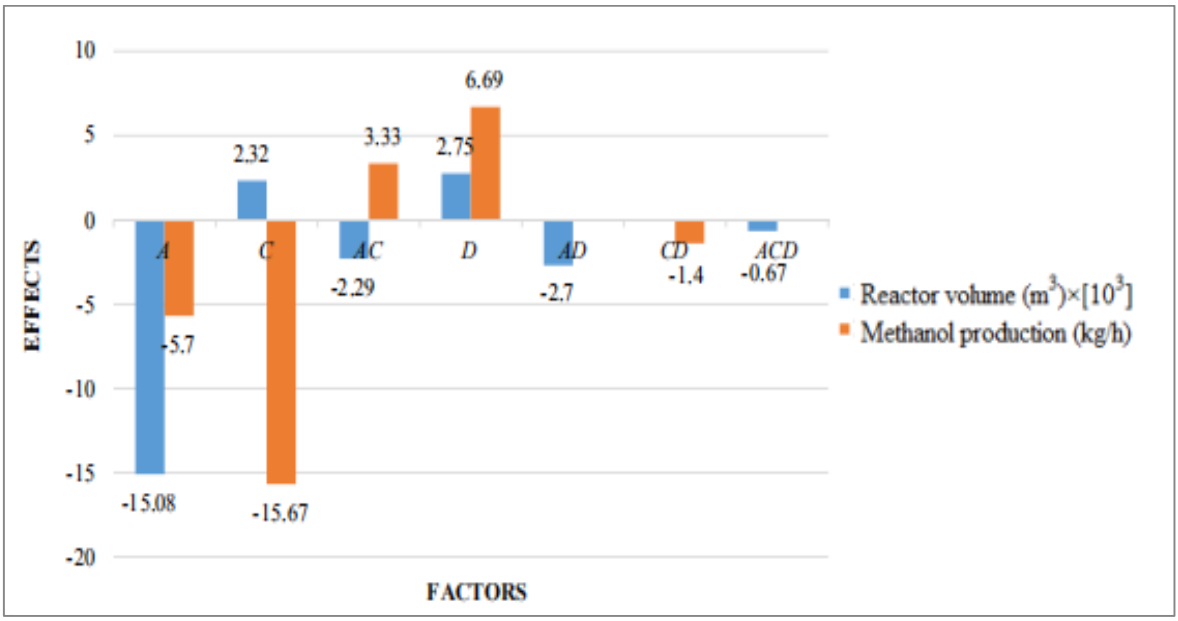


Fig. 11. Result of ANOVA analysis [15]

Based on the project, pressure and temperature were the only factors that were consider. The result for pressure factor was contradict with Figure 11. The simulation value show that pressure affect methanol production significantly. According to Table 7, the maximum mass of methanol is observed when temperature and pressure of reactor are 170°C and 80 bar. This reflect to the highest conversion of carbon dioxide to methanol.

3.2.4 Validation

When measuring the accuracy of the model, the percentage error of measurement is often used which is known as validation step. It is important for the model to have less than 10% variation

between experimental and predicted results. Based on the numerical optimization to maximize methanol production in Design Expert software, 10 starting points were developed to formulate 1 solution with optimum condition were selected for the validation which is represent in Table 11. The experimental validity on the predicted optimum conditions gave an actual mass of methanol of 21.27 kg with percentage error of 0.14%. These small errors indicated that the model was accurate in representing the actual experimental values, which can be used as a good prediction to biodiesel yield at any condition within the range studied.

Table 11
Solution of numerical optimization

Number	Temperature	Pressure	Predicted mass of methanol	Actual mass of methanol	Percent error (%)
1.	178	80	24.86	21.27	0.14

4. Conclusions

In this research, the first objective was to convert carbon dioxide to methanol using Aspen Plus simulation. There were three-unit operations to simulate methanol production. All three-unit operations have its own specific purpose for instant water scrubber was used for separation of acid gases. After that, methanol production was recorded. The second objective was to optimize methanol production by varying pressure and temperature using DOE software. Those two objectives were achieved. Based on the result, the optimum temperature and pressure for methanol production were 170 ℃ and 80 bar in which 24. 84 kg/h of methanol produced. In the future, optimization of methanol production should not only consider of temperature and pressure but also carbon dioxide conversion, methanol selectivity, H_2/CO_2 ratio.

References

[1] Bellotti, D., M. Rivarolo, L. Magistri, and A. F. Massardo. "Feasibility study of methanol production plant from hydrogen and captured carbon dioxide." *Journal of CO2 utilization* 21 (2017): 132-138.

[2] Pontzen, Florian, Waldemar Liebner, Veronika Gronemann, Martin Rothaemel, and Bernd Ahlers. "CO2-based methanol and DME–Efficient technologies for industrial scale production." *Catalysis Today* 171, no. 1 (2011): 242-250.

[3] Kothandaraman, Jotheeswari, Alain Goeppert, Miklos Czaun, George A. Olah, and GK Surya Prakash. "Conversion of CO2 from air into methanol using a polyamine and a homogeneous ruthenium catalyst." *Journal of the American Chemical Society* 138, no. 3 (2016): 778-781.

[4] Bowker, M. (2019). Methanol synthesis from CO_2 hydrogenation. ChemCatChem. doi:10.1002/cctc.201900401

[5] Kothandaraman, Jotheeswari, Alain Goeppert, Miklos Czaun, George A. Olah, and GK Surya Prakash. "Conversion of CO2 from air into methanol using a polyamine and a homogeneous ruthenium catalyst." *Journal of the American Chemical Society* 138, no. 3 (2016): 778-781.

[6] Nieminen, Harri, Arto Laari, and Tuomas Koiranen. "CO2 hydrogenation to methanol by a liquid-phase process with alcoholic solvents: a techno-economic analysis." *Processes* 7, no. 7 (2019): 405.

[7] Achinas, Spyridon, Vasileios Achinas, and Gerrit Jan Willem Euverink. "A technological overview of biogas production from biowaste." *Engineering* 3, no. 3 (2017): 299-307.

[8] Biogas Capture – Malaysian Palm Oil Board. (2017). Retrieved from http://palmoils.mpob.gov.my/publications/OPB/opb75-loh.pdf .

[9] Abdeshahian, Peyman, Jeng Shiun Lim, Wai Shin Ho, Haslenda Hashim, and Chew Tin Lee. "Potential of biogas production from farm animal waste in Malaysia." *Renewable and Sustainable Energy Reviews* 60 (2016): 714-723.

[10] Bahruji, Hasliza, Michael Bowker, Graham Hutchings, Nikolaos Dimitratos, Peter Wells, Emma Gibson, Wilm Jones, Catherine Brookes, David Morgan, and Georgi Lalev. "Pd/ZnO catalysts for direct CO2 hydrogenation to methanol." *Journal of Catalysis* 343 (2016): 133-146.

[11] Chinchen, G. C., P. J. Denny, J. R. Jennings, M. S. Spencer, and K. C. Waugh. "Synthesis of methanol: part 1. Catalysts and kinetics." *Applied Catalysis* 36 (1988): 1-65.

[12] Din, Israf Ud, Maizatul S. Shaharun, A. Naeem, S. Tasleem, and Mohd Rafie Johan. "Carbon nanofibers based copper/zirconia catalysts for carbon dioxide hydrogenation to methanol: Effect of copper concentration." *Chemical Engineering Journal* 334 (2018): 619-629.
[13] ZHUANG, Hui-dong, Shao-fen BAI, Xin-mei LIU, and Zi-feng YAN. "Structure and performance of Cu/ZrO2 catalyst for the synthesis of methanol from CO2 hydrogenation." *Journal of Fuel Chemistry and Technology* 38, no. 4 (2010): 462-467.
[14] Bowker, Michael. "Methanol synthesis from CO2 hydrogenation." *ChemCatChem* 11, no. 17 (2019): 4238.
[15] Leonzio, Grazia. "Optimization through response surface methodology of a reactor producing methanol by the hydrogenation of carbon dioxide." *Processes* 5, no. 4 (2017): 62.