SIChem
International Symposium of Indonesian Chemical Engineering - 2018
4th – 6th October 2018, Padang, West Sumatera, Indonesia

PREPARATION OF CATALYST Cu-ZnO-MgO-Al_2O_3 FOR DIRECT SYNTHESIS OF DME

Titis Swastika, Aisyah Ardy, Herri Susanto*
Department of Chemical Engineering
Institut Teknologi Bandung, Bandung 40132, Indonesia
**corresponding author: herri@che.itb.ac.id*

Abstract. DME (dimethyl ether) has been declared by the government of Indonesia in *the RUEN2017* as a partial substitution of LPG in the near future. A catalyst for direct synthesis of DME from synthesis gas were prepared using the co-precipitation method. The raw catalyst contained CuO/ZnO/Al_2O_3 with the mass ratio of about 40/27/33. Two types of catalyst were prepared, i.e. CZMA0 (without Mg) and CZMA20 (with Mg 20%). Both types of catalyst were activated by using reducing gas containing 5% H_2 and N_2 and then tested for the activity in direct synthesis of DME, by using an artificial synthesis gas with a composition (mole fraction) of 65% H_2, 28% CO and 7% N_2. Synthesis reaction was carried out in a fixed bed reactor at 5 bar, and temperature of 240ºC, 250ºC or 260ºC. In the synthesis process, CZMA20 catalyst resulted a highest CO conversion of 73% and a highest H_2 conversion of 66% (at 5 bar and 260ºC). In this study, experiments on synthesis of DME were also performed using a dual-catalyst, i.e. a bed of catalyst for methanol synthesis and a bed of catalyst for methanol dehydration to DME and the result showed CO conversion of 93% and H_2 conversion of 91% were obtained.

keywords: coprecipitation, bifunctional catalyst, catalyst for methanol synthesis, catalyst for methanol dehydration, synthesis of dimethyl ether

1. Introduction

In 2017, the government of Indonesia has established that DME (dimethyl ether) will be used for a partial substitution of LPG. At present, DME is commercially made by dehydrating methanol, including a factory in Indonesia. DME has similar properties with LPG, such as: vapor pressure at room temperature and burning characteristic. So there will not be much effort in storage, transportation and use of DME. DME is also used as propellant in many home applications. DME has been a particular concern around the world. A`large production capacity of DME will be needed in order to meet future demand [1].

DME is generally produced through two process steps. Firstly, natural gas, hydrocarbons, coal, or biomass are converted to synthesis gas containing H_2 and CO. The synthesis gas is then further processed to DME. This two step process may be expressed in the following reactions:

a. synthesis of methanol

$$CO + 2H_2 \leftrightarrows CH_3OH \quad (1)$$

b. dehydration of methanol to DME

$$2CH_3OH \leftrightarrows CH_3OCH_3 + H_2O \quad (2)$$

c. water-gas shift reaction:

$$CO + H_2O \leftrightarrows CO_2 + H_2 \quad (3)$$

The third reaction may influence the extent of the other two reactions.

Many researches are directed to develop a single step DME synthesis, directly from synthesis gas to DME without producing methanol to avoid purification and dehydration. Reaction in the single step DME synthesis is simply:

$$2CO + 4H_2 \leftrightarrows CH_3OCH_3 + H_2O \quad (4)$$

An important factor in the single step DME synthesis is the catalyst. Direct synthesis of DME (reaction 4) may be handled using Cu-based catalyst as reported in [1]. Unfortunately, this type of catalyst has low thermal stability, so development is being done to improve the catalyst resistance.

Catalyst for direct synthesis of DME may also be considered as a bifunctional catalyst: one for methanol synthesis and another one for dehydration of methanol. Metal components of bifungsional catalysts generally comprise oxides such as CuO, ZnO, MgO, Al_2O_3. In many developments, the acid-solid catalysts for synthesis of DME include γ-Al_2O_3, alumina modified with silica, TiO_2-ZrO_2, ion exchange resin, bohemite (AlOOH) and zeolites such as H-ZSM-5, HY, mordenite, SAPO, MCM , ferrierite, chabazite, and H-beta.

There are still many opportunities to develop Cu-based catalysts with various types of promoters similar to catalysts for methanol synthesis, while the catalyst supports perform as catalysts for dehydration of methanol. Addition of 20% MgO has been proved experimentally increases catalyst activity compared to those without MgO promoters, i.e.: increases in CO conversion from 19% to 37%, and in DME selectivity from 36% to 83% [1]. Therefore, Cu-ZnO-MgO-Al_2O_3 catalyst is interesting to be developed further.

The objective of this research was preparation of Cu-ZnO-MgO-Al_2O_3 catalyst for the direct synthesis of DME. Catalyst activity was evaluated based on CO and H_2 conversions. Our experimental results were compared to those of thermodynamic equilibrium and literature data [1].

2. Methodology

Direct DME synthesis research consists of (a) the catalyst preparation stage for direct synthesis, and its characterization; (b) activation of crude catalyst into active catalyst, or reduction of CuO catalyst core to Cu; (c) test of catalyst activity or the use of catalyst in DME synthesis process in fixed bed reactor.

2.1 Preparation of Raw Catalyst and its Characterization

Raw catalyst of CuO-ZnO-MgO-Al_2O_3 was prepared using the coprecipitation method [2]. At first, solutions of nitrate salts were mixed with a certain ratio in order to obtain the desired catalyst composition (see Figure 1). Carbonate salts of Cu, Zn, Mg and Al would precipitate when the solution of Na_2CO_3 was dripped. During the coprecipitation, temperature and pH were kept constant. The mixture was stirred at 700 rpm to get a homogeneous mixture and to assist in the formation of the catalyst crystals. After washing, the carbonate salt precipitates were calcined to obtain the raw catalysts of CuO, ZnO, MgO and Al_2O_3.

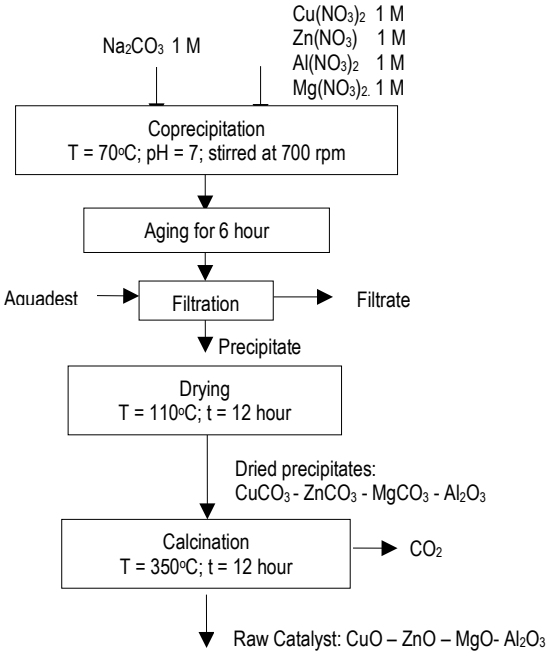


Figure 1. Preparation of catalyst using coprecipitation method

Pore property of raw catalyst was carried out using *Quantochrome Instruments Nova 300e*, in Laboratory of Analytical Instrument, Department of Chemical Engineering ITB.

2.2 Activation of Raw Catalyst (reduction of CuO to Cu)

Activation of raw catalyst must be conducted to convert CuO to Cu in the same reactor with synthesis before the use of catalyst. This reduction of CuO was done by passing a mixture of low concentration of H_2 gas (5%) and N_2. The reduction process was carried out at a pressure of 1.5 bar, and the temperature was increased step by step.

a. Purging the reactor using N_2 at a pressure of 1.5 bar and a temperature of 150°C for two hours. The flow rate of N_2 was about 80 mL/min (measured at ambient temperature of about 20°C).
b. Flowing the reducing gas (5% H_2 and N_2) into the reactor at a rate of 80 mL/min, at 1.5 bar and 150°C for 1 hour.
c. Increasing reactor temperature to 180°C, and maintained at this temperature for 1 h.
d. Increasing reactor temperature to 210°C, and maintained at this temperature for 1 h.
e. Increasing reactor temperature to 240°C, and maintained at this temperature for 1 h.
f. Increasing reactor temperature to 270°C, and maintained at this temperature for 3 h.

Started from the reactor temperature of 180°C, the progress of reduction from CuO to Cu was observed by measuring the consumption of H_2. The activation process or reduction of CuO was stopped when the H_2 concentration at the reactor effluent was the same as influent. This activation process was very critical step related to the catalyst activity in the synthesis process.

The activation and activity test of catalyst were carried out in a fixed bed tubular reactor with a a diameter of 1.3 cm and a length of 38 cm. This reactor was heated using electric heater, and provided with a temperature controller. Schematic diagram of activation and activity test of catalyst are presented in Figure 2.

2.3 Activation Test of Catalyst (direct synthesis of DME from synthesis gas)

Without opening the reactor, the reactor temperature was decreased to a desired temperature of synthesis, i.e.: 240, 250, or 260°C. The flow of reducing gas was changed with the synthesis gas (in this case, gas composition was 65% H_2, 28% CO and 7% N_2). Operating pressure 5 bar and temperature 240°C, 250°C or 260°C. The flow rate of the synthesis gas was 50 mL/min. In this study, the synthesis process was carried out for 10 hours.

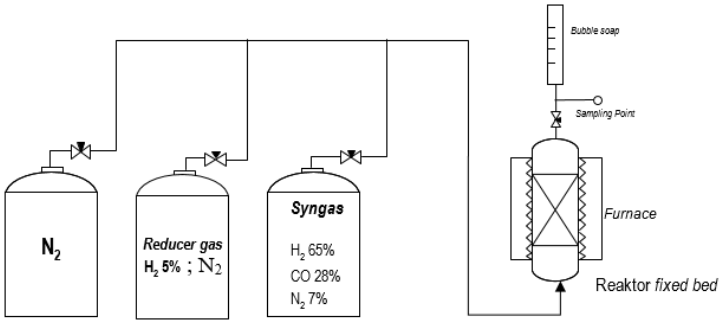


Figure 2. Flowchart of DME synthesis set of tools

2.4 Gas Analysis

The gas compositions were analyzed using two gas chromatography:
(a) Shimadzu GC-14B, with a separation column of Porapak-Q: for analysis of CH_3OH and CH_3OCH_3
(b) Shimadzu GC-2014, with a separation column of Porapak-Q and Molsieve for for analysis of H_2, CO, CO_2 and N_2

Compositions of inlet gas were checked at the beginning of experiments on catalyst activation and activity test. The gas compositions at the outlet of reactor during activation of catalyst were analyzed every 15 min (see the above mentioned procedure of reduction). This data was very important for evaluating the extent of CuO reduction.

During activity tests of catalyst, samples from the outlet gas from reactor were taken every 15 or 30 min. The samples were analysis for gaseous composition and for methanol and DME compositions.

3. Results and Discussion

3.1 Catalyst Characterization

Surface area of catalyst was considered as the most important catalyst character. This pore surface area was measured on the raw catalyst (before activation or reduction of CuO). Catalyst CZMA(0), Cu-ZnO-Al_2O_3 without addition of MgO, had a surface area of 285 m^2/g. While Catalyst CZMA(20) with addition of 20%MgO had a surface area of 125 m^2/g.

3.2 Activation of Raw Catalyst

Both catalyst CZMA(0) and CZMA(20) had similar progress in CuO reduction as indicated with H_2 conversion (Figure 3). Based on the progress of H_2 conversion, hydrogen consumption in activation of CZMA(20) was clearly more than that of ZCMA(0), as indicated by a higher H_2 conversion for CZMA(20). Activation could be considered as completely finish at after 400 min.

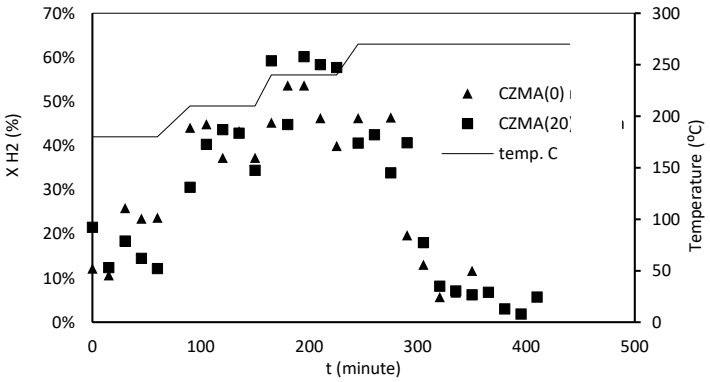
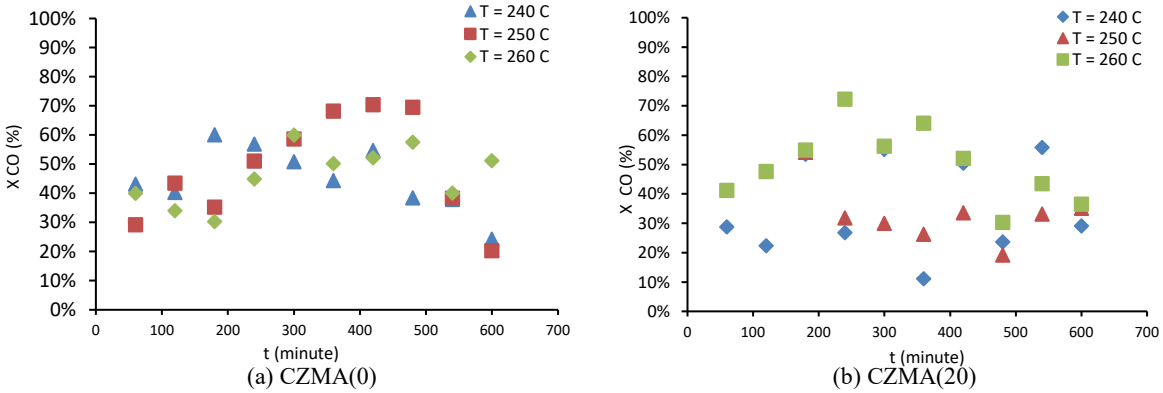


Figure 3. Average H_2 conversion

3.3 Effect of Temperature on CO Conversion and H_2 Conversions

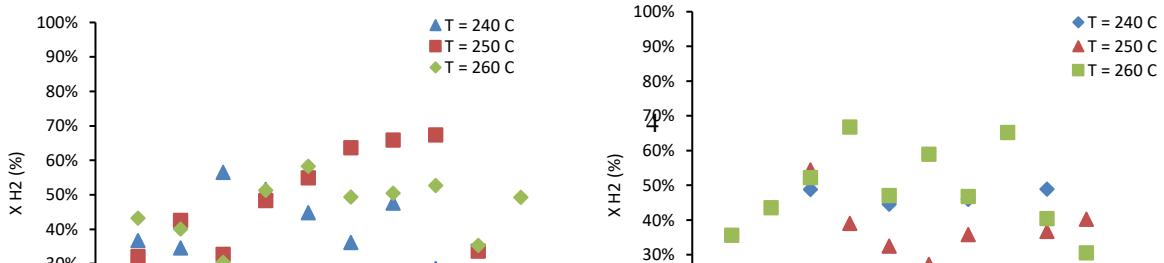
Fresh catalyst were used in each condition in the activity tests. CO conversion from CZMA(0) appeared the same for reaction time until 300 min, at three different reaction temperatures (Figure 4.a). This probably indicated that the activity of CZMA(0) could be kept constant for a certain period in the beginning of synthesis. After 300 min in process, the activity of each catalyst changed significantly, meaning that the durability of catalysts activity weas not long time. For CZMA(0) at 240°C, its activity decreased significantly after 200 min in process. Meanwhile activities of CZMA(0) at 260°C increased gradually with time, but the experiments was stopped at 650 min. Activity of CZMA(0) at 250°C was the best until 500 min in process, even it dropped drastically afterward. Thus, the quality of this catalyst was not homogeneous or the reproducibility in preparation of catalyst was not good. Discussion of this aspect was also applicably for catalyst CZMA(20).



(a) CZMA(0) (b) CZMA(20)

Figure 4. CO conversion in during activity test of catalyst for synthesis of DME
pressure, P = 5 bar; synthesis gas flow rate, Q = 50 mL/min

Despite of erratic data as shown in Figure 4, the present CO conversions were relatively higher 60% against 35% reported by Asthana et.al. with a pressure of 30 bar, in [1]. According to the thermodynamic of reaction equilibrium (calculated using *Aspen*), CO conversion might be as high as 90% at those reaction temperatures. Thus, there was a large chance to improve the catalyst.



(a) CZMA(0) (b) CZMA(20)

Figure 5. H_2 conversion in during activity test of catalyst
P = 5 bar; Q = 50 mL/min

Again, based on H_2 conversion (Figure 5), the stability of catalyst was apparently very low. Progress in H_2 conversions were quite the same as CO conversion. The highest H_2 conversion was about 60%, but surprisingly it was higher than that of thermodynamic equilibrium of 40% for DME synthesis (equation 4). Probably, there were other reactions consuming H_2 beside direct synthesis of DME according equation (4). Such as:

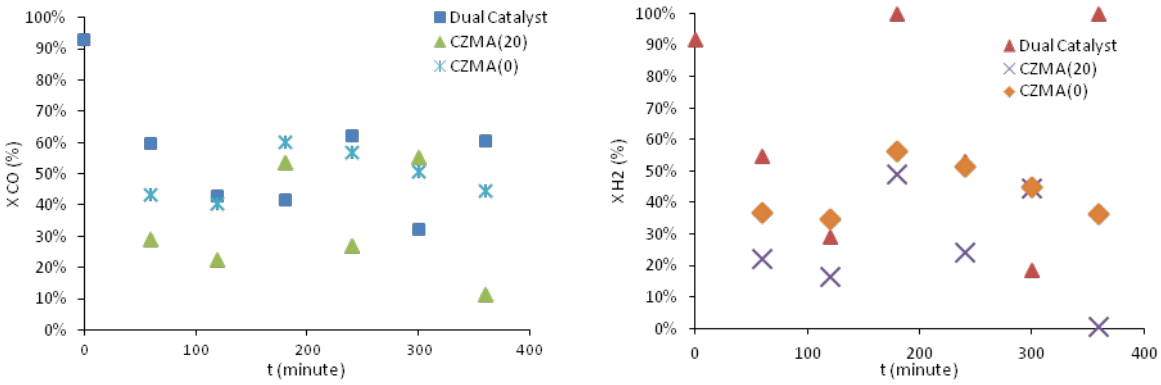
$$3H_2 + 3CO \leftrightarrows CH_3OCH_3 + CO_2 \quad (5)$$

$$H_2 + CO_2 \leftrightarrows CO + H_2O$$

$$CuO + H_2 \leftrightarrows Cu + H_2O \quad (6)$$

Reaction (5) is the sum of methanol synthesis (equation 1), methanol dehydration (equation 2) and homogeneous water shift (equation 6). Reaction (6) might be possible if: (a) the catalyst activation step was not yet completed or (b) catalyst was exposed to air so there was re-oxidation of Cu.

A series of experiments using two fixed bed was trialed with a commercial catalyst of methanol synthesis (Topsoe M151) and a methanol dehydration catalyst (γ-Al_2O_3). The ratio of those catalyst was about 1:4 respectivley. Reaction was carried at a temperature of 240^{0}C and a pressure of 5 bar. As expected the CO and H_2 conversions were significantly higher than those CZMA(0) and CZMA(20). A more stable activity of the dual catalyst was also observed (Figure 6), unfortunately the experiments was not yet carried out for sufficiently long time.



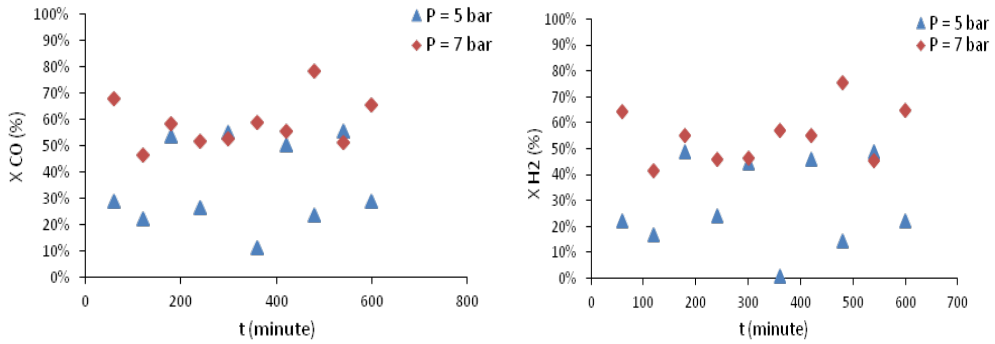
(a) CO conversion (b) H_2 conversion.

Figure 6. Comparison of activity of CZMZ(0) CZMZ(20) and dual catalyst

3.4 Effect of Pressure on CO and H_2 Conversions

Based on equation (4), a higher pressure would give a higher conversion. Indeed, our experiments with a pressure of 7 bar resulted higher CO conversion (Figure 7), as well as H_2

conversion. Surprisingly, the catalyst activity at reaction pressure of 7 bar appeared more stable than that of 5 bar, for both CZMA(0) and CZMA(20). Furthermore, activity of both catalyst also looked the same, based on CO conversion.



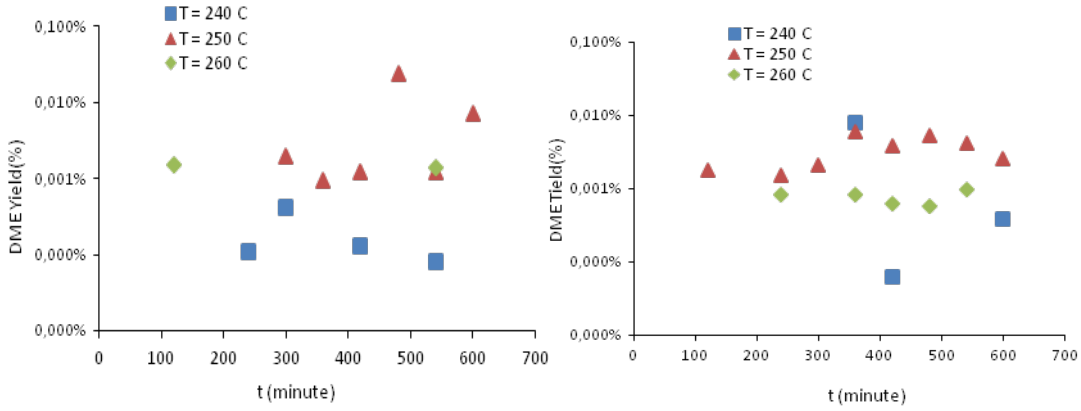
(a) CZMA(0) (b) CZMA(20)

Figure 7. Effect of pressure on CO conversion
T = 240°C

Effect of pressure would be more significant on methanol synthesis (equation 1) than on methanol dehydration reaction (reaction 2). Thus the formation of methanol would be more than that of DME, as a result increasing reaction pressure would give a higher concentration in the product. This phenomenon was reported by Prasad, et.al. [10]. So in a dual catalyst system, the amount of catalyst for dehydration should be larger than the amount of catalyst for methanol synthesis.

3.5 Yield of DME

Yield of DME was defined as a molar fraction of incoming synthesis gas (CO and H_2) converted into DME. Absolutely, the yield of DME was very disappointed, it was less than 0.01% (Figure 8).



(a) CZMA(0) (b) CZMA(20)

Figure 8. Yield of DME
P = 5 bars; Q = 50 mL/min

The best yield of DME indicated by performance of CZMA(20) catalyst which DME has begun to appear in the second hour of synthesis until the end time of synthesis. The small of yield DME obtained by a direct DME catalyst (Cu-ZnO-MgO-Al_2O_3) is not well formed for the formation reaction of dimethyl ether because the role of Al_2O_3 in this case can not really be a buffer that can accelerate the reaction towards the formation of DME. The ratio of catalyst synthesis meOH (CuO-ZnO-MgO) to dehydration catalyst (Al_2O_3) is greater than that in this experiment (1/3).

3. Conclusions

Experiments show satisfactory results in some aspects, but there are still some further development opportunities.

a. CZMA catalyst (0) has a good pore surface area, 285 m^2/gram
b. At the activation stage or CuO reduction step to Cu, CZMA catalyst (20) consumes more H_2 than CZMA (0), and takes longer.
c. In the process of synthesis or test of catalyst activity with CZMA (20) at a pressure of 5 bar, the highest CO conversion is 73% and the highest H_2 conversion is 67%. Here we see the effect of adding MgO to conversion.
d. In the process of synthesis or test of catalyst activity with CZMA (20) at 7 bar pressure, the highest CO conversion became 79% and the highest H_2 conversion reached 79%. So there is an effect of process pressure on the conversion.
e. CO conversion and H_2 conversion from this study is better than [1], but the conversion is still for below thermodynamic equilibrium conversion, about 93%.
f. Using a double catalyst configuration comprising a methanol synthesis catalyst bed and a methanol dehydration catalyst feeder being converted to DME, CO conversion and H_2 conversion may be increased again.
g. In this study, the yield of DME is still very low. This may be due to the production of byproducts, such as methanol (intermediate product), and CO_2 that is significantly detectable with chromatographic gas.

4. Acknowledgments

This study was a part of Master Thesis at Department of Chemical Engineering , ITB. The authors would like to thank to *the Indonesian Palm Oil Estate Fund* (BPDPKS) for funding our research on *Biomass to Methanol/DME*, in Fiscal Year of 2018

References

1. Asthana, S., Samantha, C., Bhaumik, A., (2016): Direct Synthesis of Dimethyl Ether From Syngas Over Cu-Based Catalysts: Enhanced Selectivity in The Presence of MgO. Journal of Catalysis 334 (2016) 89-101.
2. Hermansyah (2010): DME Synthesis Using Cu-Zn/ɣ-Al_2O_3 Catalyst in Fixed Bed Reactor, Chemical Engineering Department, Faculty of Engineering, University of Indonesia UI Campus, Depok, Chemical and Process Engineering Conference, ISSN: 1411-4216
3. Huang, M.H., Lee, H.M., Liang, K.C., Tzeng, C.C., Chen, W.H., (2015): An Experimental Study On Single Step Dimethyl Ether (DME) Synthesis From Hydrogen and Carbon Monoxide Under Various Catalyst, Institute of Nuclear Energy Research, Taoyuan 325, Taiwan and Department of Aeronautics and Astronautics, National Cheng Kung University, Tainan 701, Taiwan, *International Journal of Hydrogen Energy XXX,* I-II.
4. Kunpeng, Sun, Weiwei Lu, Fengyan Qiu, Shuwen Liu, Xianlun Xu (2003): Direct Synthesis of DME Over Bifunctional Catalyst: Surface Properties and Catalytic Performance, Lanzhou Institute of Chemical Physics, Chinese Academy of Science, Lanzhou 730000, China
5. Lee, Y.J., Jung, M.H., lee, JB., Jeong, K.E., Roh, H.S., Suh, Y.W., Bae J.W., (2014): Single Step Synthesis of Dimethyl Ether from Syngas on Al_2O_3-modified CuO-ZnO-Al_2O_3/Ferrierite Catalyst: Effects of Al_2O_3 Content, Korea
6. M. Gadek, R. Kubica, E. Jedrysik., (2013): Production of Methanol and Dimethyl Ether from biomass derived syngas-a comparison of the different synthesis pathways by means of flowsheet simulation, Department of Chemical and Process Apparatus Construction, Silesian University of Technology, Poland
7. Moradi, G.R., Ahmadpour, J., Yaripour, F., (2007): Effect of The Hybrid Catalyst Preparation Method Upon Direct Synthesis of Dimethyl Ether from Synthesis gas, Catal, Commun, 598-600
8. Ng, K. L., D. Chadwick and B. A. Toseland., (1999): Kinetics and Modelling of Dimethyl Ether Synthesis From Synthesis Gas, Chemical Engineering Science. 54, 3587-3592
9. Nursiam, R., (2013): Industrial Chemical Industry Process Paper Synthesis Dimethyl Eter, Samarinda
10. Prasad, P.S., Bae, J.W, Kang, S.H., Lee, Y.J., Jun, K.W, (2008): Single Step Synthesis of DME from Syngas on Cu-ZnO-Al_2O_3/Zeolite Bifunctional Catalyst; The Superiority of Ferrierite

Over The Other Zeolites, Korea Research Institut of Chemical Technology, Republic of Korea, Fuel Processing Technology, 89, 1281-1286

11. Qingjie Ge, Youmei Huang, Fengyan Qiu, Shuben Li (1997): Bifunctional Catalyst for Conversion of Synthesis Gas to Dimethyl Ether, Lanzhou Institute of Chemical Physics, Chinese Academy of Science, China
12. Sung-Hwan Ahn, Song-Hyoung Kim, Kwang-Bo Jung, dan Hyun-Sik Hahm, (2007): Effect of Pressure on Direct Synthesis of DME from syngas over Metal-pillared IleritesI, Korean J. Chem. Eng., 466-470