

Synthesis of dimethyl ether using a fixed bed of dual catalyst for methanol synthesis and its dehydration

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Abstract. Experimental study on direct synthesis of DME (dimethyl ether) has been conducted using tubular reactor. The synthesis of DME was performed with two commercial catalysts, ie methanol synthesis catalyst (M151, Cu-based) and methanol dehydration catalyst (γ -Al₂O₃). A mixture of H₂, CO, and N₂ was used as a model for synthesis gas. Gas flow rate was set at 20 mL/min (5 bar and 240°C). The reaction held at: pressure of 5 bar and a temperature of 240°C. This experiment was conducted by arranging a series of two types of catalysts in a fixed bed reactor. The methanol synthesis catalyst was placed in the upstream to ensure the reaction of methanol formation, then proceed with dehydration of methanol to DME. The objective of this experiment was to find out the best dual catalyst composition to produce a high concentration of DME. The experiment has shown that the best combination of methanol catalyst to dehydration catalyst was a mixture of 20% methanol catalyst (ratio 1/4). CO conversion was 62% and the product ratio of DME/methanol was 40%.

1 Introduction

Dimethyl ether (DME) is an environmentally friendly fuel that is being widely considered as an alternative fuel to replace petroleum fuels. DME can also be used as a propellant material and another intermediate product [1]. DME can be used as a substitute of LPG as fuel for rural energy. Government of Indonesia has been stated that DME will be used as blending material of LPG to suppress LPG imports (General Plan of National Energy in Indonesia, RUEN 2017).

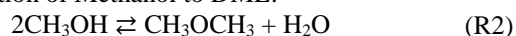
In line with RUEN 2017, the objective of current research is to develop a process of converting biomass into DME/Methanol. Synthesis gas production through biomass gasification is expected to provide an adequate H₂/CO ratio for DME synthesis. The recommended H₂/CO ratio for DME synthesis is 1-2 [2, 3].

Synthesis of DME could be done with two synthesis paths, namely direct synthesis and indirect synthesis. Reaction of direct synthesis of DME was an overall reaction from methanol synthesis and methanol dehydration. Some reactions in synthesis process are as follows.

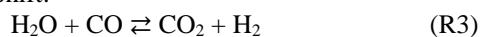
Methanol synthesis:



Dehydration of Methanol to DME:



Water Gas Shift:



Direct synthesis of DME:



In the present study, the experiment focuses on the development of catalyst for the direct synthesis of DME from syngas. Generally direct synthesis is carried out at

pressures above 20 bar [2], but this experiment has been done of direct synthesis of DME at 5 bar. The challenge in this study is to find the right combination to be able to handle the DME synthesis process at low pressure.

2 Materials and methods

2.1 Materials

In this experiment, we used two kinds of catalyst: M151 as commercial catalyst for synthesis of methanol and γ -Al₂O₃ as catalyst for dehydration of methanol to DME. Combination of both catalysts was used as catalyst of direct synthesis of DME from syngas. To obtain a good catalyst combination, the experiments were carried out in the ratio of methanol catalyst and methanol dehydration (M/D) the range of 10% - 90%.

Gas mixture containing 7% H₂ and N₂ was used for reduction of CuO in the raw catalyst of methanol synthesis catalyst. N₂ was used as inert for purging the reactor. A syngas model was made of 65% H₂, 28% CO and N₂.

2.2 Catalysis characterization

Characteristic of both catalysts were determined by nitrogen absorption at 77,3 K in Quantochrome Instruments Nova 300e. Brunauer-Emmett-Teller (BET) method was used to analyst of surface area of catalyst, and pore volume and diameter volume used Baret-Joyner-Halenda (BJH).

2.3 Experimental procedure

Experiments were carried out in three steps i.e purging of reactor, reduction of CuO in catalyst and synthesis of

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DME (**Fig.1**). Purging was carried out to remove O₂ and other gases inside the reactor. Ultra High Purity (UHP) of N₂ at 100 mL/min was used to this process. Reduction was performed to activate the catalyst. CuO in methanol catalyst was converted to Cu⁰ (**R5** and **R6**). Catalyst was activated by 7% H₂ at 60 mL/min and 1,5 bar. The reduction process temperature was increased from 150°C to 270°C with a heating rate of 30°C/h. Reduction temperature was hold at 270°C for 3 hours.

Reduction of CuO in Cu based catalyst:

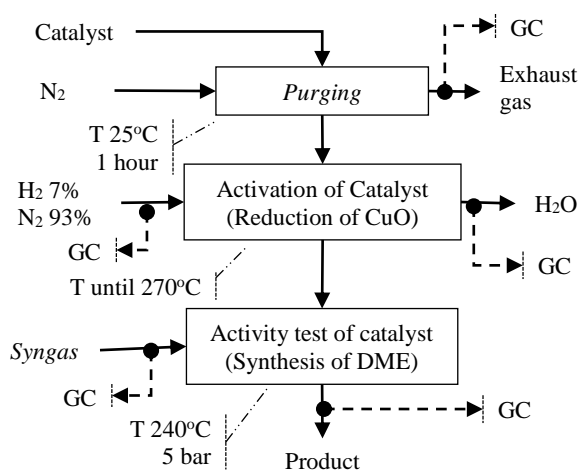
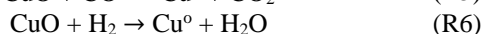
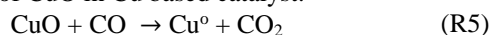


Figure 1. Procedure of direct synthesis of DME

Experimental study on direct synthesis of DME has been conducted using tubular fixed reactor (**Fig. 2**). The reactor consists of 15 cm stainless steel (SS316, 1.5 cm O.D), in where catalysts were placed for direct synthesis of DME. A mixture of H₂, CO, and N₂ was used as a model for synthesis gas. Gas flow rate was set at 20 mL/min (5 bar and 240°C) and Gas Hourly Space Velocity (GHSV) was about 4,837 h⁻¹ to methanol catalyst. The reaction conditions were set at: pressure of 5 bar and a temperature of 240°C. Gas product was analyzed using gas chromatography.

2.4 Procedure of analysis

Composition of product of synthesis was done using two kind of gas chromatography (GC). GC-2014 Shimadzu was used to analyses CO, CO₂, N₂, H₂ and CH₄. Thermal conductivity (TCD) detector uses Porapak Q – Molecular sieve 5A in parallel column. The temperature of GC was operated by in the following conditions: injector of 200°C, detector of 150°C, column of 200°C, and Argon as carrier gas. The heating rate was 10°C/min and current 70 mAh. The flow rate of carrier gas into each column was set to 15 mL/min and sample injected for analyst was 1 mL.

Analyst of N₂, CH₃OH, and CH₃OCH₃ was done using GC 14-B Shimadzu. TCD detector and Porapak Q column was used in this gas chromatography. Operating conditions were injector of 120°C, column of 80°C,

detector of 200°C and current 50 mAh. N₂ was used as carrier gas at 30 mL/min.

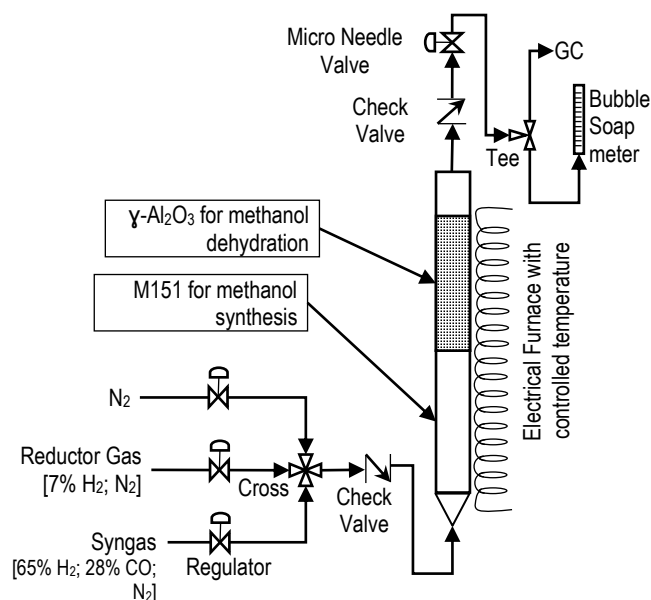


Figure 2. Experimental device

3 Results and discussion

3.1 Characteristics of catalyst

The results show that catalyst for methanol synthesis has smaller surface area, pore volume and pore diameter than $\gamma\text{-Al}_2\text{O}_3$ (**Table 1**). M151 has smaller textural properties than METS-1 as methanol commercial catalyst. METS-1 having a surface area of 76.6 m²/g and pore volume of 0.257 cm³/g [4].

Surface area of M151 catalyst was also smaller than Cu-ZnO/Al₂O₃ (CZMA(0)) catalyst used by Swastika et al [5]. Mass ratio of CZMA(0) was 40/27/33. But the activity of methanol catalyst used in this study was higher than CZMA(0) catalyst. Specific surface area of catalyst decreased at higher Cu concentration [6].

$\gamma\text{-Al}_2\text{O}_3$ was solid acid catalyst for dehydration of methanol to DME. $\gamma\text{-Al}_2\text{O}_3$ has a high selectivity for DME production [7]. It has good performance as support of catalyst. Result shown that $\gamma\text{-Al}_2\text{O}_3$ has good activity and selectivity of DME.

Table 1 Pore properties of catalysts

Catalyst	Surface Area (m ² /g)	Pore Volume (cm ³ /g)	Pore Diameter (Å)
M151 (Cu based)	37.8	0.126	66.6
$\gamma\text{-Al}_2\text{O}_3$	194.4	0.536	112.3

3.2 Activation of catalyst

In the activation process, H₂ was used as reducing gas and N₂ gas as an inert gas [8]. Catalyst reduction was carried out at temperatures of 180 to 270°C (**Fig. 3**).

The increase in the reduction temperature was set to 30°C and held for one hour at each temperature. The reduction process was stated to have been completed if concentration of output H₂ has been same as input of H₂. Process of reduction of catalyst has been completed at 270°C (Fig. 3).

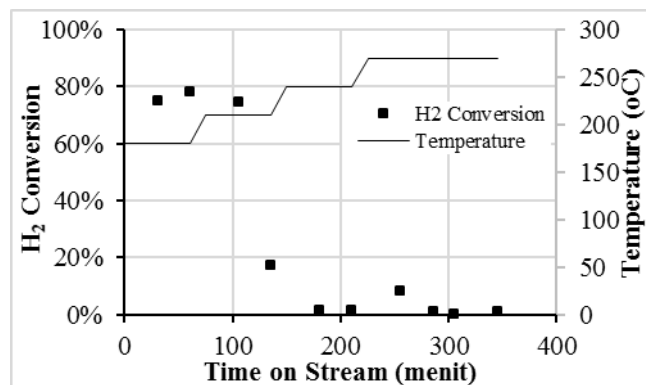


Figure 3. Typically profile of reduction process

Conversion of H₂ reached 80% in the first hour of reduction reaction. It indicates the consumption of H₂ for reduction of CuO to Cu on the M151 catalyst. The conversion result shows the reduction reaction of catalyst M151 was stopped at a reaction temperature of 240°C. Conversion was constant at 0% when the reduction reaction has lasted for 3 hours.

3.3 Catalytic activity of catalyst

Direct synthesis of DME was conducted by dual bed catalyst (M151 and γ -Al₂O₃). Same experiment was done by Palaez et al [4]. Palaez used METS-1 as methanol catalyst and also used γ -Al₂O₃ as methanol dehydration catalyst. The objective of our experiment was finding out the best dual catalyst composition for direct synthesis of DME.

Activity of catalyst was analyzed at various combination (Table 2). In fixed bed reactor the bed catalyst was arranged in series. First, syngas reacted in M151 and formed methanol, and then dehydration methanol in γ -Al₂O₃ to formed DME.

Table 2. Composition of dual catalyst

No	M/D Ratio (wt)	Mass of M151 (gram)	Mass of γ -Al ₂ O ₃ (gram)	Legend in Fig. 4
1	1/9	1	9	10%
2	1/4	2	8	20%
3	1/2	2	4	33%
4	2/3	2	3	40%
5	1/1	2	2	50%
6	2/1	2	1	67%
7	4/1	2	0.5	80%
8	9/1	2	0.22	0.536

* ratio of methanol synthesis catalyst to dehydration catalyst

According of R4 reaction and feed of reactor, limiting reactant of direct synthesis of DME was CO. So

identification of activity of catalyst was based on conversion of CO gas. The highest conversion of CO and stability for 6 hours operation was 20% of catalyst of methanol synthesis (mass ratio of catalyst for methanol to dehydration of 1/4) at 240°C and 5 bar (Fig. 4). CO conversion was 62% and ratio of DME to methanol was 40% as product of reactor.

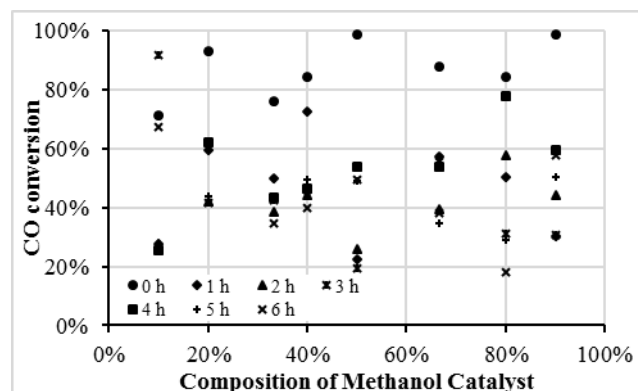


Figure 4. Activity of dual catalyst on direct synthesis of DME

Swastika et al (2018) conducted a test of the activity of catalysts in the same conditions as this experiment, namely pressure of 5 bar and temperature of 240°C using a bifunctional catalyst CZMA(0) containing of CuO/ZnO/Al₂O₃ with ratio 40/27/33 [5]. CO conversion was 60% on stream time that it was not much different from this study, i.e. 64%. But yield and selectivity of DME products obtained in this study was higher than CZMA(0) catalyst.

γ -Al₂O₃ catalyst has an important role of yield and selectivity of DME product. The high of yield and selectivity of DME product proved that γ -Al₂O₃ has good activity as catalyst of methanol dehydration. γ -Al₂O₃ activity (this study) has been proven by the experiment of dehydration of methanol. Catalyst convert up to 90% of methanol at high methanol concentrations in feed reactor with selective products to DME.

CO conversion was high at the beginning of reaction (93%) and decrease at first hour of operation. conversion was constant at 3 hours operation (Fig. 4). This indicates that CO is consumed to activate the catalyst which has not been fully activated at the beginning of the reaction. This statement was supported by the results of the reactor product composition. CO₂ and H₂O have formed at the beginning of the reaction, while methanol and DME were formed slightly. CO₂ and H₂O were formed from the conversion of CuO to Cu⁰ as active site of methanol catalyst (R5 and R6).

The formation of CO₂ in the R5 reaction caused a shift at equilibrium of water gas shift reaction form H₂O (R3). The presence of H₂O made a decrease in dehydration methanol catalyst activity. H₂O would compete with methanol in adsorption on the surface of γ -Al₂O₃. These made a decrease of DME production [9]. This could be anticipated by impregnation of metals such as Si and P over γ -Al₂O₃ catalyst.

The water gas shift reaction has a tendency to take place at temperature below 1,165°C, and forms CO₂ and H₂ [10]. Since the experiments in this study were carried

out at a temperature of 240°C, the water gas shift reaction likely to take place.

Cu-based catalysts also promote the water gas shift reaction. Cu/ZnO/Al₂O₃ catalyst with ratio of copper to zinc of 1:2 was used as catalyst of water gas shift reaction (WGS) in a Low Temperature Shift Converter (LTSC) with an inlet temperature of 200°C [8]. So CO₂ could be formed through two reactions, i.e. the water gas shift reaction and reduction of CuO to Cu⁰.

Another reason for the low of methanol synthesis catalyst activity in this study that CuO was not completely reduced to Cu⁰ (active site of methanol catalyst). So it also caused low of DME production and deactivation due to H₂O on the catalyst surface. CO₂ which was a by-product of the water gas shift reaction had a composition above 94% of all reaction products (Fig. 5). The presence of high CO₂ concentrations caused a decrease in DME production [11, 12].

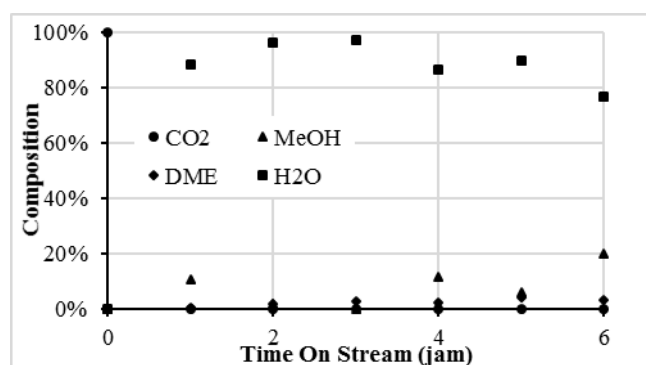


Figure 5. Composition of outlet gas from direct synthesis of DME

Yields of methanol and DME at this process were 0.08% and 0.14% respectively (Fig. 6). Yields of methanol and yield of DME in this experiment still increased during the 6 hours of reaction. These indicated that reactions were not reached its equilibrium. Yield of DME might be improved as a longer reaction time. Modification of γ -Al₂O₃ will be done in the next experiment.

Selectivity of DME was defined as the mole ratio of produced DME to all by product. The highest DME selectivity in this process only reached 4.6% (Fig. 7). In this process the more dominant product was CO₂ from reduction of CuO to Cu⁰ and water gas shift reaction.

The selectivity of DME products might be increased by suppressing the CO₂ formation. This might also reduce the formation of H₂O which causes deactivation of methanol dehydrated catalysts. The decrease of CO₂ could also increase methanol formation as the DME intermediate substance.

4 Conclusion

Experiment on a dual catalyst were carried out successfully with a commercial catalyst M151 as a catalyst for methanol and γ -Al₂O₃ as a catalyst of dehydration of methanol at 5 bar and 240°C. The results

shown that CO conversion reaches 64% in a combination of 20% methanol catalyst. The activation of methanol

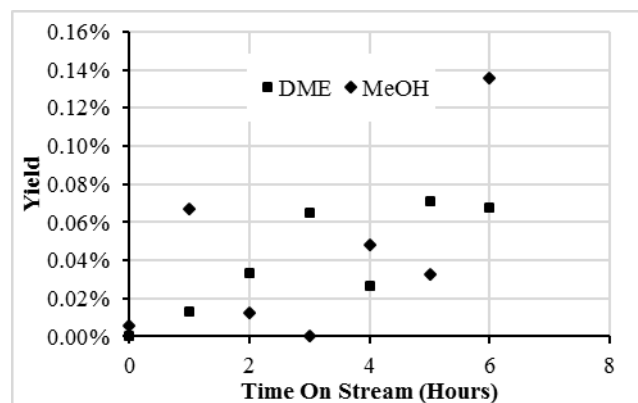


Figure 6. Yield of DME and methanol at 20% of methanol catalyst

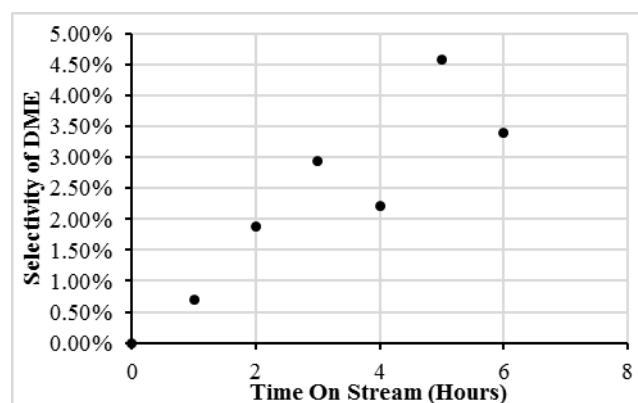


Figure 7. Selectivity of DME at 20% of methanol catalyst

synthesis catalyst (reduction of CuO to Cu⁰) was the important step. The presence of CO₂ and H₂O as a byproduct of the reduction of CuO catalyst caused a decrease in DME production. The presence of CO₂ in the reaction system might cause a low yield of DME of 0.14% and a low DME selectivity of 4.6%. Furthermore, the presence of H₂O form in the shift reaction cause a low γ -Al₂O₃ activity.

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