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Article

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Simulation of single-step dimethyl ether synthesis from syngas

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Abstract

Dimethyl ether (DME) is an alternative energy that simplest ether. DME has 2 ways to synthesis from syngas. The single-step DME synthesis combined methanol synthesis and methanol dehydration in one reactor. This study is focusing on DME production from synthesis gas by used catalyst as $\text{CuO-ZnO-Al}_2\text{O}_3/\gamma\text{-Al}_2\text{O}_3$. For the simulation we simulated in Aspen Plus V8.8 and used Langmuir–Hinshelwood Hougen–Watson (LHHW) kinetic model for the reaction rate of DME synthesis in a plug flow reactor with catalyst. Simulation is varying the temperature range between 220 °C to 300 °C and pressure between 20 bar to 80 bar to find the suitable condition for the single-step DME synthesis with $\text{CuO-ZnO-Al}_2\text{O}_3/\gamma\text{-Al}_2\text{O}_3$ catalyst.

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Keywords: Dimethyl ether; Simulation of DME; Kinetic parameter; Aspen plus; DME synthesis

1. Introduction

DME is alternative energy that used as transportation fuel, fuel sources for power generation, chemical (e.g. aerosol, propellant) and precursor of hydrogen production. DME has a property close to LPG but with a good cetane number, ultra-low exhaust emissions and high energy efficiency, which can be used as a clean burning alternative that it can replace LPG, LNG and diesel. DME has a similar vapor pressure of LPG, hence it can be used in existing structures for storage and transportation [1,2]. DME can synthesis in 2 ways as shown in Fig. 1. First called two-steps synthesis that has methanol synthesis and methanol dehydration in another reactor. Second called single-step synthesis that combined methanol synthesis and methanol dehydration in one reactor by used bi-function catalysts [3,4].

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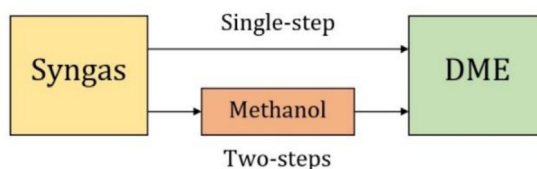


Fig. 1. DME synthesis diagram.

Many researches of single-step DME synthesis focused on catalyst part such as Kim et al. [5] did the experiment about the single-step DME synthesis from syngas by used Cu/ZnO/Al₂O₃ as a bi-function catalyst. Nie et al. [6] studied about the kinetic model of single-step DME synthesis from syngas by used bi-function catalyst. From this studied they got kinetic model of single-step DME synthesis. There are a lot of research that studies about simulation and modeling the single-step DME synthesis. Inayat et al. [7] investigated and simulated about the production of DME by used empty fruit branch of palm wastes as a raw material in Aspen HYSYS. They studied about the variable that effect to DME yield such as pressure, temperature and steam/biomass ratio. The optimum of process is 1000 kPa and temperature is 140 °C.

In previous work, we did in part of biomass gasification that can convert biomass to syngas [8]. So, we will use the results to simulate in DME synthesis. The purpose of this work is focusing on DME synthesis that produces from syngas by using Aspen Plus V8.8 that apply kinetic parameters to simulate for designing the process.

2. Reaction kinetics

For the DME synthesis that produces from syngas can be synthesis from the reactions as shown below.



Reaction (1) is a methanol synthesis that produces from carbon monoxide and hydrogen. Reaction (2) is a methanol synthesis that produces from carbon dioxide and hydrogen. Reaction (3) is methanol dehydration. Reaction (4) is a water gas shift reaction.

In single-step DME synthesis that combined methanol synthesis and methanol dehydration in one reactor by used bi-function catalyst [4]. The methanol synthesis uses metallic as a catalyst and the methanol dehydration uses acidic catalyst. For the single-step DME synthesis use CuO/ZnO/Al₂O₃ as a metallic catalyst and γ -Al₂O₃ as an acidic catalyst [6,9]. The reaction rates as shown below and kinetic parameters are shown in Table 1 [6].

$$r_{\text{CO}} = \frac{k_1 f_{\text{CO}} f_{\text{H}_2}^2 - \frac{k_1 f_{\text{CH}_3\text{OH}}}{K_{f_1}}}{(1 + K_{\text{CO}} f_{\text{CO}} + K_{\text{CO}_2} f_{\text{CO}_2} + K_{\text{H}_2} f_{\text{H}_2})^3} \quad (5)$$

$$r_{\text{CO}_2} = \frac{k_2 f_{\text{CO}_2} f_{\text{H}_2}^3 - \frac{k_2 f_{\text{CH}_3\text{OH}} f_{\text{H}_2\text{O}}}{K_{f_2}}}{(1 + K_{\text{CO}} f_{\text{CO}} + K_{\text{CO}_2} f_{\text{CO}_2} + K_{\text{H}_2} f_{\text{H}_2})^4} \quad (6)$$

$$r_{\text{DME}} = \frac{k_3 f_{\text{CH}_3\text{OH}} - \frac{k_3 f_{\text{DME}} f_{\text{H}_2\text{O}}}{K_{f_3} f_{\text{CH}_3\text{OH}}^2}}{(1 + \sqrt{K_{\text{CH}_3\text{OH}} f_{\text{CH}_3\text{OH}}})^2} \quad (7)$$

$$r_{\text{WGS}} = \frac{k_4 f_{\text{H}_2\text{O}} - \frac{k_4 f_{\text{CO}_2} f_{\text{H}_2}}{K_{f_4} f_{\text{CO}}}}{1 + K_{\text{CO}} f_{\text{CO}} + K_{\text{CO}_2} f_{\text{CO}_2} + \sqrt{K_{\text{H}_2} f_{\text{H}_2}}} \quad (8)$$

Table 1. Kinetic parameters [6].

	A(i)	B(i)
k_1	7380	−54,307
k_2	5059	−57,515
k_3	1062	−43,473
k_4	7.3976	−20,436
K_{CO}	3.934×10^{-6}	37,373
K_{CO_2}	1.858×10^{-6}	53,795
K_{H_2}	0.6716	−6476
K_{CH_3OH}	3.480×10^{-6}	54,689

Parameter = $A(i)\exp(B(i)/RT)$.

3. Methodology

3.1. Syngas feed

In previous work, we did in part of biomass gasification that used eucalyptus wood chips as a raw material feed stock with 30 wt% moisture content. Eucalyptus wood chip fed to fluidized bed gasifier. Syngas is cleaned by dry cleaning, wet cleaning and CO₂ removal and then stored in a gas holder that pressurized at 20 bar. The syngas composition from biomass gasification is consist 30% H₂, 25% CO, 29% CO₂, 10% CH₄, 1% C₂H₄ and 5% N₂ at 20 °C, 20 bar [8].

3.2. Process description

The syngas that use as raw material is consist 30% H₂, 25% CO, 29% CO₂, 10% CH₄, 1% C₂H₄ and 5% N₂ at 20 °C, 20 bar has 0.13 mol/h of total flow rate. Syngas feed is going to compressor to increase pressure to 40 bar and pre-heat to 220 °C. The reactor model that uses in simulation is a plug flow reactor. The dimension of reactor is 0.6 m and 0.024 m in diameter. The catalyst that use in this simulation is CuO–ZnO–Al₂O₃/γ–Al₂O₃. We use kinetic parameters as shown in Table 1 to simulate the single-step DME synthesis that applies by Langmuir–Hinshelwood Hougen–Watson (LHHW) model. The suitable form for LHHW is shown in Eqs. (9)–(12) [10].

$$r = \frac{(\text{kinetic factor}) \times (\text{driving force expression})}{(\text{adsorption term})} \quad (9)$$

$$\text{kinetic factor} = k \left(\frac{T}{T_0} \right)^n e^{(-Ea/R)(\frac{1}{T} - \frac{1}{T_0})} \quad (10)$$

$$\text{driving force} = K_1 \prod C_i^a - K_2 \prod C_i^b \quad (11)$$

$$\text{adsorption} = \sum K_i \left(\prod C_i^\gamma \right) \quad (12)$$

After we put the rate reaction in plug flow reactor with the suitable form for LHHW model, we simulate the single-step DME synthesis in Aspen Plus V.8.8. The products of single-step DME synthesis come out from reactor.

4. Results and discussion

The simulation result of the single-step DME synthesis model that use as a catalyst in a plug flow reactor with specified temperature in Aspen Plus V.8.8 are shown in Table 2. The results are shown about the CO, H₂, DME and H₂O in mole fraction (%) with varying of temperature between 220 °C and 300 °C, pressure between 20 bar and 80 bar.

4.1. Effect on temperature

Effect on temperature of single-step DME synthesis that has catalyst loading in the reactor is studied about mole fraction of DME and the ratio between DME and CO with the varying of temperature from 220 °C to 300 °C by fixed pressure at 60 bar as shown in Fig. 2(a).

Table 2. The results of single-step DME synthesis (out of reactor) in mol%.

No	T (°C)	P (bar)	$x_{CO,in}$	$x_{CO_2,in}$	$x_{H_2,in}$	$x_{CO,out}$	$x_{H_2,out}$	x_{H_2O}	x_{DME}
1	220	20	25	29	30	9.266	3.928	6.242	10.974
2	220	80	25	29	30	8.208	2.817	6.333	11.553
3	260	20	25	29	30	2.501	0.487	4.845	13.656
4	260	80	25	29	30	2.371	0.393	4.842	13.725
5	300	20	25	29	30	0.644	0.075	4.179	14.125
6	300	80	25	29	30	0.631	0.065	4.190	14.131

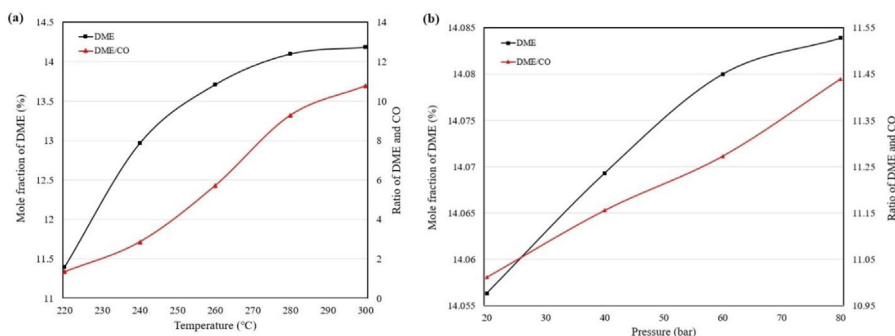


Fig. 2. (a) The mole fraction of DME and ratio of DME and CO when varying temperature between 220 °C and 300 °C with fixed pressure at 60 bar; (b) The mole fraction of DME and ratio of DME and CO when varying pressure between 20 and 80 bar with fixed temperature at 280 °C.

Starting with 220 °C, temperature increased until 300 °C. We found that the temperature increased mole fraction of DME and ratio between DME and CO are also increased. For the mole fraction of DME is significantly increased until 280 °C. After 280 °C, mole fraction of DME is silently increased the previous temperature. The ratio between DME and CO is also significantly increased until 280 °C, after that ratio between DME and CO is silently increased the previous temperature. Because, at high temperature the activity of catalyst in methanol dehydration is lower than methanol synthesis that cause the decreasing of DME production. The optimum condition of temperature is 280 °C.

4.2. Effect on pressure

The effect on pressure of simulation is studied about mole fraction of DME and the ratio between DME and CO with the varying of pressure from 20 to 80 bar by fixed temperature at 280 °C as shown in Fig. 2(b). Starting with 20 bar, pressure increased until 80 bar. From the simulation, we found that when we increased pressure mole fraction of DME also increased. When we increased pressure, mole fraction of DME is significantly increased until 60 bar after that it silently increased.

The ratio between DME and CO when we increased pressure is also increased, it means that when pressure increased CO can convert to DME better than the low pressure. Increasing the pressure will increase rate reaction of methanol synthesis particularly and other reaction because methanol synthesis favors a high pressure. So, mole fraction of DME and ratio between DME and CO will increase when pressure increase and the optimal condition of pressure is 60 bar.

5. Conclusion

The simulation of single-step DME synthesis from syngas by used kinetic parameters of catalyst with Langmuir–Hinshelwood Hougen–Watson (LHHW) model. This simulation is studied by Aspen Plus V.8.8. When we got a suitable from of reaction rate, we studied the effects of temperature and pressure by varying between 220 °C and 300 °C, 20 and 80 bar. We found that the ratio of DME and CO is also increased when pressure and temperature increased. In case of the temperature increased value significantly increased until 280 °C. After 280 °C, value silently increased than previously. So, the proper temperature and pressure of single-step DME synthesis for this model are 280 °C and 60 bar that got 14.078 mole fraction of DME (%).

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