JBAT 7(1) (2018) 48 – 53
p-ISSN 2303 0623
e-ISSN 2407 2370

Jurnal Bahan Alam Terbarukan

Terakreditasi: SK No.: 36b/E/KPT/2016
http://journal .unnes.ac.id/nju/index.php/jbat

Kinetic Modeling of Series Reaction CH_4-CH_3OH-DME with CuO-ZnO/γ-Al_2O_3 Catalyst

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DOI 10.15294/jbat.v7i1.11403

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Article Info

Article history:
Received
October 2017
Accepted
December 2017
Published
June 2018

Keywords :
Kinetic;
DME;
Catalyst;
Conversion.

Abstract

A kinetic model was proposed for the synthesis of methane to be dimethyl ether (DME) in one reaction step from ($CH_4 + O_2$) and (CH_3OH) to dimethyl ether using kinetic CuO-ZnO /γAl_2O_3 catalyst parameters. The bifunctional catalyst of the series kinetic reaction model according to the experimental results obtained under isothermal conditions in a pipe flow reactor under various operating conditions: 225-325 ° C; 10 bar gauge; Residence time, 16-57.0 (g Catalyst) hour (mole CH_4) $^{-1}$. An important step for modeling is the synthesis of methanol from ($CH_4 + O_2$) and the synthesis of (CH_3OH to DME) is methanol dehydration (very fast), and water-shifting and CO_2 (equilibrium) reactions. The effects of water inhibition and CO_2 were also taken into account in the synthesis of methanol and the formation of hydrocarbons. The dehydration advantage of methanol can achieve higher yields above 60 % methanol that was converted to DME and the remaining 5% methanol if ($CH_4 + O_2$) comes in at 10 bar gauge and 375 ° C. At higher temperatures produces CO_2 and H_2O. Methane-methanol-DME series reaction model follows single-order gas phase reaction to methane and methanol with k_1 = 0.195 minutes^{-1} and k_2 = 0.115 minutes^{-1} The time and maximum concentration occurs in the formation of methanol constituents 9.5 minutes and 0.44 mole

**This is a revised and extended version of an article which had been presented at SNTK UNNES 2017, Semarang, Indonesia, September 20th, 2017.*

INTRODUCTION

The model of methane series reaction engineering into a dimethyl ether (DME) is an alternative design that can be applied in the model of kinetics of parallel reactions. The design of gas phase parallel reaction model is easily designed and has the advantage which is raw materials are relatively cheaper and renewable, because it uses raw materials from plant-based material. The latest innovation to be developed in the focus of this topic is to combine a single biogas reaction into biomethanol and biomethanol to DME through a series reaction in the gas phase. This research is combining single reaction biogas to biometanol with single reaction biometanol to DME by the method of kinetics reaction model. Series reaction kinetics model of biogas become biogasoline is series reaction process which run simultaneously and continuously in gas phase with reaction kinetics model and constant reaction rate which can be implemented in experimental.

This reaction phenomenon is an innovation/breakthrough in the field of renewable energy and the kinetic is very interesting to be modeled. The methanol parallel reaction route to DME and CO_2 has not been discovered and described its kinetic and current modeling and there

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ISSN 2303-0623
e-ISSN 2407-2370

is not much information available on the effect of bioenergy kinetics phenomena on the gas phase parallel reaction. Complete modeling of kinetic parallel reactions is a modeling concept for chemical reactions by studying the basic reactions of each component. The overall parallel reactions are modeled by initiation and termination initiation steps. The series-parallel reaction model will be based on the reaction mechanism. The process of modeling the parallel reactions identifies the parameters and the effects of the reaction. The reaction occurring within the reactor is rarely found in only one reaction (single reaction) but most of what will happen is a multiple reaction type of final product determined through path way reaction that is different in accordance with kinetic criterion.

Based on Akarmazyan (2012) the conversion of methanol to dimethyl ether was conducted by modification of alumina gamma catalyst, silica-alumina by one stage using CO_2 hydrogenation. Modification of gamma alumina with 1% by weight of silica is more active and the catalyst will become inactive due to water formation. CO_2 gas has no effect on the dehydration of methanol to DME.

Based on Arcuomanis (2008) Synthesis of dimethyl ether from methanol using H-ZSM 5 catalyst and HZMS 5 catalyst with metal reinforcement Mg, Na, Zr, Al and Zn all catalyst results are characterized by AAS, BET, XRD, and TPD. The TPD results show the amount of acid strength increased on the surface portion of Na, Zn and Mg modified with HZSM 5, while the intermediate acid strength increased in Zn and Al modified with HZSM 5 having 94% activity and 99% selectivity of the modified material with HZSM 5 as well as very stable.

Based on Bercic (1992) DME production process consists of four parts synthesis of natural gas, absorb CO_2 from natural gas, DME synthesis reactor and purification and separation DME. The syngas process from natural gas to DME uses a single bed reactor. Laboratory experimental results were then simulated with Aspen plus generating DME data which can be used commercially.

Based on Gayubo (2004) reaction kinetics and dynamic reactor modeling for trans-formation syngas in dimethyl ether using a mixture of metal oxides (CuO, ZnO, and Al_2O_3) and acid components (γ-Al_2O_3) as a catalyst. Kinetic measurements were performed using a fixed-bed micro reactor catalytic. The operating temperature range was 230 ~ 300°C and the pressure was 8 bar gauge (barg).

Based on Alexandro (2005) The kinetic model for the synthesis of dimethyl ether in a single step reaction of (H_2 + CO) and (H_2 + CO_2), and kinetic parameters had been calculated for CuO-ZnO-Al_2O_3 / β-Al_2O_3 bifunctional catalyst. The kinetic model was in accordance with the experimental results obtained in the fixed isothermal bed reactor under various operating conditions of the clock. The highest yield of 60% carbon was converted to DME and 5% to methanol.

Based on Aguayo (2007) Clinoptilolite, natural zeolite converted menja catalyzed to dehydration methanol to dimethyl ether. The catalyst was tested in a fixed bed reactor at 300 °C, 16 atm, and WHSV = 52.5 h^{-1} conversion of 67.02% and selectivity of 99.74%

Based on Heriyansyah (2010) DME can be used as sulfur free fuel for diesel engines without particulate formation and low NOx emissions compared to oil and gas. DME can be used as a substitute of LPG. Dimethyl ether (DME) is produced directly from synthesis gas in a fixed bed reactor. In this study, Cu-Zn / γ-Al_2O_3 was used as a direct dimethyl ether bifunction synthesis catalyst. This catalyst is characterized by BET, XRF, and XRD. Catalyst activation test was conducted on the operating conditions of pressure of 20 bar and temperature of 220°C. The best catalyst activity test results showed CO conversion of 70 %, dimethyl ether selectivity by 80%, and 54% dimethyl ether yield.

Based on Sierra (2010) Model of adiabatic fixed bed reactor for catalytic dehydration of methanol to dimethyl ether. Fixed bed reactor with a diameter of 1.5 mm γAl_2O_3 as catalyst and operated in various temperatures as 543 – 603 K at atmospheric pressure. The maximum conversion was obtained at 603 K with WHSV of 92.87 h^{-1} of 67.3%.

Based on Xu M. (1997) the hydrothermal route and containing Al/Si atomic ratios ranging from 0.03 and 0.18 were tested in dehydration of methanol to DME. The Optimum Al/Si ratio was 0.09 for the impregnated DME synthesis showing a very high DME yield values at low temperatures of 250 °C Selectivity DME75 and 73% conversion.

Table 1. Catayst characteristic

Type of catalyst	Surface area (g/m^2)	Pore volume (cm^3/g)	Pore Diameter (nm)
CuO-ZnO/γ Al_2O_3 (1 : 1 : 1)	75.3	0.34	23.1

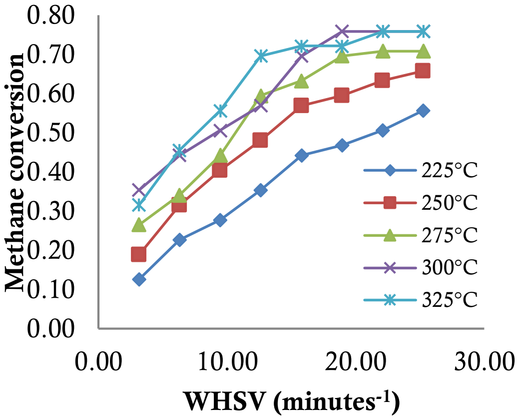

Figure 1. Methane conversion and space velocity

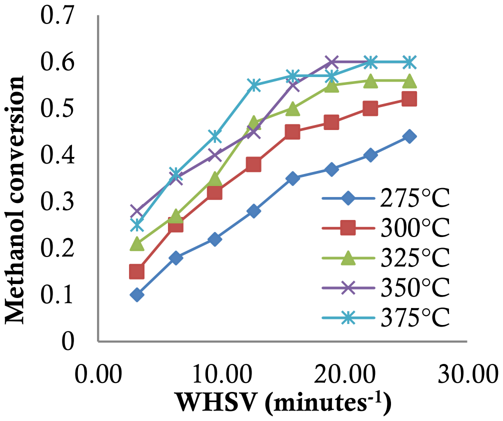

Figure 2. Methanol conversion and space velocity

RESEARCH METHODOLOGY

Catalyst Preparation Step

Mixing $ZnSO_4$ 1 M and $CuSO_4.5H_2O$ 1 M and Na_2SO_4 solutions were stirred until homogeny into beaker glass containing demineralized water for 30 minute at a flow rate of 5 ml/minute at a fixed pH of 50 °C (323 K) using a magnetic stirrer. Then set aside for 3 hours then filtered and washed with hot water 50 °C (323 K). The sieves added with gamma alumina and stirred are then dried at 90 °C for 18 hours. It was then calcined at 800°C for 18 hours.

Reaction of Methane into DME Test Step

Plug flow reactors of ½ "and 20" diameter sizes are loaded with the catalyst as a fixed bed and flown with N_2 for 30 ml/minute. The methanol reaction stage takes place at a temperature of 325 °C and a pressure of 10 bar gauge. The next step converts the liquid phase methanol into a gas phase by heating it with a temperature range of 40-50 °C in support with the bubbled N_2 gas stream into liquid methanol at 25 ml per minute. The pipe reactor flow temperature is operated in the temperature range 250-375°C isothermally pressured at 10 bar gauge. The reaction products analyzed include methanol, DME and CO_2 content using GC-MS Shimadsu.

RESULTS AND DISCUSSION

The reaction model is the consecutive reaction of the product-formed reactant simultaneously transformed into another stable product. The path way reaction model that occurs forms the rate of the reaction with different routes.

One type of heterogeneous catalyst having alkaline properties is Cu and Zn and provides an adsorption and absorption site for converting the intermediate reaction of methanol to DME. The surface area results show that CaO and ZnO are more active in granular micro form because they have larger surface area. Catalysts that have larger surface area have more contact area with reactant molecule so as to produce more DME and have higher catalyst activity.

In Figure 1 and 2 the initial conditions of reaction are relatively constant at WHSV 3 per minutes of conversion difference at 350°C and 375°C there is unconverted methane because CO_2 formation as by product is too fast. The conversion increased at 350°C greater than 375°C with WHSV 20 per minutes influenced by the amount of CO_2 gas that will affect the catalyst activity but not reached the deactivation of the catalyst yet. The condition was almost the same at 325 °C having a conversion greater than 300°C at WHSV 12 per minutes. This condition occurs that CO concentrations of intermediate reaction products are not sufficiently stoichiometric to support pressurized and high temperature reactions.

Synthesis of methane into dimethyl ether (DME) contains no sulfur and nitrogen content. The resulting DME is not corrosive to metals because there is no CO_2. In the synthesis of methane reaction to dimethyl ether (DME) there are two main reaction routes and through three steps (1)

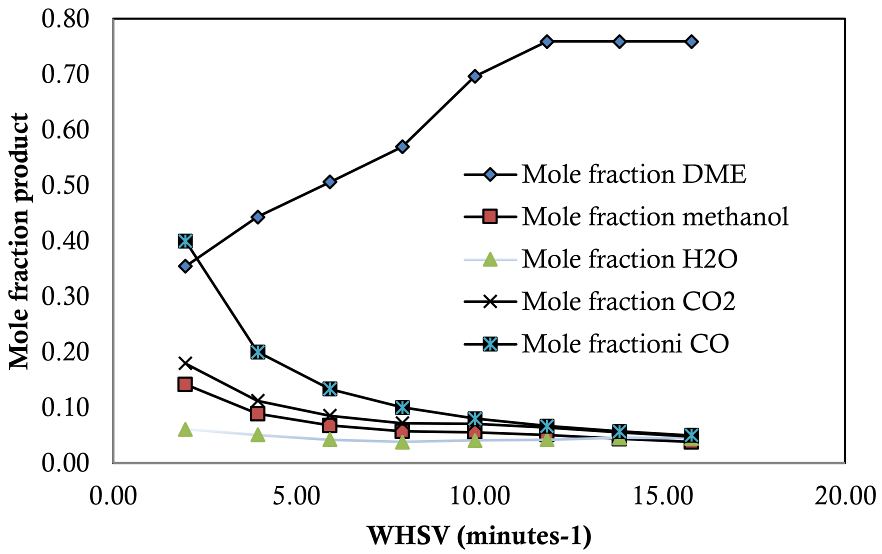

Figure 3. mole fraction of product function WHSV minutes^{-1}

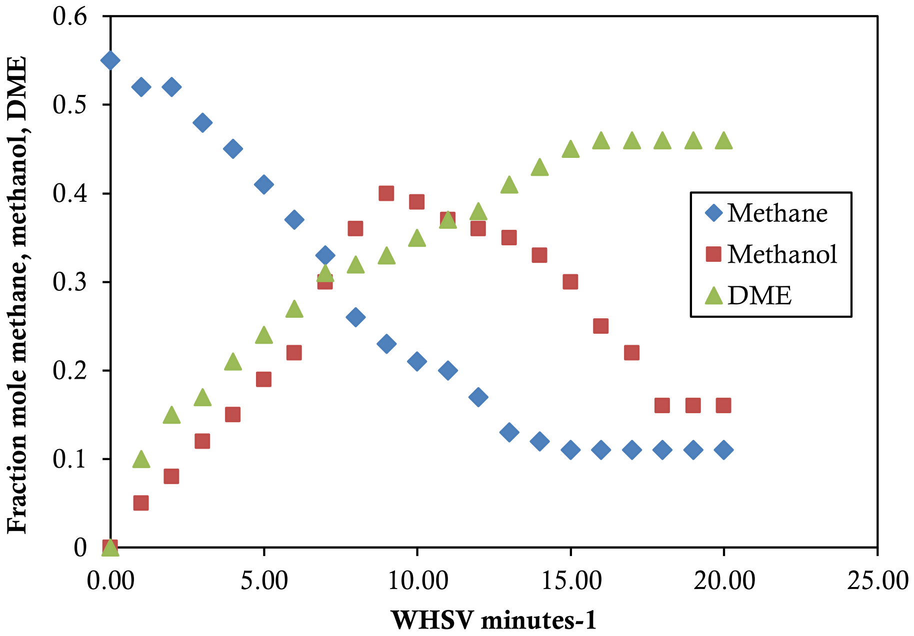

Figure 4 Profile modeling of series reaction CH_4-CH_3OH-DME

combustion reaction (2) methanol dehydration reaction (3) combustion reaction and dehydration reaction. In Figure 1 the product distribution reaction for various linear temperatures and relatively constant corresponds to the pathway reaction.

$$2CH_4+O_2+CO_2 \rightarrow 3CO+3H_2+H_2O \quad (1)$$

$$3CO+3H_2 \rightarrow CH_3OCH_3 \text{ (DME)}+CO_2 \quad (2)$$

$$2CH_4+O_2 \rightarrow CH_3OCH_3 \text{ (DME)}+H_2O \quad (3)$$

The overall reaction mechanism for methane to DME was a product of CO_2 gas at each step of the reaction because of the low pressure of the reactor in the reactor. The kinetics model is proposed as a representation of the kinetic model reaction mechanism in series to CO and water.

The proposed series reaction scheme is shown in Eq. 4.

$$2CH_4 + 0.5O_2 \overset{k_1}{\rightarrow} 2CH_3OH \overset{k_2}{\rightarrow} CH_3OCH_3 \quad (4)$$

In Figure 3 the conversion of methane into dimethyl ether (DME) results in a maximum product distribution. The overall reaction to DME and by-products is a reversible reaction. Synthesis of methane to DME was through the intermediate reaction of CO and H_2. The ratio of H_2/CO to the product affects the reaction rate as a conversion function. The reaction route is affected by the ratio of $CuO\text{-}ZnO/\gamma Al_2O_3$ which has the function as catalyst. The acid properties present in the catalyst will form reaction and equilibrium conversion.

Model of CH_4 → CH_3OH → DME series reaction equations:

$$C_{methanol} = k_1 C_{methane}\left(\frac{e^{-k_1\tau}}{k_2 - k_1} - \frac{e^{-k_2\tau}}{k_2 - k_1}\right) \quad (5)$$

In Figure 4 the methane series reaction profile becomes methanol and methanol to DME is a first-order reaction to methane and methanol. The conversion of methane to methanol significantly occurred in the WHSV range of 2.5-12.5 minutes^{-1} then relatively constant after WHSV 15 minute^{-1} due to the effect of carbon compounds transitioning to methanol. This condition leads to the conversion of methanol to DME resulting in optimum conditions achieved WHSV 9.5 minutes^{-1}, methane conversion to methanol and methanol to DME relatively constant at WHSV 18-20 minutes^{-1} because CO_2 and H_2O are converted to methanol and hydrogen.

CONCLUSION

Dimethyl ether (DME) is a clean energy and alternative fuel that can be produced from renewable raw materials (methane). The of chemicals and physica; characteristic of DME that resemble LPG has the potential to become fuel generator, transportation and household needs. DME products do not contain sulfur and are not corrosive to metals. The innovation of methane processes into DME needs to be developed by modifying competitive, efficient and character-specific catalysts. Achieved 76 % conversion, 79 % selectivity and 80 % yield. The kinetic model follows a first order reaction.

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