

Effect of Pressure and Syngas Composition on Direct Synthesis of Dimethyl Ether using Dual Bed Catalyst

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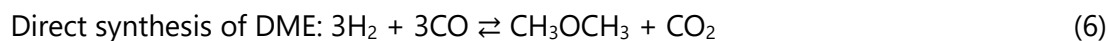
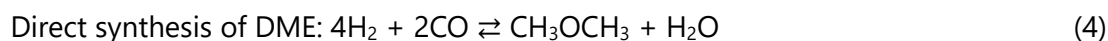
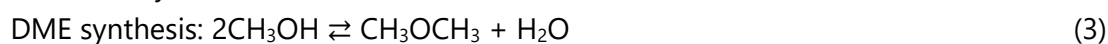
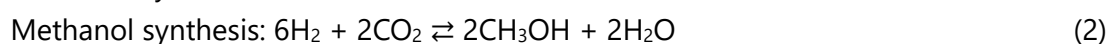
National General Energy Plan of Indonesia 2017 (RUEN 2017) stated that dimethyl ether (DME) is appointed as a blending of LPG to reduce LPG imports. DME can be made with two reaction pathways, namely direct synthesis and indirect synthesis. The objective of this study was to determine the effect of pressure and syngas composition on the direct synthesis of DME using dual fixed bed catalyst. The research was carried out with two types of catalyst: M-xxx as a commercial catalyst for methanol synthesis and γ -Al₂O₃ as catalyst for dehydration of methanol to DME. The later was prepared in our *Laboratory of Chemical Reaction Engineering and Catalysis, ITB*. The dual catalyst experiment was carried out at 5 and 7 bars, and a fixed temperature of 240°C. The mass ratio of the M-xxx to γ -Al₂O₃, so-called M/D ratios, were varied from 1/9 to 9/1. Two type of syngas were used, i.e. SA containing only H₂ and CO with a SN of 2,3 and SB containing 4% CO₂ with SN of 1,8. The dual bed with a M/D ratio of 1/4 gave a CO conversion up to 62% at 5 bars and 240°C (SA). As pressure increased, the conversion of CO and H₂ increases to 85% and 83% at 7 bar and 240°C (SA). The presence of CO₂ (SB) decreases catalyst activity, as indicated by the decrease in conversion of CO and H₂ to 56% and 54%, at 7 bar and 240°C.

Keywords: Dimethyl ether, direct synthesis, dual bed catalyst, stoichiometric number, γ -Al₂O₃

INTRODUCTION

DME (dimethyl ether, CH₃OCH₃) has been known as an environment-friendly fuel. DME can be liquefied at a pressure of about 6 atm (in room temperature) or at a temperature of about -25°C (in an atmospheric pressure), so it can be stored or distributed like LPG. Based on the

aforementioned reason, DME will be used as partial substitution of DME in Indonesia. DME has a high cetane number in the range of 55-60, which is higher than diesel fuel (40-55). Thus, it is also interested for substitution of diesel fuel (Akarmazyan et al., 2014). The DME synthesis involves several reactions, as shown in Eqs. 1-6 (Cai, 2015).



All reactions written in Eqs. 1-6 are exothermic. Thus, care must be taken to control reaction temperature in order to optimize the equilibrium conversion and the rate of reaction. DME synthesis can be done with two synthesis pathways, i.e. direct or indirect synthesis. This study dealt with the direct synthesis of DME from synthesis gas using a dual bed catalyst, for methanol synthesis and dehydration of methanol to DME. The direct synthesis in this study was conducted at a pressure below 10 bar, instead of 20 bar or more (Cai, 2015). The use of a lower reaction pressure was intended for developing an appropriate small-scale processing unit for biomass to DME. The objective of this study is to determine the effects of pressure and syngas composition on the performance of a direct synthesis DME reaction system.

EXPERIMENT

Material

In this experiment, commercial Cu-based catalyst of M-xxx and $\gamma\text{-Al}_2\text{O}_3$ made in ITB were used respectively for methanol synthesis and dehydration of methanol to DME. Catalyst $\gamma\text{-Al}_2\text{O}_3$ was prepared in our *Laboratory of Chemical Engineering and Catalysis, ITB*. The synthesis was done at a ratio of

catalyst M/D of 1/1 and 1/4. This configuration was considered from our previous works (Swastika et al., 2019, Ardy et al., 2019), that the rate of methanol dehydration was lower than that of methanol synthesis.

A gas mixture containing 5% H_2 and N_2 was used as the reducing gas to activate M-xxx catalyst. Two kinds of syngas model used for synthesis, as presented in Table 1. The synthesis was conducted at a fixed temperature of 240°C , and two different pressure of 5 and 7 bar. The gas inlet flow rate was adjusted to get a GHSV (gas hourly space velocity) of 2057 h^{-1} . The stoichiometric number, SN is calculated from the gas composition, as shown in Eq. 7.

$$SN = \frac{[\text{H}_2] - [\text{CO}_2]}{[\text{CO}] + [\text{CO}_2]} \quad (7)$$

Table 1. Composition of syngas model

No	component	Syngas model SA	Syngas model SB
1	H_2	65%	65%
2	CO	28%	28%
3	CO_2	-	4%
4	N_2	7%	3%
mol ratio of $\text{H}_2/\text{CO} = 2.32$			
stoichiometric number			
5	SN	2.3	1.8

Characterization of Catalyst

Elemental composition of the catalyst was analyzed using X-Ray Fluorescence (XRF). Average of pore diameter and pore volume of the catalyst was characterized using Brunauer-Emmett-Teller (BET).

Experimental Set up

The direct synthesis of DME was carried out using a stainless-steel tubular reactor (ID 3 cm, see Fig. 1). In this reactor, the catalyst beds of M-xxx and γ -Al₂O₃ are placed. The outlet gas of the reactor was analyzed by a gas chromatography (Shimadzu 2014) with separation columns of porapack-Q and molsieve 5A, to get the concentrations of CO, H₂, CO₂, and N₂. Conditions of GC were as follows: injector temperature of 150°C, column 70°C, TCD detector 200°C, current 50 mA, Argon as a gas carrier at 50 mL/min.

Experimental Procedure

The experiment was done in three steps (Fig. 2), i.e. purging, reduction or activation of the methanol catalyst, and catalytic activity test or synthesis and dehydration of methanol. Purging was carried out to eliminate air or other gases that may interfere the activity test. Purging was done using UHP-N₂ with a flow rate of 100 mL/min (measured at room condition of about 1 bar and 27°C). During this purging, the temperature of reactor was increased from the room to a specified reduction condition. When the purging finished, the flow of N₂ was then changed with the reducing gas containing 5% H₂ and N₂. The reduction was carried out at a fixed temperature of 340°C and reactions shown in Fig. 2 took place.

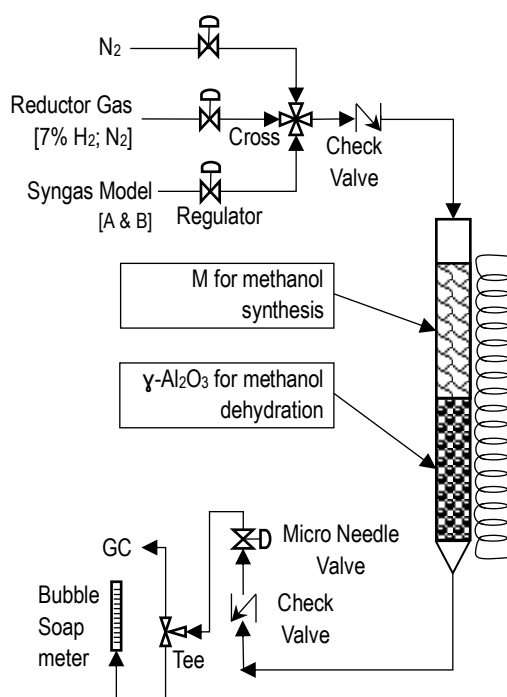


Fig. 1: Scheme of the experimental device

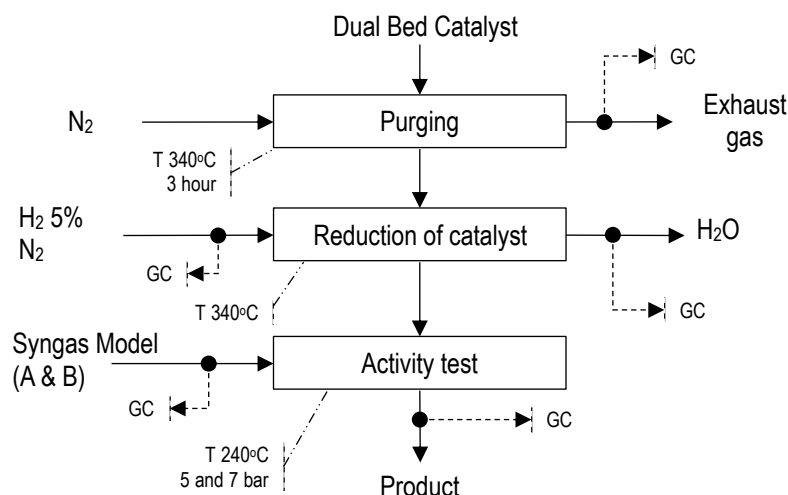


Fig. 2: Procedure of experiment

Table 1. Characteristic of dual bed catalyst

Characteristic	M-xxx, Cu-based commercial	γ -Al ₂ O ₃ , prepared in ITB	MEST-1 (Peláez et al., 2017)	γ -Al ₂ O ₃ (Peláez et al., 2017)
A. Pore Properties				
Surface area (m ² /g)	37.80	194.40	79.90	239.90
Volume (cm ³ /g)	0.13	0.54	0.26	0.55
Diameter (Å)	66.60	112.30	153.00	64.00
B. Major minerals				
CuO	63.41%			
ZnO	26.01%			
Al ₂ O ₃	10.01%	100.00%		

During the reduction, the H₂ conversion or H₂ concentration at the reaction outlet was observed. After reduction, as indicated with a no-more H₂ conversion, the reactor was flushed with N₂ at a temperature of 240°C.

RESULTS AND DISCUSSION

Characteristic of Catalyst

Pore characteristic of M-xxx and γ -Al₂O₃ catalysts are presented in Table 1. For comparison, pore characteristics

of other commercial catalysts are also presented. The higher surface area, the higher contact between reactant on the surface active site of catalyst. If the composition of Cu on Cu-based catalyst is higher than 16%, the surface area of Cu-based on the catalyst will be lower (Nagaraja et al., 2004). The M-xxx catalyst had a CuO content of 63%, which is a higher than METS-1 (Pelaez et al, 2017).

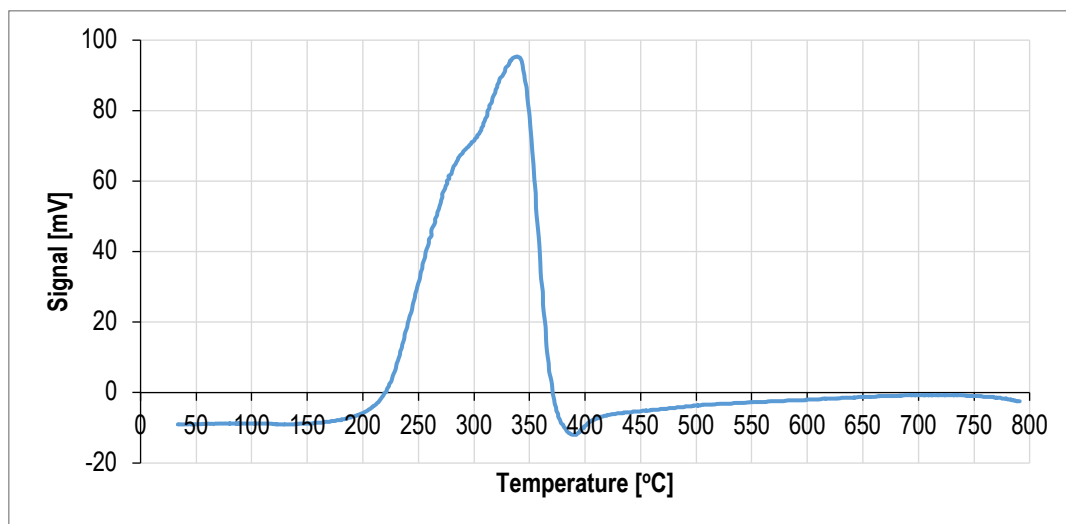


Fig. 3: Temperature programmed reduction (TPR) analysis of M-xxx catalyst

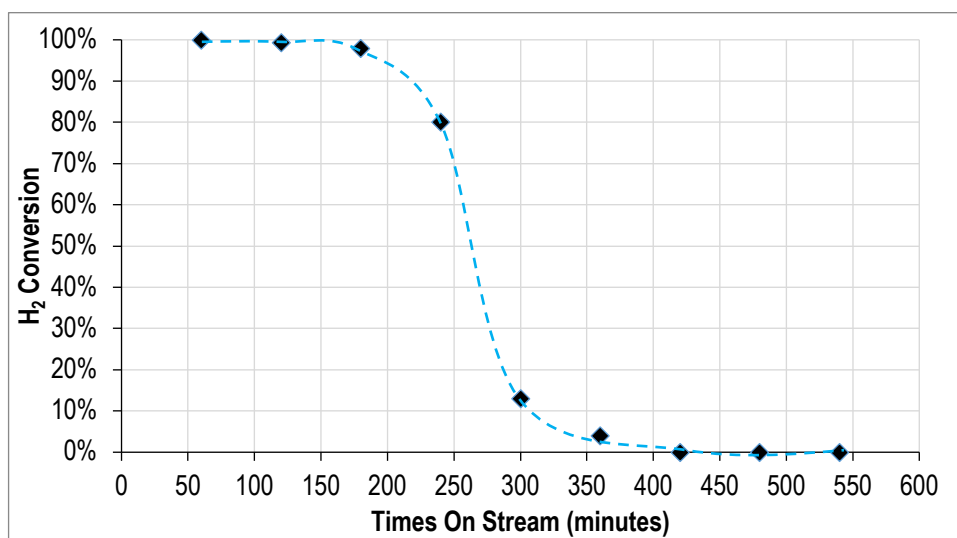


Fig. 4: Typically profile of CuO reduction on M-xxx catalyst

Reduction Catalyst

The reducing temperature of M-xxx catalyst was estimated using the temperature programmed reduction analysis (TPR, Fig. 3). This analysis suggested that the reducing temperature of M-xxx catalyst should be at 340°C, as the above procedure. From the time course of H₂ conversion, the reduction process was clearly completed for about 7 hours (times on stream of 420 min, Fig. 4). From this

observation, CuO in M-xxx catalyst was considered to change completely into Cu⁰.

Catalytic Activity Test

Based on previous research (Ardy et al., 2019, Swastika et al., 2019) it was found that the best catalyst M/D ratio was 1/4 (Fig. 5). The highest CO conversion was 62% at 5 bar and 240°C.

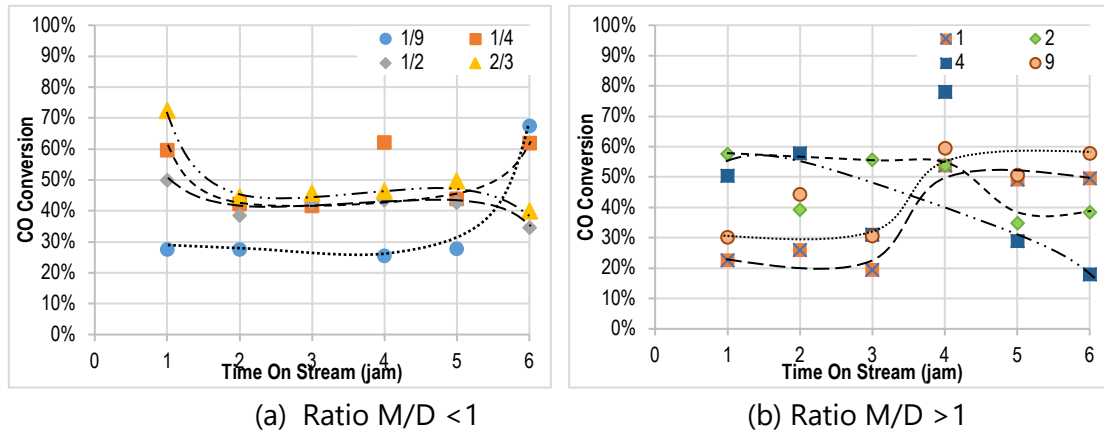


Fig. 5: Activity of dual bed catalyst at various ratio of M/D (gas model SA, 5 bars, and 240°C)

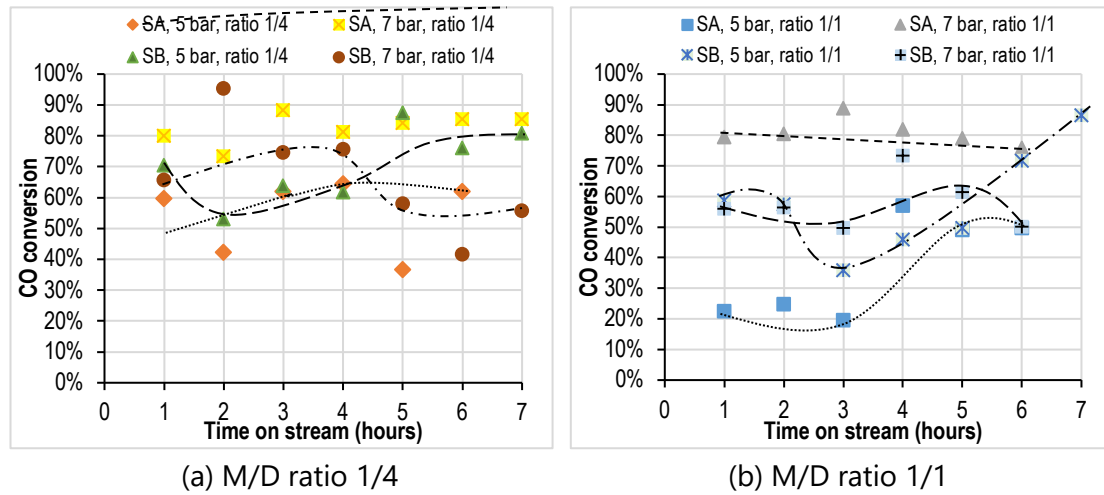


Fig. 6: CO conversion during synthesis

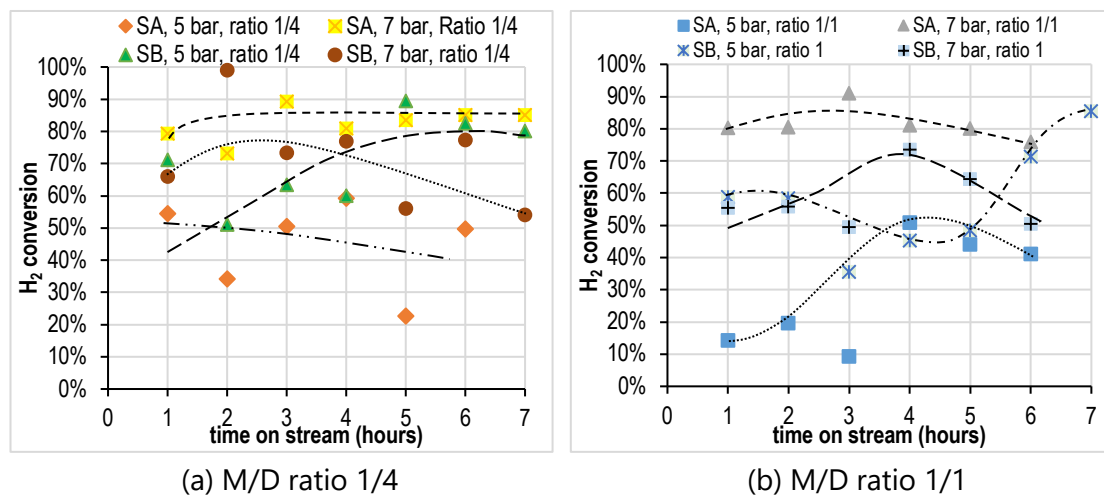


Fig. 7: H₂ conversion during synthesis

As predicted, the dual bed with M/D ratio of 1/4 gave higher CO conversion than that of 1/1, as presented in Figure 6.a and Figure 6.b. Similar trends for the H₂ conversion were also observed (Fig. 7). These results might indicate that the rate of dehydration was lower than that of methanol synthesis. Therefore, a study has to be conducted to improve the activity of dehydration catalyst

Although the pressure variation were only 5 and 7 bar, an increase in pressure resulted in higher conversions of CO (Fig. 6) and that of H₂ (Fig. 7). This phenomenon is in accordance with the stoichiometric of the methanol synthesis from H₂ and CO (Eq. 1), as well as that from H₂ and CO₂ (Eq. 2). Moreover, trends of CO conversion were more or less similar H₂ conversion. This might indicate the overall process was dictated by these stoichiometric (Eq. 1 and Eq. 2).

The effect of syngas composition on the performance of dual bed

reactor could also be observed in Figs. 6 and 7. In general, the conversions of CO and H₂ from the syngas model SA (SN 2.2) were higher than conversion from SB (containing 4% CO₂, with SN 1.8). Theoretically, methanol synthesis from a syngas containing no-CO₂ has a SN 2 (Eq. 7), while the gas model SA has a SN of 2.2 or in excess of H₂. Hence, there might be direct synthesis of DME (Eq. 4, and Eq. 6), resulted in a more conversion of CO. On the other hand, gas model SB has a SN of 1.8 and contained CO₂, so the conversion of CO was lower than that from SA.

When using syngas model containing CO₂ (SB), it was interesting also to evaluate the conversion of CO₂. These results are presented in Figure 8. The conversion of CO₂ seemed to be affected by the pressure of the reaction, in which a lower pressure resulted on a higher conversion of CO₂. In addition to that, CO₂ conversion were also affected by the M/D ratio.

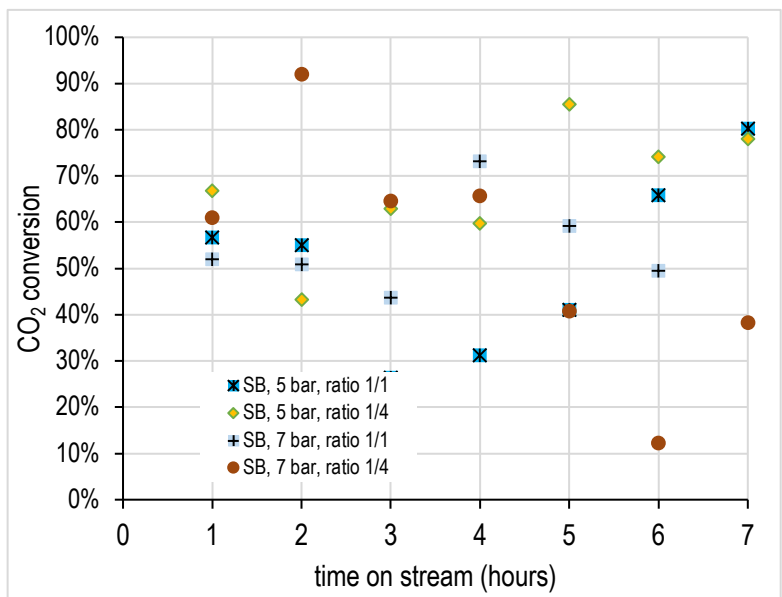


Fig. 8: Conversion of CO₂ during synthesis SB (4% CO₂)

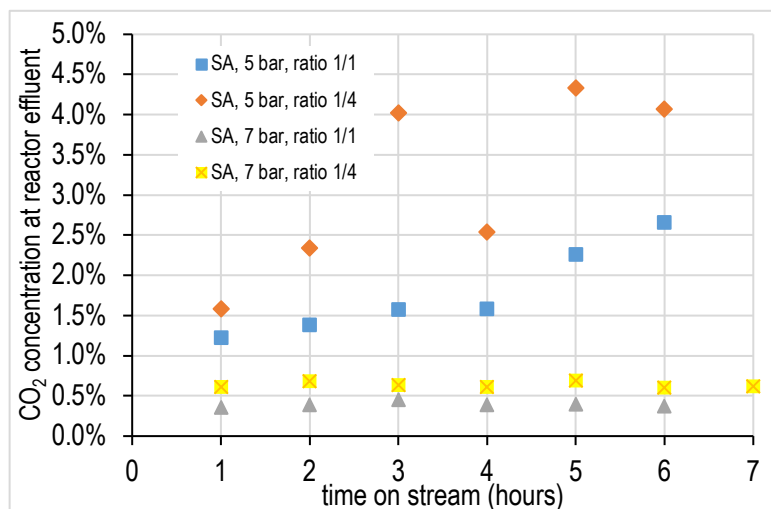


Fig. 9: Generation of CO₂ during synthesis using SA (no-CO₂)

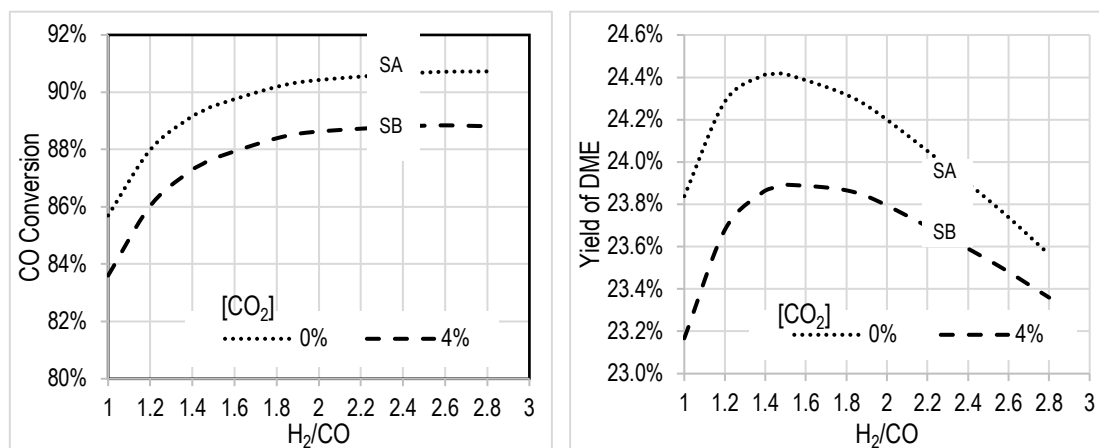


Fig. 10: Simulation of the effect of H₂/CO and CO₂ content on direct synthesis of DME (P = 30 bar; T = 240°C)

When the synthesis was carried out using gas model SA (containing no-CO₂), it was found that the effluent of the synthesis reactor contained CO₂ (experimental data on generation of CO₂ presented as concentration is presented Fig. 9). Since the generation of CO₂ was more significant in the synthesis with a pressure of 5 rather than 7 bar, the direct synthesis of DME (Eq. 6) seemed to be more profound than the shift reaction (Eq. 5). Remarkably, the generation of CO₂ was also affected by the M/D ratio. The lower the M/D ratio, the higher the

CO₂ generation.

To provide an overview on the yield of DME, a thermodynamic simulation has been done. Based on this simulation using gas models with a H₂/CO mol ratio of 2.32, the conversion of CO (Figure 10.a) achieved an optimum value of about 90% and 89% for SA and SB, respectively. But the calculated yields of DME of about 24% (for SA) and 23% (SB) had been in a decreasing region.

CONCLUSION

The direct synthesis of DME in the dual bed reactor containing a commercial catalyst of methanol synthesis and a self-made catalyst of methanol dehydration have been carried out at a temperature of 240°C, and other various process conditions. The configuration of dual bed affects the performance of the synthesis proses as presented in the conversions of H₂ and CO. The dual bed configuration with the M/D ratio of 1/4 gave a reactor performance in two types of feed without (SA) and with CO₂ (SB).

Using SA as feed and the reaction pressure of 7 bar, the conversions of CO and H₂ reached 85% and 83% respectively. Besides the conversion of CO and H₂, the use of gas model SA (contained no -CO₂) generated CO₂ as a product of a direct synthesis from H₂ and CO to DME. While in the use of gas model SB (containing 4% CO₂) as feed, conversion of CO₂ was also observed. This indicated that the methanol synthesis from H₂ and CO₂ took place.

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