Reaction Kinetics Study of Methanol Dehydration for Dimethyl Ether (DME) Production Using Dealuminated Zeolite Y Catalyst

Luqman Buchori*, Didi Dwi Anggoro

Department of Chemical Engineering, Faculty of Engineering, Diponegoro University, Jl. Prof. Soedarto, SH, Tembalang, Semarang, Indonesia 50275
luqman.buchori@che.undip.ac.id

Dimethyl ether is classified as an alternative material that can be renewed and used for diesel engines, diesel fuel, and gas stoves as a household fuel. Dimethyl ether production was carried out by dehydration of methanol. The catalyst used in this process was dealuminated zeolite Y. This study aims to determine the effect of temperature on conversion, reaction rate constants, activation energy, and collision factor (A) in the synthesis of dimethyl ether. The reaction was carried out in a fixed bed catalytic reactor where the temperature was varied at 225-325 ^{o}C. The gas product was analysed by Gas Chromatography-Mass Spectrometry (GCMS), while the liquid product was analysed by High-Performance Liquid Chromatography (HPLC). The calculation of reaction kinetics was carried out using MATLAB. The results showed that the highest conversion was obtained at a reaction temperature of 225 ^{o}C which was 75.58 %. The reaction rate constant was obtained at 0.1795 l/mol.h with the activation energy and the collision factor values are 1.044 x 10^{3} cal/mol and 0.0589, respectively.

1. Introduction

Energy is a basic human need that continues to increase in line with the level of life. Oil fuel or fossil energy is one of the non-renewable energy sources that has been the mainstay of meeting energy needs in all activity sectors (Chen et al., 2021). Currently, petroleum is still the primary energy source to meet the needs of people in Indonesia. Like the consumption of petroleum, consumption of LPG (Liquid Petroleum Gas) is continuously increasing from year to year. LPG demand is estimated to increase from 7.2 million tons in 2017 to 17.4 million tons in 2050 or an average increase of 2.7 % per year (Agency for the Assessment and Application of Technology, 2019). Current LPG production in Indonesia is only 2.0 million tons, so importing LPG is required to meet this demand. However, it is feared that the increase in LPG imports will burden Indonesia's current trade balance. The increase in consumption of fossil-based energy, especially LPG (Liquid Petroleum Gas), which is not balanced with the availability of energy reserves, demands the development of other abundant and environmentally friendly alternative energy.

Dimethyl ether is a simple ether compound produced from various raw material sources such as natural gas, coal, and biomass. Dimethyl ether (DME) has a high cetane number and has properties close to that of LPG, such as viscosity, boiling point, and pressure (Rosadi et al., 2020), so it is imperative to study the possibility of using DME to replace or reduce the use of diesel and LPG in Indonesia. Dimethyl ether not only can be used in industry and transportation as well as power generation as a substitute for diesel oil, but also possesses the opportunity to replace LPG as a fuel in the household, commercial, and industrial sectors (Azizi et al., 2014), which are currently mostly imported (Agency for the Assessment and Application of Technology, 2019). Dimethyl ether is classified as an alternative material that can be renewed and used for diesel engines, diesel fuel, gas stoves fuel as a multi-source and multi-use household fuel (Makos et al., 2019).

In general, the DME production process can be carried out in two stages: methanol synthesis from the conversion of biomass or the reaction of carbon monoxide or carbon dioxide gas with hydrogen, then followed by the methanol dehydration process to produce DME and water molecules (Azizi et al., 2014). Zeolite is one

type of catalyst that is commonly used in the DME manufacturing process due to its abundant stock in Indonesia. Moreover, zeolite is a solid catalyst that can help the dehydration process of methanol into DME products. However, the catalyst used should have specifically required characteristics. The properties of the zeolite-based catalyst can be improved through dealumination and calcination processes (Anggoro et al., 2020). Dealumination is the most common method for increasing the SiO_2/Al_2O_3 ratio resulting in mesoporosity in zeolites with high Si/Al ratios, to the newly created porosity produced by preferential extraction of the Si frame due to hydrolysis in the presence of OH^- ions (Borges and de Macedo, 2016). Zeolite Y has an acidity comparable to amorphous silica-alumina supports, so it has similar selectivity (Dik et al., 2014). Calcination is a way to remove water content or organic molecules by heating to activate the material, creating pore structures from the available structures (Gualtieri, 2006).

Several researchers have studied on the reaction kinetics model of the DME synthesis (Hosseininejad et al., 2012; Ng et al., 1999; Nie et al., 2005; Ortega et al., 2018). Ng et al. (1999) studied the kinetics of the synthesis process of methanol and DME with a commercial $CuO/ZnO/Al_2O_3$ catalyst (in the methanol formation) and γ-alumina catalyst (in the dehydration process). They used the Vanden Bussche and Froment kinetics models for methanol + DME synthesis and the Bercic and Levec kinetics models for methanol dehydration. Nie et al. (2005) investigated the intrinsic kinetics of the synthesis of dimethyl ether from syngas in a bifunctional catalyst mixed with methanol synthesis catalyst and methanol dehydration catalyst with a mass ratio of 1:1 in a tubular integral reactor at 3-7 MPa and 220-260 ^oC. Three reactions including methanol synthesis from CO and H_2, CO_2 and H_2, and methanol dehydration were selected as independent reactions. Meanwhile, Ortega et al. (2018) explored the intrinsic kinetics of the conversion of methanol to dimethyl ether using the ZSM-5 catalyst. The kinetic test was carried out in a fixed bed external recycling reactor, without temperature and concentration gradient. Kinetics studies on converting methanol to dimethyl ether using a dealuminated zeolite Y catalyst have not been found in previous studies. Therefore, the purposes of this work are to determine the effect of temperature on the conversion of methanol into DME, the effect of temperature on the reaction rate constants of DME formation and evaluate the activation energy and collision factor (A) of DME synthesis reaction from methanol.

2. Materials and methods

2.1 Materials

The raw material used in this study was zeolite Y obtained from Surabaya, Indonesia. Methanol (99.99 %), sulfuric acid pro analyst grade, and ammonia solution (25 %) were purchased from Merck. The distilled water was supplied from the Integrated Laboratory, Diponegoro University, Indonesia.

2.2 Dealumination of zeolite Y

The zeolite Y catalyst dealumination was carried out using sulfuric acid solution. The sulfuric acid solution was first prepared at a concentration of 8.5 N. The acid solution was then filled into a three-neck flask. A total of 15 grams of zeolite Y was added to the sulfuric acid solution. The mixture was heated to a temperature of 50 ^oC and maintain the temperature using temperature control. The dealumination process was performed at 50 ^oC for 3.5 h in constant stirring. The mixture was then filtered using Whatman 42 filter paper under vacuum condition using suction pump (Krisbow 1/3HP KW19-533). The solid obtained was dried in an oven Memmert UN 55 B214.0281 for 1 h at 110 ^oC. The acquired dry solid was calcined in the furnace (Ney Vulcan D-550-240 V) at 550 ^oC for 3 h. The resulting product was a dealuminated zeolite Y. The equipment set used for the dealumination process is shown in Figure 1A.
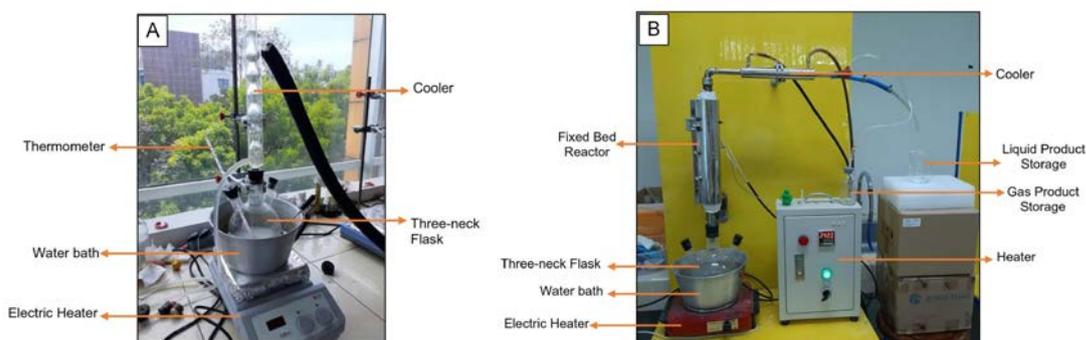
Figure 1: (A) Experimental set up of catalyst dealumination process, (B) Experimental set up of methanol dehydration process

2.3 Synthesis of dimethyl ether

The synthesis of dimethyl ether was performed in a fixed bed catalytic reactor with operating temperatures varied at 225, 250, 275, 300, and 325 ^{o}C. The reactor with an inner diameter of 1 in (2.54 cm) was filled with 15 grams of dealuminated zeolite Y catalyst. First, 200 mL of liquid methanol was put into a three-neck flask and heated using an electric heater to convert its phase into the gas phase. Then, methanol gas was fed into the reactor for the synthesis process (methanol dehydration). The reactor was heated with a heater and the temperature was adjusted according to the desired variable. The synthesis of dimethyl ether was performed for 1 h. The two-phases product was separated and analysed for its composition. Gaseous product composition was analysed using GCMS (Shimadzu, Restex RTX1-MS column) and the liquid product was evaluated using HPLC (Shimadzu, LC-20AD/T). The experimental equipment set-up of methanol dehydration process is presented in Figure 1B.

2.4 Reaction kinetic parameters evaluation

In this study, kinetics modelling was carried out based on the stoichiometric of the methanol dehydration reaction into dimethyl ether. The methanol dehydration reaction is as follows:

$$2 CH_3OH \underset{k_2}{\overset{k_1}{\rightleftharpoons}} CH_3OCH_3 + H_2O$$
$$\quad A \qquad \quad B \qquad \quad C$$
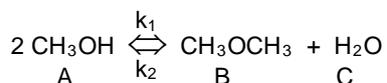
Methanol conversion is calculated using Eq(1).

$$Methanol\ conversion\ (X_A) = \frac{moles\ of\ reacted\ methanol}{moles\ of\ initial\ methanol} x100\%$$
(1)

The known data obtained from the experiment, such as conversion (X_A), methanol concentration (C_A), dimethyl ether concentration (C_B), and water concentration (C_C) were inputted into the MATLAB program to evaluate the value of reaction rate constants (k_1 and k_2). The calculation algorithm of the reaction rate constants evaluation is schematically depicted in Figure 2. The mathematical model of reaction rates was solved using the fourth order Runge-Kutta method, multivariable optimization, and Sum of Square Error (SSE). The activation energy (E_a) and the collision factor (A) were estimated using linear regression of the Arrhenius equation as a function of temperature.
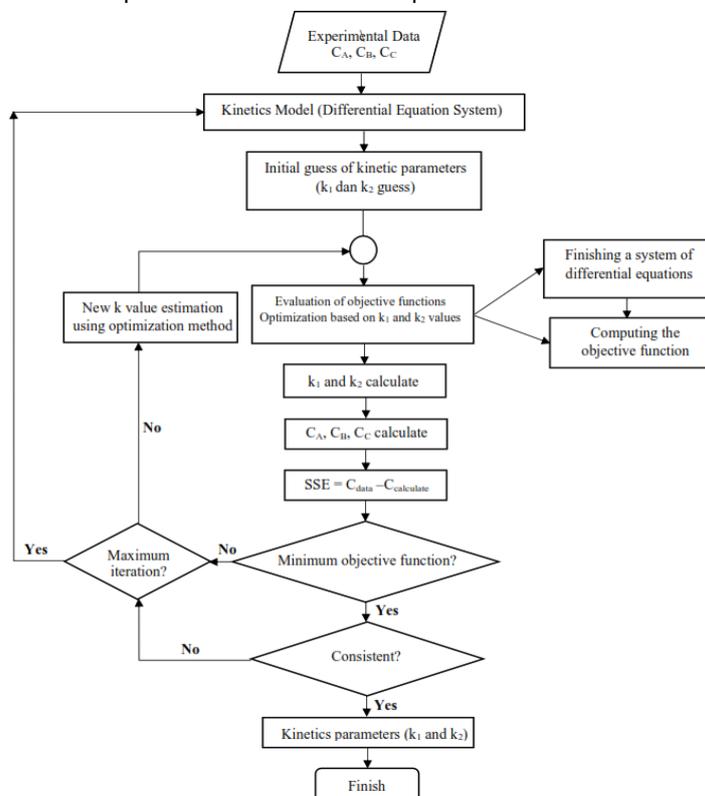
Figure 2: Schematic algorithm of reaction rate constants (k_1 and k_2) evaluation using the MATLAB program

3. Results and discussions

This research is focused on the synthesis of dimethyl ether using methanol dehydration process with dealuminated zeolite Y as catalyst. The reaction temperature was varied to obtain the maximum DME conversion. The reaction rate constant at each reaction temperature was evaluated. Meanwhile, the activation energy and the collision factor were found for each reaction rate constant.

3.1 Effect of operating temperature on methanol conversion in dimethyl ether synthesis

Temperature is a factor that affects the reaction rate of methanol dehydration to produce DME. High temperatures can affect the amount of methanol that evaporates (Iranshahi et al., 2017). According to this study, the methanol conversion into DME varied as the reaction temperature changed. The effect of operating temperature on the methanol conversion is presented in Figure 3.
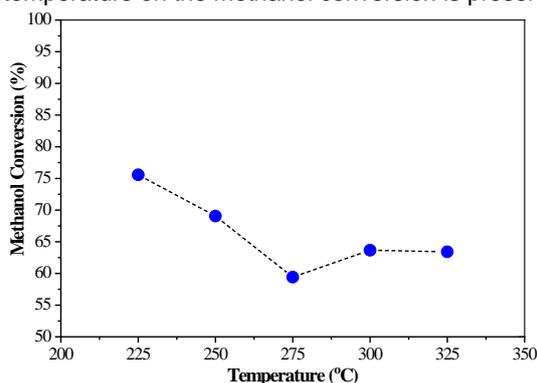
Figure 3: Methanol conversions at various reaction temperatures

Figure 3 indicates that temperature influences the reaction of methanol dehydration to dimethyl ether. Figure 3 shows that methanol conversion decreases with increasing temperature. The methanol conversions obtained were 75.58, 69.06, 59.42, 63.67 and 63.42 % at operating temperatures of 225, 250, 275, 300, and 325 $^{\circ}$C, respectively. The results showed that the highest methanol conversion was obtained at a temperature of 225 $^{\circ}$C, which was 75.58 %. At this temperature, the yield for dimethyl ether was 54.32 %. In Figure 3, the higher the operating temperature, the lower the methanol conversion. This phenomenon is because more by-products are formed at higher temperatures due to the acidity of the zeolite Y catalyst. Zeolite Y catalyst tends to produce hydrocarbons at higher temperature which causing a decrease in the yield of dimethyl ether produced (Ajami and Shariati, 2016). The zeolite-based catalyst activity must be stable over a wide temperature range due to the exothermic reaction. The inappropriate temperature can cause the formation of side reactions such as hydrocarbon by-products (Kim et al., 2017).

The results of this study are in accordance with the previous study conducted by Ajami and Shariati (2016). They used the H-ZSM-5 catalyst in the conversion of methanol to dimethyl ether and found that methanol conversion increased steadily with the increasing of reaction temperature from 200-240 $^{\circ}$C and the conversion relatively constant at temperature above 240 $^{\circ}$C. The highest conversion is obtained in the temperature range of 240-250 $^{\circ}$C. At temperatures above 250 $^{\circ}$C, conversion decreases slowly as more by-products are formed. The study conducted by Kim et al. (2017) showed that methanol conversion increased from 23.9 % at 190 $^{\circ}$C to 78.3 % at 220 $^{\circ}$C. Kim et al. (2017) used K-modified HZMS-5 as a catalyst in the catalytic dehydration of methanol to dimethyl ether.

In the research conducted by Lourentius et al. (2005), Cu-Zn-Al/γ-Al$_2$O$_3$ catalyst was used and the highest conversion was achieved at temperature of 240 $^{\circ}$C where at this temperature range, the catalyst can work actively. However, relatively high amount of water was also formed as by-product. Therefore, the generation of water in the reaction significantly decreased the yield of dimethyl ether produced.

3.2 Effect of temperature on reaction rate constant (k)

The value of the reaction rate constant was evaluated using the numerical method 4th order Runge-Kutta. The calculation was carried out using the MATLAB software. The evaluation results of the rate constant value of the methanol dehydration reaction at various reaction temperatures are presented in Table 1. It shows that the value of the reaction rate constant for reverse reaction (k_2) is greater than the reaction rate constant for forward reaction (k_1). The possible answer for this phenomenon is the thermodynamic equilibrium behaviour of exothermic reaction where the high reaction temperature causes the forward reaction rate constant (k_1)

decreases relatively while the reverse reaction rate (k_2) increases. The reaction rate constant or the reaction rate coefficient (k) is the constant ratio between the forward and reverse reaction rates of the reactant concentrations which affects the reaction rate. The reaction rate constant always increases along with the increasing of reaction temperature (Aboulkas and Harfi, 2008). However, this study shows that the higher reaction temperature, the lower the reaction kinetics constant value, where the best reaction rate constant was obtained at 225 ^{o}C with k_1 value of 0.1795 l/mol.h. This result is due to the thermodynamic properties of the exothermic formation reaction of DME where the higher temperature, the lower resulting conversion (Lourentius et al., 2005). As a result, when the conversion of DME formation decreases, the reaction rate for DME formation also decreases. Table 1 also shows that at 300 ^{o}C the reaction rate constant slightly increases. This result could be due to the increasing of methanol conversion into side reaction by-products of methane formation at high temperatures. As comparisons, the previous study conducted by Bandiera and Naccache (1991) found the kinetic parameters of the methanol dehydration reaction to dimethyl ether using sulfonated polystyrene catalyst at temperature of 250 ^{o}C was 147 mmol/h or 0.147 mol/h. Meanwhile, Bates and Gounder (2020) reported the kinetic parameters of the methanol dehydration reaction to dimethyl ether using zeolite chabazite catalyst at 250 ^{o}C obtained the k value of 1.69 x 10^{-4} mol/s.

Table 1: The reaction rate constant at various temperatures

Reaction rate	Temperature (^{o}C)				
	225	250	275	300	325
k_1 (l/mol.h)	0.1795	0.1653	0.1248	0.1606	0.1222
k_2 (l/mol.h)	1.0982	1.3126	1.7808	2.2071	1.4915

3.3 Activation energy and collision factors

Activation energy (E_a) and collision factor (A) are the kinetic parameters that can be determined based on the linear regression method the known reaction rate with the assistance of MATLAB software. The activation energy and collision factors for methanol dehydration reaction based on this study are presented in Table 2.

Table 2: Value of activation energy and collision factor

E_a	Activation energy (E_a)	A	Collision factor
E_{a1} (cal/mol)	1.044 x 10^3	A_1	0.0589
E_{a2} (cal/mol)	2.487 x 10^3	A_2	14.9846

Table 2 presented that the value of E_a and A obtained from this experiment were 1.044 x 10^3 cal/mol for E_{a1}, 2.487 x 10^3 cal/mol for E_{a2}, 0.0589 for A_1 and 14.9846 for A_2. The experiment revealed that the value of the activation energy (E_{a2}) and the collision factor (A_2) at k_2 were greater than those of k_1. These results show that the dehydration reaction of methanol to dimethyl ether is reversible. Therefore, the activation energy (E_{a1}) and the collision factor (A_1) forward reaction to desired product are smaller than those of reverse reaction. This fact is due to the thermodynamic property of the DME reaction formation. This reaction is exothermic in that the higher the temperature, the lower the resulting conversion. Thus, the reaction rate constant decreases with the increasing reaction temperature which makes the E_a value becomes lower as well. The acidity of the catalyst also plays an important role in affecting the activation energy (Moreno-Castilla et al., 2001). The catalyst acidity at higher temperature was getting lower. The previous work reported by Moreno-Castilla et al. (2001) also obtained the E_a methanol dehydration to dimethyl ether at 115 kJ/mol. The reaction experiments were conducted at temperature range of 177-302 ^{o}C. A similar study was also conducted by Xu et al. (1997) on the formation of DME using γ-Al_2O_3 catalyst resulted the activation energy of 25 kcal/mol. Meanwhile, Akarmazyan et al. (2014) obtained the E_a for methanol dehydration of 18.5 kcal/mol using α-Al_2O_3 as catalyst. The variation in activation energy values of methanol dehydration reaction obtained by previous researchers and this work was possibly influenced by the variation of Si/Al ratios and the type of catalyst used (Xu et al., 1997).

4. Conclusions

The reaction temperature is significantly affected the reaction behaviour for the synthesis of DME from methanol dehydration process. The best temperature that reached highest methanol conversion was obtained at 225 ^{o}C with the methanol conversion of 75.58 %. The reaction rate constants for the formation of DME at 225 ^{o}C were 0.1795 l/mol.h and 1.0982 l/mol.h for k_1 and k_2, respectively. In the formation of DME, the activation energy value at forward reaction (k_1) 1.044 x 10^3 cal/mol with a collision factor (A_1) of 0.0589.

Meanwhile, the value of the activation energy at k_2 is 2.487 x 10^3 cal/mol and the collision factor (A_2) is 14.9846.

References

Agency for the Assessment and Application of Technology, 2019, Indonesia Energy Outlook 2019: The Impact of Increased Utilization of New and Renewable Energy on the National Economy, Center of Assessment for Process Industry and Energy, Jakarta, Indonesia.

Aboulkas A., Harfi K.E., 2008, Study of the kinetics and mechanisms of thermal decomposition of Moroccan Tarfaya oil shale and its kerogen. Oil Shale, 25(4), 426–443.

Ajami H., Shariati A., 2016, Effect of acidic H-ZSM-5 catalyst in conversion of methanol to dimethyl ether. Energy Sources, Part A: Recovery, Utilization and Environmental Effects, 38(19), 2845–2853.

Akarmazyan S.S., Panagiotopoulou P., Kambolis A., Papadopoulou C., Kondarides D.I., 2014, Methanol dehydration to dimethyl ether over Al_2O_3 catalysts. Applied Catalysis B: Environmental, 145, 136–148.

Anggoro D.D., Oktavianty H., Sasongko S.B., Buchori L., 2020, Effect of dealumination on the acidity of zeolite Y and the yield of glycerol mono stearate (GMS). Chemosphere, 257, 127012.

Azizi Z., Rezaeimanesh M., Tohidian T., Rahimpour M.R., 2014, Dimethyl ether: A review of technologies and production challenges. Chemical Engineering and Processing: Process Intensification, 82, 150–172.

Bandiera J., Naccache C., 1991, Kinetics of methanol dehydration on dealuminated H-mordenite: Model with acid and basic active centres. Applied Catalysis, 69(1), 139–148.

Bates J.S., Gounder, R., 2020, Clustering of alkanols confined in chabazite zeolite: implications for dehydration of methanol-ethanol mixtures. Journal of Catalysis, 390, 178–183.

Borges L.D., de Macedo J.L., 2016, Solid-state dealumination of zeolite Y: Structural characterization and acidity analysis by calorimetric measurements. Microporous and Mesoporous Materials, 236, 85–93.

Chen J., Xie Q., Shahbaz M., Song M., Wu Y., 2021, The fossil energy trade relations among BRICS countries. Energy, 217, 119383.

Dik P.P., Klimov O.V., Koryakina G.I., Leonova K.A., Pereyma V.Y., Budukva S.V., Gerasimov E.Y., Noskov A.S.. 2014, Composition of stacked bed for VGO hydrocracking with maximum diesel yield. Catalysis Today, 220–222, 124–132.

Gualtieri M., 2006, Synthesis and Characterization of Zeolite Films and Membranes. Doctoral Thesis, Luleå University of Technology, Luleå, Sweden.

Hosseininejad S., Afacan A., Hayes R.E., 2012, Catalytic and kinetic study of methanol dehydration to dimethyl ether. Chemical Engineering Research and Design, 90(6), 825–833.

Iranshahi D., Saeedi R., Azizi K., 2017, Maximization of dimethyl ether production from synthesis gas by obtaining optimum temperature profile and water removal. Fuel, 190, 386–395.

Kim S., Kim Y.T., Zhang C., Kwak G., Jun K.W., 2017, Effect of reaction conditions on the catalytic dehydration of methanol to dimethyl ether over a K-modified HZSM-5 catalyst. Catalysis Letters, 147(3), 792–801.

Lourentius S., Roesyadi A., Mahfud, 2005, Pengaruh loading metal dalam katalis Cu-Zn-Al/γ-Al_2O_3 terhadap konversi pada hidrogenasi karbon monoksida menjadi dimethyl ether, Reaktor, 9(2), 26-33.

Makos P., Słupek E., Sobczak J., Zabrocki D., Hupka J., Rogala A., 2019, Dimethyl ether (DME) as potential environmental friendly fuel, E3S Web of Conferences, 116, 1-8.

Moreno-Castilla C., Carrasco-Marín F., Parejo-Pérez C., López Ramón M.V., 2001, Dehydration of methanol to dimethyl ether catalyzed by oxidized activated carbons with varying surface acidic character. Carbon, 39(6), 869–875.

Ng K.L., Chadwick D., Toseland B.A., 1999, Kinetics and modelling of dimethyl ether synthesis from synthesis gas. Chemical Engineering Science, 54(15–16), 3587–3592.

Nie Z., Liu H., Liu D., Ying W., Fang D., 2005, Intrinsic kinetics of dimethyl ether synthesis from syngas. Journal of Natural Gas Chemistry, 14(1), 22–28.

Ortega C., Rezaei M., Hessel V., Kolb G., 2018, Methanol to dimethyl ether conversion over a ZSM-5 catalyst: Intrinsic kinetic study on an external recycle reactor. Chemical Engineering Journal, 347(April), 741–753.

Rosadi I., Athikaphan P., Chantanachat P., 2020, The catalytic activity of Co/kaolinite catalyst for dimethyl ether synthesis via methanol dehydration, Energy Reports, 6, 469–473.

Xu M., Goodman D.W., Bhattacharyya A., 1997, Catalytic dehydration of methanol to dimethyl ether (DME) over Pd/Cab-O-Sil catalysts. Applied Catalysis A: General, 149(2), 303–309.