International Journal Of Engineering Research And Development
e- ISSN: 2278-067X, p-ISSN: 2278-800X, www.ijerd.com
Volume 15, Issue 4 (April 2019), PP.41-44

Study of Kinetics Model "Shifting Order Reaction" Dehydration of Ethanol to Become Diethyl Ether (Dee) With Catalystcuo-Zno/γ-Al_2o_3

Achmad Chumaidi[1,a], Dwina Moentamaria[2,b,*], danHeny Dewajani[3]
[1] *Achmad Chumaidi, Dwina Moentamaria Departmentof Chemical Engineering State Polytechnic of Malang*
[2] *Heny Dewajani Departmentof Chemical Engineering State Polyrechnic of Malang*
Corresponding Author: Achmad Chumaidi

ABSTRACT.*The dehydration reaction of ethanol to diethyl ether (DEE) takes place in a batch reactor by pyrolysis and pressure. The "shifting order reaction" kinetics model was examined to assess the suitability of reaction mechanisms for parameters in the reaction speed equation. The "shifting order reaction" point is the point of shifting elementary reaction orders from one order to another where it is a significant location for "shifting order reaction". The purpose of this modeling is to find the kinetic model of "shifting order reaction" ethanol to diethyl ether is a reaction process Elementary which runs simultaneously and continuously in the liquid phase and gets a reaction order and reaction speed constants that can be implemented in the form of laboratory experiments The research method uses a 8 bar pressurized batch reactor and 60^oC temperature for 2 hours the liquid phase using a CuO-Zno / γ-Al_2O_3 catalyst. The results of the study were analyzed by GC MS Shimadzu with liquid phase chromatogram and ethanol gas phase, diethyl ether, CO gas, CO_2, ethylene. Reaction rate constants k_1 = 0.012 minutes^{-1} and k_2 = 1.2 minutes^{-1}. The kinetic model of "shifting order reaction" is 1.45 having the following equation:*

$$-r_{DEE} = \frac{k_1 C_{Ethanol}^2}{1 + k_2 C_{Ethanol}}$$

In accordance with the concept of "shifting order reaction" this investigation ensures thedehydrationreaction of ethanol to diethyl ether has a linear regression equation.

Keywords:*Shifting order, pyrolysis, DEE, catalyst..*

Date of Submission: 25-11-2019 Date of acceptance: 07-12-2019

I. INTRODUCTION

The kinetics of chemical reactions are related to the speed of chemical processes. Each chemical process can be broken down into a sequence of one or more one-step processes known as elementary processes, elementary reactions, or elementary steps. Elementary reactions usually involve a single reactive collision between two molecules, which we call a bimolecular step, or dissociation / isomerization of a single reactant molecule, which we call a unimolecular step. Very rarely, under conditions of very high pressure, a thermolecular step can occur, which involves the simultaneous collision of three reactant molecules. The very important thing to recognize is that many reactions written as single reaction equations in fact consist of a series of basic steps. This will be very important when many studies on the theory of chemical reaction rates. Process optimization in the chemical industry requires proper knowledge of the chemical reaction model system, which consists of one or more reaction steps. Therefore, the design and optimization of chemical reactions as a core element of this process is of particular concern. Generally reaction designs are based on equilibrium equations, which contain thermodynamic and kinetic models. The kinetic model is a mathematical description of the reaction sequence for each reaction step as a function of components in the system. Kinetic modeling is a fully parametric model for describing each reaction step from the reaction mechanism step. Chemical Reaction Techniques provide the possibility to make kinetic measurements and kinetic modeling. For this, several continuous and batch laboratory scale reactors are available allowing a variety of different parameters and whose settings are adapted to various requirements. Diethyl ether is a chemical product that is useful as an alternative fuel to substitute fossil energy. Diethyl ether is classified as an alternative material that can be renewed and can be used for diesel engines and for gas stoves as household fuel. The process of producing diethyl ether through the dehydration reaction has been carried out mainly using homogeneous catalysts such as sulfuric acid. The use of homogeneous catalysts has disadvantages such as catalysts cannot be re-used and requires further steps such as the catalyst separation stage which certainly requires additional production costs. The process of converting ethanol into DEE with a homogeneous solid catalyst. To support the government's target, this research will do its utmost to accelerate the growth of technological innovations with high

commercial value in order to strengthen domestic technological and industrial competitiveness, while enhancing national energy security and formulating strategic steps in the application of research results in the use of DEE as an alternative fuel substitute diesel as an input for policy makers and real solutions for users. Renewable fuels that can substantially overcome the increasing contribution of exhaust emissions to global climate change. In the transportation sector, ethanol produced from biomass promises as a future fuel to be converted into diethyl ether DEE) because it has high octane quality. Ethanol can be easily converted through a dehydration process to produce diethyl ether (DEE), which is an excellent compression flame fuel with a higher energy density than ethanol. DEE has long been known as a pioneer of fuel users, but no one has used DEE as an important component in a mixture or as a substitute for diesel fuel.This research is targeted to find DEE performance produced from biomass ethanol. Some compounds that have been produced by reactive processes.distillation and provide considerable benefits are Methyl acetate and MetylTertier Butyl Ether (MTBE) (Taylor, 2010). In the process of making diethyl ether from ethanol with sulfuric acid catalyst, it produces diethyl ether compound, ethanol sulfate. Diethyl ether compounds have very low boiling points compared to the components inside. Thus it is possible to make diethyl ether by reactive distillation process. (Widayat 2005) has conducted research into the manufacture of diethyl ether using a reactive distillation process. The results showed that the reactive distillation process can be used to manufacture diethyl ether compounds, which are shown in the top products which are mostly diethyl ether compounds. In this research, an optimization process is carried out on the manufacture of diethyl ether compounds by reactive distillation process. One alternative energy that is currently being developed is ethanol because of its renewable nature and low emissions of carbon monoxide (Bryden, 2002). However, there are some disadvantages of ethanol as a fuel, namely the availability of ethanol as a fuel is still limited, the volumetric heat value, and the Reid vapor pressure are smaller than gasoline, causing difficulties in ignition in cold weather and initial ignition (Jain, JR and Pillai CN 2007) . So that ethanol used as fuel currently requires a high concentration of absolute ethanol. To obtain high concentrations of ethanol, a high energy separation process is needed. This is due to the nature of ethanol and water which forms azeotropic solution at atmospheric pressure and temperature of 78^oC with 95% azeotropic point (Kosaric, et al, 2009). According to (Chumaidi 2016) modeling the biogas series reaction into biogasoline with ZnO / SiO_2 catalysts is an initial symptom of DEE results with a low yield of 5%, the pattern of increased conversion can be approached by changing the homogeneous catalyst paradigm into a heterogeneous catalyst. The most direct production process of diethyl ether in the world is sulfuric acid or Barbet process. Conversion of diethyl ether produced was 94-94% (Ullman, 2007). The weakness of this process is the separation of catalysts is still difficult and expensive and the catalyst is corrosive so it requires quite expensive equipment investment. Therefore, this research was conducted to overcome these weaknesses by developing heterogeneous catalysts. Catalysts that can be used in dehydration processes other than alumina are MgO and Silica Alumina and WO_3 (Thomas 2011). In addition Golay (2012) has also conducted research on the ethanol dehydration process by using an alumina catalyst modified with Mg^{2+}. Haber et al. (2002) used catalysts of potassium and silver salts from tungstophosporic acid (HPW), namely $KxH_{3-x}PW_{12}O_{40}$ and $Ag_xH_3PW_{12}O_{40}$. Another study was carried out by (Zaki 2005) using a catalyst mixture of metal oxides containing iron and manganese oxide with alumina and / without silica gel. (Kito T, 2004) found the mechanism of dehydration reaction of ethanol into diethyl ether with conversion and selectivity reaching 76% and 78% with aluminaopathospat alumina catalyst in the temperature range of 200 - 300^oC at 11 psia pressure. (Thanh 2013) Catalytic conversion of ethanol to diethyl ether (DEE) using alumina, MFI zeolite, FER and USY, silica-alumina and calcination of hydrotalcite. Zeolite, alumina and active silica-alumina in the temperature range of 453-573 Dilek V 2007 Exchange of ZSM-5 iron ions with a Si / Al ratio of 25-300 prepared by three ions successively used for dehydration of ethanol to ethylene. ZSM-5 exchanged iron (Si / Al = 25) catalyst with an iron content of 0.46% by weight giving 97% -99% yield of ethylene at 98% -99% conversion of ethanol at 260 ° C and speed of 0.81 per hour. High performance is maintained for 60 seconds. X-ray diffraction.Rahmanian 2013 Non-stoichiometric activity of aluminum phosphate-hydroxyapatite for continuous dehydration of ethanol for diethyl ether (DEE) under sub and supercritical conditions was investigated. The catalyst was characterized, using different methods namely, XRD, FT-IR, BET, TGA, EDX. The optimum conditions for ethanol flow rates from 0.17 mL min-1 (WHSV = 1.01 h-1), 340 ° C, and 200 bar, DEE results, selectivity, ethanol conversion, and liquid selectivity reach above 75%, 96 %, 78%, and 97%, VIjaj V. 2011 dehydration of dilute vapor phase of bio-ethanol (EtOH) to ethylene (E) and diethyl ether (DEE) are relevant industries. Ethylene is an important raw material for many petrochemical products and Diethyl ether (DEE) can be used as an alternative fuel.

II. EXPERIMENT METHOD

The raw material used by the ethanol fermented from drops at a rate of 12% is distilled in a "bubble cap column distillation" until it reaches 96% ethanol content.The equipment used in this experiment was a 1.2 liter batch reactor.The 96% ethanol content used was 800 cc then added Cuo-ZnO / γ-Al_2O_3 catalyst (1: 1: 1) by ensuring that the stirrer was a magnetic stirrer, then a pyrolysis operation was prepared by adding notrogen gas

in the reactor until it reached a pressure of 8 bar andset the temperature of 60^{o}C for 2 hours.At the end of this experiment, analyzing gas and liquid products with GC MS.

III. RESULT AND DISCUSSION

The basic contribution of this experiment is to find a pattern of a simultaneous and continuous model in the gas phase with a reaction order kinetics model and reaction speed constants.Engineering this kinetic model is designed to route the reaction by taking into account the intermidiate reaction pathway.The reaction speed equation shows the effect of changing the reactant concentration on the reaction speed, to find out about the reaction order and the reaction speed constant (k) under the influence of temperature, pressure and catalyst.

Path way reaction yang terjadi

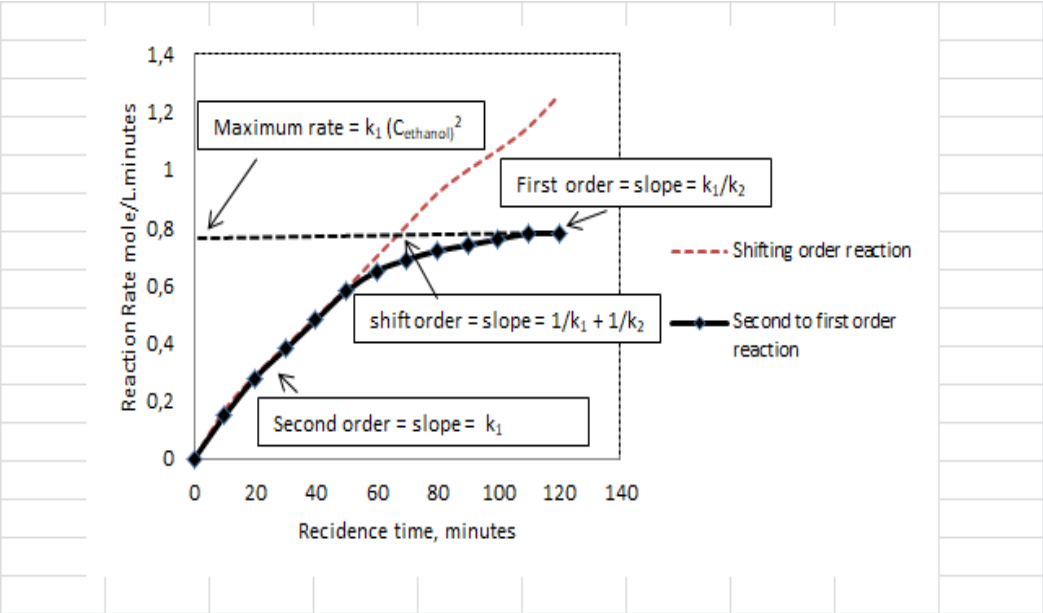
$$C_2H_5OH \xrightarrow{k_1} C_2H_4 + H_2O$$

$$2C_2H_5OH \xrightarrow{k_2} C_2H_5OC_2H_5\,(DEE) + H_2O$$

$$C_2H_4 + 2{,}5\,O_2 \xrightarrow{k_3} CO + CO_2 + 2\,H_2O$$

The equation of the "shifting order reaction" dehydration of ethanol to diethyl ether (DEE)

$$r_{DEE} = \frac{k_1 C_{Ethanol}^2}{1 + k_2 C_{Ethanol}}$$



This kinetic model follows the findings of the LAIDLER kinetic model, in this case a brief "shifting order reaction" will be discussed through the process of dehydration of ethanol into diethyl ether (DEE). The reaction process of dehydration of ethanol into diethyl ether (DEE) through several stages including the transfer of reactant mass to the surface, adsorption of reactants to the surface, chemical reactions to the surface, desorption from the surface of liquid and gas products, mass transfer of the product. This dehydration process uses heterogeneous catalysts which are very closely related to adsorption theory. The dehydration process takes place by pyrolysis proposing intermidiate compounds so that there are several routes that must be passed until it becomes DEE. The speed equation shows the effect of changing the reactant concentration on the reaction speed, to find out about all other things (such as temperature, pressure and catalyst) that can also change the reaction speed, by entering these parameters into the equation, called the reaction speed constant (k). By changing the reactant concentration, the speed remains constant, but if variations in temperature, pressure or catalyst are observed then the constant speed will change accordingly.

Reaction orders give details about the stoichiometry of the speed of the reaction determining the steps of the entire reaction. A reaction can have more than one sequence depending on the different reactant

concentrations. Furthermore the relationship between reactant / product concentration and reaction speed. It also shows that the extent to which reactant concentrations affect the reaction speed, as well as which components have the greatest effect. Similarly, "shifting order reaction" is a reaction that can have more than one sequence depending on the concentration of different reactants. The law of reaction velocity is found to have a second order initially when the reactants are at high concentrations, whereas the reaction order shifts to the first order at the end of the reaction when the reactant concentration is low. Constant price decreases when chemical reactions take place. This reduction is proof for the initial concentration of reactants to be reduced during the reaction. At the time of high concentration the reaction order follows first order while at low concentration the reaction order follows the second order reaction.

IV. CONCLUSION

The dehydration reaction of ethanol into diethyl ether has a shifting order reaction kinetics model."shifting order reaction" has a price of $k_1 = 0.012$ and $k_2 = 1.2$ n = 1.45. Dehydration reaction ofethanol to diethyl ether type of parallel reaction.Maximum reaction speed of 0.8 mol/l.min

REFERENCES

[1]. Buren (2009) , Catalytic conversion of Ethanol to Gasoline Range Hydrocarbons, Catalysis Today. 96 (2004) 155-160.
[2]. Bryden, K. etal (2012), "ModellingThermallythicof Wood", Biomass and Bioenergi, 22, 41-53.
[3]. Chumaidi A. (2015) "Parallel reaction kinetic modelling of biogas to biomethanol with ZnO/SiO2 nanoparticles International Journal of Engineering Research and Development (IJERD) e-ISSN: 2278-0675, p-ISSN: 2278-8004
[4]. Chumaidi A. (2015) " Pengembangan model kinetic reaksi biogas menjadibiometanolberbasisCuO-ZnO/Al2O3 Seminar Nasional "Sustainnable Energy and Mineral Proocessing for National Competitiveness" 12-13 Oktober 2015 UGM Yogyakarta hal 172.
[5]. Chumaidi A. (2016) Dehidrasi methanol menjadi DME dengankatalisCuO-ZnO/alumina Seminar SENTIA 2016
[6]. Golay (2009), Prosess Studies on the Conversion of Methanol to Gasoline, Ind.Eng.Chem.Process Des.Dev.,17, 255-260.
[7]. J. Laider, in "Chemical kinetics" (Harper & Row, New York, 1987) p. 230.
[8]. Jain, J. R. and Pillai C. N. 2007.Catalytic Dehydration of Alcohols over Alumina – Mechanism of Ether Formation.Journal of Catalyst.Volume 9 (322- 330).Department of Chemistry.Indian Institute of Technology. India.
[9]. Kito T 2004 "Prepr. Pap.-Am. Chem. Soc"., Div. Fuel Chem.2004, 49(2),856
[10]. Nicolas V. 2016 "Diethyl ether pyrolysis study in a jet-stirred reactor. Journal of Analytical and Applied PyrolysisVolume 121, September 2016, Pages 173–176
[11]. Ullman, 2007, Proses Produksi Dietil Eterdengan Dehidrasi Etanolpada Fase Cair, Jurusan Tekinik Kimia FakultasTeknik Universitas Diponegoro, Semarang.
[12]. Thanh 2015 "Diethyl ether cracking and ethanol dehydration: Acid catalysis and reaction paths" Volume 272, 15 July 2015, Pages 92–101
[13]. Thomas 2011, Kinetic Study on Methanol Dehydration to Dimethyl Ether Applying Clinoptilolite Zeolite as the Reaction Catalyst, J.Mex.Chem.Soc., 53(4), 233-238.
[14]. Widayat, dan A.H. Jestyssa., 2010 "Optimasi Proses AktivasiKatalisZeolitAlamDenganUji Proses Dehidrasi Etanol" Seminar Rekayasa Kimia, Universitas Diponegoro, Semarang.
[15]. Zaki2005., "DehidrasiEtanol Menjadi Etilen", Tesis, FakultasPascaSarjana, Universitas Gadjah Mada, Yogyakarta.

Achmad Chumaidi "Study of Kinetics Model "Shifting Order Reaction" Dehydration of Ethanol to Become Diethyl Ether (Dee) With Catalystcuo-Zno/□-Al2o3" International Journal Of Engineering Research And Development , vol. 15, no. 4, 2019, pp 41-44