Mechanism Reaction of Methane-Methanol-Dimethyl Ether (Dme)With Catalyst CuO-ZnO/γ-Al$_2$O$_3$

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ABSTRACT: Design modeling of the reaction kinetics of methane-methanol-DME is a single reaction series of parallel methane to dimethyl ether (DME). The reaction scheme is explained through a single reactants that can be converted into several products with different kinetic equations different. The reaction of series successive reactions through the reaction intermediate which then reacts to form products. Development of kinetic models mathematically through simulation consecutive reactions. In this research study will be conducted to obtain data on the kinetic parameters of series reaction of methanol into DME with a catalyst CuO-ZnO/γ-Al$_2$O$_3$ with main composition of 1:1:1 were prepared using ZnSO$_4$ solution and CuSO$_4$.5H$_2$O. Data taken reaction kinetics model experiments with a temperature range of 250 to 350°C and a pressure of 3 atm. Modelling reaction kinetic was tested with a series derived from the catalyst surface reaction mechanisms. Kinetic model that best fit the experimental results is the phase of termination (formation DME) faster than the formation of intermediate (CO$_2$ production). series of reaction kinetic parameters obtained in the form of the reaction rate constants of methane to methanol and methanol into DME conversion 76%, selectivity 79% and a yield of 80%

Keywords: DME, catalyst, methane, methanol

I.   INTRODUCTION

The model of metallic parallel reaction engineering into dimethyl ether (DME) is an alternative design that can be applied in the kinetic model of parallel reactions. The design of gas phase parallel reaction model is easily designed and has the advantage that raw materials are relatively cheaper and renewable, because it uses raw materials from vegetable elements. The latest innovation to be developed in the focus of this topic is to combine a single biogas reaction into biomethanol with biomethanol to DME through a series reaction in the gas phase. This study combines a single reaction of biogas to biomethanol with a single reaction of biomethanol to biogasoline through a series reaction kinetics modeling method. Biogas series reaction kinetics model into biogasoline is a series reaction process that runs simultaneously and continuously in gas phase with reaction kinetics model and reaction speed constant that can be implemented in experimental form This reaction phenomenon is a new innovation / breakthrough in renewable energy field and very interesting for Modeled kinetically. The metallol parallel reaction route to DME and CO$_2$ has not been discovered and described its kinetic and current modeling and there is not much information available about the effect of bioenergy kinetics phenomena on gas phase parallel reactions. Complete modeling of kinetic parallel reactions is a modeling concept for chemical reactions by studying the basic reactions of each component. The overall parallel reaction is 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 reactions occurring within the reactor are rarely found in only one reaction (single reaction) but most of what will happen is the multiple reaction type of final product determined through Path way reaction is different according to kinetics criteria.

There are two strategies for the production of DME fromsynthesis gas: (i) a two-step process (methanol synthesis on a metallic catalyst and subsequent dehydration of methanol on an acid catalyst); (ii) a single step using a bifunctional catalyst. It is note worthy that the steps in strategy i have been studied separately with the aim of attaining either methanol synthesis or the production of DME, although in the latter case methanol dehydration is considered an intermediate step in the transformation of methanol into hydrocarbons.The interest in CO2 capture justifies the present efforts for its incorporation in methanol synthesis, given that it is a process involving high pressure requirements. The selective transformation of methanol into DME has become an important objective, due to the aforementioned interest in DME.The main advantage of DME synthesis in a single step on a bifunctional catalyst is the lower thermodynamic limitation than methanol synthesis (due to the

low concentration of methanol in the reaction medium, which shifts the thermodynamic equilibrium of methanol synthesis) and the fact that it can be carried out at higher temperature and lower pressure. Consequently, CO_2 incorporation in the feed is more feasiblethan in the synthesis of methanol, given that it requires lowerpressure. Over the mid-to-long term, energy consumption in the Asian region is expected to increase substantially during the 21st century. In realizing sustained growth in this region in the future, energy supply and environmental problems associated with mass energy consumptionwill be major problems. High expectations are placed on dimethyl ether (DME) as a new fuel which can be synthesized from diverse hydrocarbon sources, including natural gas, can be handled as easily as liquefied petroleum gas (LPG), and causes a small load on the environment. Thus, if DME can be produced and distributed at low cost and in large quantities, this fuel can make an important contribution to solving the energy supply problems and environmental problems resulting fromexpanded energy consumption expected in the future.

The synthesis of dimethyl ether (DME) has received considerable attention in the literature, because of itspotential use as a multipurpose fuel. Another reason is that it can be produced from a variety of resources,such as natural gas, coal and biomass, which contributes to reducing the energy dependence on oil(Semelsberger, 2006). DME can be used either as a gasoline additive, or directly as an automotive fuelalternative to diesel fuel (Arcoumanis et al., 2008). Moreover, DME is a strategic raw material which couldreplace methanol in the production of hydrocarbons (such as light olefins and BTXE) and chemicals (dimethylsulphate, methyl acetate). In addition, it is suitable to be used as an aerosol propellant as a green substitutefor CFCs, which were banned because they cause the depletion of the ozone layer (Fleisch et al., 2012).The catalytic dehydration of methanol over solid-acid catalysts is a suitable process for DME synthesis, whichis the previous stage in the transformation of methanol into hydrocarbons (MTG process) or olefins (MTOprocess). Another possibility is the synthesis of DME from synthesis gas in one reaction step over bifunctionalcatalysts, process in which methanol dehydration is essential to shift the thermodynamic equilibrium ofmethanol synthesis (Ereña et al., 2005). In both processes, the selective production of DME is mainly relatedto active sites of weak and medium acidity, being γ-Al2O3 the most commonly used acid function.The kinetics of the selective dehydration of methanol to DME has been extensively studied in the literature.Some authors have proposed either the dissociative adsorption of methanol (Figueras et al., 1971; Klusačekand Schneider, 1982; Bercic and Levec, 1992) or the molecular adsorption (Gates and Johanson, 1971) as

the controlling step. Nevertheless, most of the kinetic models proposed were derived from experimentsconducted in conditions not found in an industrial reactor (where methanol dehydration reaction takes place at high conversion levels), or over catalysts with a low stability and reproducibility. Furthermore, the water produced during the dehydration of methanol considerably lowers the reaction rate, and the kinetic models donot take into account this effect.The presence of water in the reaction medium has a considerable unfavourable effect, as it causes adecrease in the equilibrium values of DME yield and selectivity. Moreover, it may have several negativeeffects on the catalyst, such as i) the attenuation of the activity of the acid function, due to its adsorption onactive sites and ii) the partial dealumination of the catalyst, due to the presence of vapour at high temperature,which is important in HZSM-5 zeolite above 400 ℃ and leads to irreversible deactivation by the loss of Al in zeolite framework (Gayubo et al., 2004).

Akarmazyan (2012) converts methanol to dimethyl ether by a modified gamma alumina 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.

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 acidity of the berthabha on the surface portion of Na, Zn and Mg modified with HZSM 5, while the intermediate acid strength is increased in Zn and Al modified with HZSM 5 having 94% activity and 99% selectivity of the material modified by HZSM 5 and very stable. **Bercic** (1992) The DME production process consists of four synthesis parts of natural gas, absorbs CO2 from natural gas, DME synthesis reactor and purification and separation of DME. The syngas process from natural gas to DME uses a single fixed bed reactor. Laboratory experimental results then simulated with Aspen plus generating DME data can be used commercially.

Gayubo (2004) reaction kinetics and dynamic modeling of reactors for trans-formation syngas in dimethyl ether using a mixture of metal oxides (CuO, ZnO, and Al_2O_3) and component acid (γ-Al_2O_3) as catalysts. Kinetic measurements were performed using a fixed-bed microreactor catalytic. The operating temperature range is 230 ~ 300°C and the pressure is 8 bar guage (barg).

Aquayo (2005) A 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 has been calculated for γ-Al_2O_3bifunctional catalyst CuOZnO Al_2O_3. The kinetic model fits according to the experimental results obtained in fixed bed isothermal reactors under various operating conditions: 225 - 325 ° C; 10 bar space time, 1.6 57.0 hours (mol H_2) 1. Highest yield of

60 % carbon converted to DME and 5% to methanol. Aguayo (2007) Clinoptilolite, natural zeolite is converted to catalyst for the dehydration of methanol to dimethyl ether. The catalyst was tested in a fixed bed reactor at 300 ºC, 16 atm, and WHSV = 52.5 h^{-1} conversion of 67.02% and selectivities of 99.74 %. **Heriyansyah** (2010) DME can be used as sulfur free fuel for diesel engines without particulate formation and low NOx emissions when compared to oil and gas. DME can be used instead of LPG. Dimethyl ether (DME) is produced directly from synthesis gas in a fixed bed reactor. In this study, Cu-Zn / γ-Al₂O₃ was used as a direct dimethyl ether synthesis bifunction catalyst. This catalyst is characterized by BET, XRF, and XRD. The catalyst activity test is carried out under operating conditions of 20 bar pressure and temperature of 220ºC. The best catalyst activity test results showed CO conversion of 70%, dimethyl ether selectivity of 80%, and 54% dimethyl ether yield. Sierra (2010) The adiabatic fixed bed reactor model for catalytic dehydration of methanol to dimethyl ether. Fixed bed reactors with 1.5 mm γ-Al₂O₃ diameter as catalyst and operated in various temperatures from 543 to 603 K at atmospheric pressure. Results, maximum conversion was obtained at 603.15 K with WHSV of 72.87 h^{-1} of 67.3%.

Xu M. (1997) hydrothermal route and containing Al / Si atomic ratios ranging from 0.03 and 0.18 were tested in dehdrasimethanol to DME. The optimum ratio of Al / Si is 0.09 for the synthesis of the DME that is teripregnated shows very high DME result value at low temperature 250 ° C. Selectivity DME 75 and 73% conversion.

Experiment
Preparation catalyst

Mixing a 1 M and aqueous ZnSO₄.5H₂O 1 M and CuO₄ M as well as Na₂SO₄ solution were stirred homogeneously into a beaker glass containing demin water for 30 min at a rate of 5 ml / min at a fixed pH and 50 ° C (323 K) using a magnetic stirrer. Then stand for 3 hours then filtered and washed with hot water 50ºC (323 K). The sieves added with gamma alumina and stirred are then dried at 90 ° C for 18 hours. Then calcined at 800ºc for 18 hours.

Synthesis in plug flow reactor methane – methanol – DME

Two pipe flow reactors are each filled with nanocatalyst-based for conversion of biogas to methanol and methanol to dimethyl ether (DME) according to their individual requirements. Then install a condenser that serves to condense the biogasoline product. The next step sets up the temperature of both reactors at 325 ° C while flushing by nitrogen to remove oxygen in the reactor. After reaching the desired operating temperature, the nitrogen flow as a gas carrier with a nitrogen velocity of 5 ml / min (constant) and biogas flow as raw material from 5 ml / min to 25 ml / min which is accommodated in the mixer is then streamed into a fixed nanocatalis based bed reactor Continuously and periodically sampling the initiation, intermidiation and termination. Taking 30 grams of nanocatalyst inserted into the RAP reactor that operates there is a temperature of 400oC and a pressure of 1 atm. Then the methanol solution was bubbled with a N2 gas carrier at a rate of 5 ml per minute and reacted with the nanocatalyst to produce dimethyl ether (DME).

II.   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 to form reaction speed with different routes.

Jenis katalis	Luas permukaan (g/m²)	Volume pori (cm³/g)	Diameter pori (nm)
CuO-ZnO/γ Al₂O₃ (1 : 1 : 1)	75,3	0,34	23,1

One type of heterogeneous catalyst having alkaline properties is Cu and Zn and provides an adsorption and absorption site for converting the intermidiate reaction of methanol to DME. The surface area results show that CaO and ZnO are more active in the form of granular microstructure 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 yield and larger catalyst activity. Methane synthesis into dimethyl ether (DME) contains no sulfur and nitrogen content. The resulting DME is not corrosive to metals because it is not oxygenated CO₂ gas. In the synthesis of methane reaction to dimethyl ether (DME) there are two main reaction routes and through three steps (a) combustion reaction (b) methanol dehydration reaction (c) combustion reaction and dehydration reaction. In Figure 1 the distribution of the reaction product for various linear temperatures and is relatively constant according to the pathway reaction.
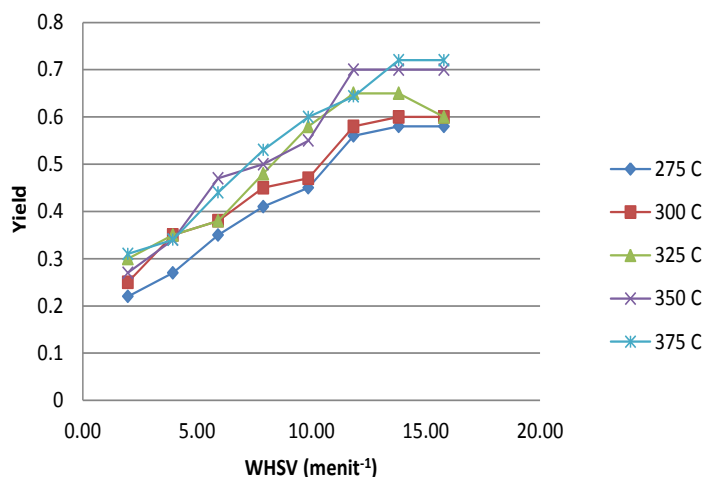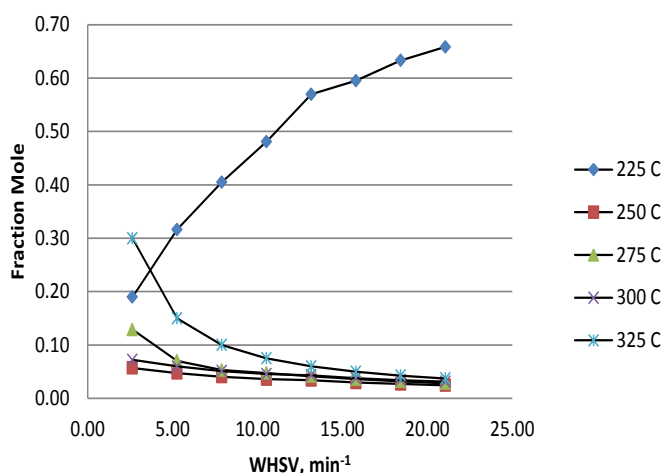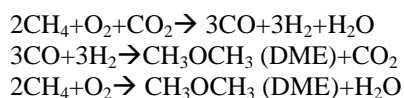
Figure 1 Relationship between space velocity and yield

$2CH_4 + O_2 + CO_2 \rightarrow 3CO + 3H_2 + H_2O$
$3CO + 3H_2 \rightarrow CH_3OCH_3 \text{ (DME)} + CO_2$
$2CH_4 + O_2 \rightarrow CH_3OCH_3 \text{ (DME)} + H_2O$

Figure 2 mol fraction of the product is a WHSV function (min^{-1})

The overall reaction mechanism for methane to DME is the product of CO_2 gas at each step of the reaction because of the low pressure of the reactor in the reactor. The proposed kinetic model as a reprentation of the kinetic model reaction mechanism in parallel to the CO and CO gas products.
The proposed reaction scheme
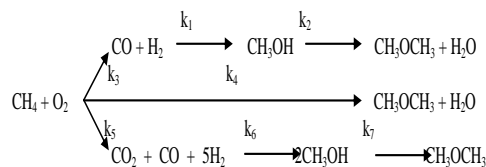
In Figure 2 methane becomes dimethyl ether (DME) resulting in a maximum product distribution. The overall reaction to DME and byproducts are reversible. Synthesis of methane to DME through CO and H_2 intermediate reactions. The ratio of H_2 / CO to the product affects the reaction speed as a conversion function. The reaction route is influenced by the catalyst ratio of CuO-ZnO / γAl_2O_3 which acts as a bifunction catalyst. The acid properties present in the catalyst will form the reaction and equilibrium conversion.
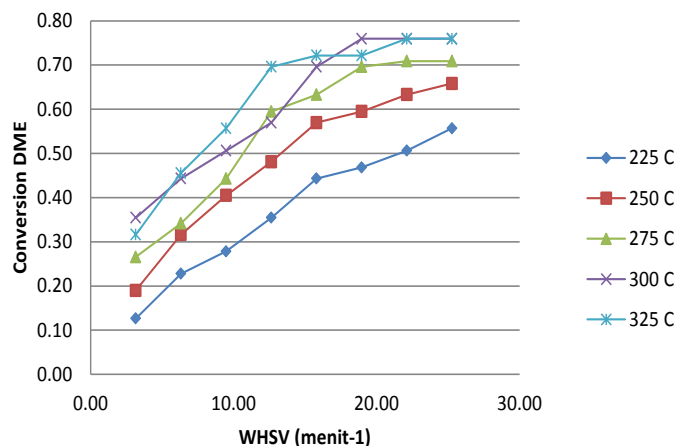
Figure 3 conversion DME and SV

In Figure 3 The initial condition of the reaction is relatively constant at WHSV 3 per minute of conversion difference at 300 ° C and 325 ° C there is unconverted methane because CO_2 loading as by product is too fast. The conversion increased at 300 ° C greater than 325 ° C with WHSV 20 per minute influenced by the amount of CO2 gas that will affect the catalyst activity but not yet reached the deactivation of the catalyst. The condition is almost the same at 325 ° C having conversion greater than 300oC at WHSV 12 per minute. This condition occurs that CO concentrations of intermediate reaction products are not sufficiently stoichiometric to support pressurized and high temperature reactions. kinetic model is proposed for singlestepDME synthesis based on experimental results obtained onaCuO-ZnO/γ-Al2O3 catalyst prepared for attaininghigh DME activity and selectivity. Simple kinetic modelswith a clear physical meaning have been chosen for the singlestepDME synthesis, and the thermodynamic equilibriumconstants of the individual steps have been incorporated.Moreover, relevant aspects concerning process conditions of great significance in the kinetic modeling have been considered,as are the following: the inhibiting effect of water in the kineticsteps and the formation of hydrocarbons from synthesis gas.These peculiar circumstances of DME synthesis in a single stepand especially the synergetic effect of in situ methanoltransformation justify the need for a specific kinetic model forthis process. Furthermore, the simplicity of the kinetic modelfor zero time on stream is an interesting objective, given thatthis model is to be the basis for establishing the kinetic modelby coke deactivation in future papers. This model is essentialfor the design of the reactor and for establishing an optimumreaction-regeneration strategy that will condition the viabilityof the process at industrial scale.

III.   Conclusion

Dimethyl ether (DME) is a clean energy and alternative fuel that can be produced from renewable raw materials (methane). The DME nature of chemicals and physics that resemble LPG has the potential to become fuel for power generation, transportation and household needs. DME products do not contain sulfur and are not corrosive to metals. The innovation of the methane process into DME needs to be developed by modifying a specific, efficient and character-specific catalyst. Achieved 76% conversion, 79% selectivity and 80% yield.

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