IOP Conference Series: Materials Science and Engineering

PAPER • **OPEN ACCESS**

Production of Diethyl Ether Over Cr-Co/γ-Al_2O_3 Catalyst

To cite this article: M J Marbun *et al* 2019 *IOP Conf. Ser.: Mater. Sci. Eng.* **543** 012058

IOP Conf. Series: Materials Science and Engineering **543** (2019) 012058 doi:10.1088/1757-899X/543/1/012058

Production of Diethyl Ether Over Cr-Co/γ-Al_2O_3 Catalyst

M J Marbun[1,], F Kurniawansyah[1], D H Prajitno[2], A Roesyadi[1*]

[1] Chemical Reaction Engineering Laboratory, Department of Chemical Engineering, Faculty of Industrial Technology, Sepuluh Nopember Institute of Technology, Surabaya, 60111, Indonesia.
[2] Department of Industrial Chemical Engineering, Vocational Faculty, Institute Technology of Sepuluh Nopember, Surabaya, 60111, Indonesia.

Email: aroesyadi@yahoo.com

Abstract. Diethyl ether (DEE) is an important chemical in practical application. This substances actually very interesting to be object of study because its can be substitute the fuel oil such gasoline from the fossil. Its mean that DEE is one of alternative sources of energy. In this study the production of DEE was based on ethanol dehydration over a granule Cr-Co/γ-Al_2O_3 catalyst. The reaction was conducted in a fixed bed reactor at range temperature of 100 to 200^0 C and atmospheric pressure. Un nitrogen gas is fed in reactor to push the ethanol vapor. Sampling the product of reaction is taken after the condition is steady state. The catalyst was analyzed by the BET and XRD method and the result indicated that the prepared catalyst has surface area of 162,840 m^2/g with pore diameter of 0,3178 cc/g. The ethanol conversion under the variable condition attaints of 93.122% of and DEE yield is 0.34%.

1. INTRODUCTION

Ethanol is one of the organic chemicals can be used a solvent for diethyl ether production. Diethyl ether can be produced using a heterogeneous catalyst [1]. Diethyl ether (DEE) is one of the most important chemicals in industrial application. Diethyl ether was commonly used to dissolve oils, gums, resins, microselulose, parfumes, alkynid, and butadiene. Other than that application DEE is also used as anesthetic [2]. In the field of renewable energy DEE can also be utilized mixture or substitue fuel, mixed with gasoline to overcome the shortage of fuel [3]. The mixed of DEE with gasoline more compatible than ethanol- gasoline because the different of their boiling point.and also has the advantage of being a renewable energy source because very low carbon monoxide emissions [4].

DEE can be utilized to increase the octane number in the use of gasoline fuel. DEE compound began to utilize as octane level on the material diesel or biodiesel because has a high cetane number. The use of heterogeneous catalyst is very developed in the industrial chemicals. The most important factor in a heterogeneous catalyst is a acidity, surface area, porosity, mechanical properties, and stability. One of the developments in this field catalyst sectors is the preparation of nano-catalyst to improve their performance to accelerate the reaction. Nano-catalyst is a catalyst which has size of 1-100 nm. Dimension reduction of catalyst into nano-sized catalyst would increase the catalyst surface area and consequently increase the activity of catalysts in certain reactions. DEE is compound colors with distinctive aroma small and very low boiling point. Diethyl ether generally is made though the dehydration process of ethanol (Barbet process) using sulfuric acid catalyst (homogeneous catalyst).

IOP Conf. Series: Materials Science and Engineering **543** (2019) 012058 doi:10.1088/1757-899X/543/1/012058

This process has weaknesses of difficulty of catalyst separation after the reaction. To avoid this difficulty homogeneous catalysts are replaced by heterogeneous catalysts. The heterogeneous catalyst generally used for dehydration of ethanol to DEE is Al_2O_3 with promotor Cr-Co. γ-Al_2O_3 has been known for having a large surface area with acidic and alkaline active sides. Butt et al., (1962), and De boer et al., (1967). have studied reaction kinetics of dehydration of ethanol to DEE. The results shown that reaction is similar than mechanism theory formed Langmuir Hinshelwood reaction mechanics simultaneously. An excessive effort is very necessary to produce diethyl ether as an better energy resources. This research used granulated Cr-Co/ γ-Al_2O_3 catalyst prepared by impregnation method. Then, to test the activity of prepared Cr-Co/ γ-Al_2O_3 nano-catalyst. Ethanol dehydration reaction was carried out in a fixed bed reactor.

2. EXPERIMENTAL

2.1 Materials

The chemicals were used in this experiment are: $Al(NO_3)_3.9H_2O$, NH_4OH, HCl and 99% ethanol. This study was used the Al_2O_3 catalyst purchased at the Merck company, Aluminium nitrate nonahydrate (Merck), $Cr(NO_3)_3.9H_2O$, $Co(NO_3)_2.6H_2O$, molecular sieve, nitrogen gas (PT. Aneka Gas Industry) were also employed.

The starting materials, fructose (D-(-)-type, Sigma-Aldrich, 99%), silver nitrate ($AgNO_3$, AR, QRëC™), titanium tetraisopropoxide (TTIP, Sigma-Aldrich, 97%) and absolute ethanol (EtOH, HmbG® Chemicals) were used as the precursor for carbon microspheres, silver, and TiO_2 microspheres, respectively.

2.2 Preparation of catalyst

The first Al_2O_3 was synthesized using the precipitation method. Alumina nitrate monohydrate was prepared with different concentration different (0.2, 0.3, 0.4, 0.5, and 1 M) was dissolved in a solution of HCl (0.5 M). the precipitation was carried out by adding ammonium nitrate into the solution. The precipitate formed was stirred with variation of time between (3.4.5 and 6 hours) at 60, 70, 80, 90, 100^oC. Furthermore, the precipitate was filtered and washed by using distilled water and ethanol and then dried at 75^o C for 24 hours. The solid precipitate calcined for 6 hours at 600^o C with air flow to produce catalyst γ-Al_2O_3. γ-Al_2O_3 in synthesis using XRD and BET. Size of crystal calculated by using Scherrer formula based on the data of XRD analysis. Scherrer formula used is:

$$D = \frac{\kappa \lambda}{\beta \cos \theta} \quad (1)$$

Where D is the diameter of the crystal, κ is the shape factor with a value of 0.9-1.4 (generally used ~ 0.9), λ is the wavelength of X-ray (0.15406 nm), θ is the Bragg angle (radians), and β is the FWHM (Full Width Half maximum) of the highest peak (radians).

2.3 Preparation of Cr-Co/γ-Al_2O_3 Catalysis

γ-Al_2O_3 as a support was impregnated with $Cr(NO_3)_3.9H_2O$ and $Co(NO_3)_2.6H_2O$ metal salt solution using the Dry Impregnation method with loading 10%. Phase stage as follows: The impregnation $Cr(NO_3)_3.9H_2O$) on γ-Al_2O_3 is done by spraying metal solution to γ-Al_2O_3. In stirring using magnetic stirrer at temperature 80 ^0C for 3 hours. After which the catalyst is dried at temperature of 110 ^0C for 12 hours. $Co(NO_3)_3.9H_2O$) is impregnated in same manner. and then dry catalyst was calcined with N_2 at 550 ^0C for 3 hour and followed by a reaction reduction with H_2 at a temperature of 600 ^0C for 6 hour and characterized.

2.4 The production process of diethyl ether (DEE)

The catalytic production of diethyl ether was conducted in fixed bed reactor using 3 g of catalyst. This temperature operation was of 100 – 200 ^{0}C, and in atmospheric pressure in the reactor. The ethanol and liquid products were analyzed using gas chromatography with a FID detector and using helium with a flow rate of 27,4 mL/min, temperature operation of 125-250 ^{0}C. Arrangement of equipment used for the production process DEE is shown in Figure 1 below.

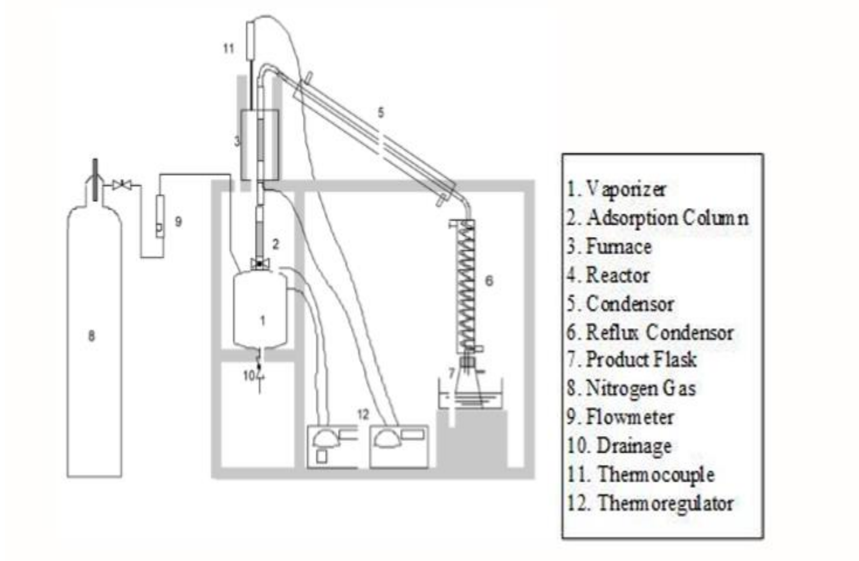

Figure 1. Diethyl Ether Production Equipment

3. RESULTS AND DISCUSSION

3.1 *Surface area and pore volume analysis of catalyst by BET*

The specific surface area, average pore diameter, and pore volumes of the γ-Al_2O_3 and Cr-Co/γ-Al_2O_3 catalyst shown in Table 1. The specific surface area for the γ-Al_2O_3 catalyst is 162.84 m^2/g. After impregnation of Cr and Co on to the γ-Al_2O_3 catalyst reduced the surface area, is 133.499 m2/g. the results indicated that the impregnation of Cr and Co particle blocked of the γ-Al_2O_3 catalyst [5].

Table 1. BET catalyst analysis results of Cr-Co/ γ-Al_2O_3

Catalyst	Specific Surface Area (m^2/g)	Average Pore Diameter (nm)	Pore volume (cm^3/g)
γ-Al_2O_3	162.840	0.3178	3.4276
Cr-Co/ γ-Al_2O_3	133.499	0.2288	3.9027

3.2 The production process of diethyl ether (DEE)

3.2.1 GC-MS analysis

Figure 2 show the chromatogram results of the DEE production process at a gas rate of 600 mL/min. At temperature of 150 ^{0}C the ethanol component was detected at retention time of 3.985 minute, while DEE detected at retention time of 5.367 minutes. From chromatogram, diethyl ether compounds was detected

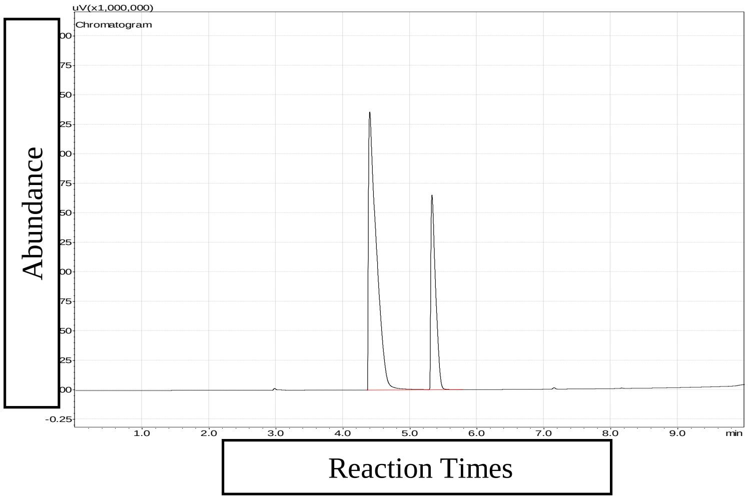

Figure 2. Chromatogram of liquid product in DEE production process using catalyst Cr-Co/ γ-Al_2O_3 of reaction temperature

Figure 2 show that at nitrogen rate 200 mL/min, the conversion of ethanol more significant value compared with 400 mL/min nitrogen gas rate. The largest conversion produced at rate of 200 mL/min is 93.12% at temperature of 100^0 C. For the conversion of 400 mL/min nitrogen gas rate 93.03% at 100 ^{0}C and at conversion rate of 600 mL/min nitrogen gas was 84.40% at temperature of 100 ^{0}C. This indicate that the greater the rate of carrier gas caused then the smaller the contact time between ethanol with surface area of the catalyst [6]. Increased temperatures can increase the conversion of ethanol according to the Arrhenius equation. In this equation, the increase of temperature will increase the reaction rate constants that will increase the rate of reaction [7].

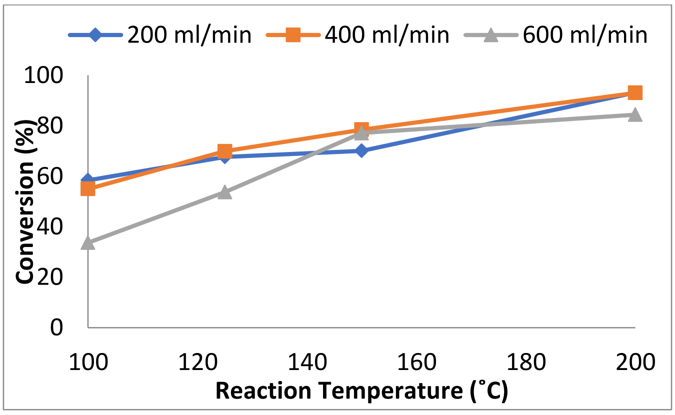

Figure 3. Ethanol conversion vs reaction temperature of dehydration (^{0}C).

Figure 3 shows that the nitrogen gas rate of 600 mL/min produce diethyl ether greater compared which rate of nitrogen gas 200 mL/min and 400 mL/min. The higher yield of DEE in this experiment attaint 0.3 % with N_2 gas rate 600 mL/min at temperature of 200 ^{o}C. As shown in Figure 4, the Increasing reaction temperature can increase the yield of DEE. Using of catalyst generally produce dehydration reaction cenvertion hight. This is happened because it has been know that the catalyst has greater surface area. Greater surface area will increase the convertion of ethanol because it can increase the opportunity for the convertion process.

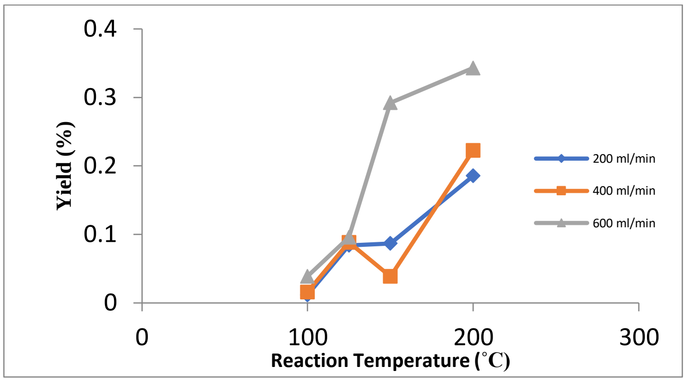

Figure. 4 Relationship between yield DEE % with temperature (^{0}C)

Figure 4 show that the nitrogen gas rate of 600 mL/min produce diethyl ether greater compared which rate of nitrogen gas 200 mL/min and 400 mL/min. The higher yield of DEE in this experiment attaint 0.3 % with N_2 gas rate 600 mL/min at temperature of 200 ºC. As shown in Figure 5, the Increasing reaction temperature can increase the yield of DEE. due to more minimum (more negative) value of the Gibbs energy change (ΔGreaction) make the reaction more easy to be occurred [8].

4. CONCLUSION

Based on this research, it may be concluded that diethyl ether can be produced by using. The ethanol dehydration with γ-Al_2O_3 as a catalyst and Cr-Co as metal. The catalyst prepared in the granular state has surface area from 162.84 m^2/g to 133.499 m^2/g, and the catalyst pore volume from 3.4276 cm^3/g to 3.9027 cm^3/g. The higher conversion of ethanol attain 92,12% and yield 0.3 % of DEE yield was biggest conversion reaction has been 93.12% from temperature of 100^0 C. The biggest DEE yield was resulted at temperature of 200 ^{0}C.

ACKNOWLEDGEMENT

The authors would like to thank Ministry of Research Technology and Direktorat Riset dan Pengabdian Masyarakat–Direktorat Jenderal Penguatan Riset dan Pengembangan–Kementerian Riset, Teknologi, dan Pendidikan Tinggi Republik Indonesia for financial support under grant PTUPT Scheme for the year of 2018 granted through Institute for Research and Community Services Sepuluh Nopember Institute of Technology.

REFERENCES

[1] Cárdenas-Guerra J C, Figueroa-Gerstenmaier S, Hernandez S and Reyes-Aguilera J A 2018 Simulation study of a reactive distillation process for the ethanol production *Chem. Eng. Trans.* **69** 613-18
[2] DA Pacas, Kito-Borsa T, Selim S and Cowley S W 1998 Properties of an ethanol-diethyl ether-water fuel mixture for cold-start assistance of an ethanol-fueled vehicle *J. Ind. Eng. Chem.* **37** 3366-74
[3] Bailey B J, Eberhardt S, Erwin J and Goguen 1997 *SAE Trans.* **972** 78
[4] Sunaardi W and Yulia I 2007 Study of 2- propanol catalyst conversion reaction using catalyst and catalyst support γ-Al2O3. *Bull. Chem. React. Eng. Catal.* **2** 56-61
[5] Abdullah B, Dai-Viet V N, Sow Lock I M and Sow Lock S M 2017 Influence of palladium on Ni-

based catalysts for hydrogen production via thermo-catalytic methane decomposition *Chem. Eng. Trans*. **57** 343-48.
[6] Akira Tand Wei C X 1989 The Effects of temperature and residence time on the secondary reactions of volatiles from coal pyrolysis *Amsterdam Elsevier Science Publishers*
[7] Doğu T and Varişli D 2007 Alcohols as alternatives to petroleum for environmentally clean fuels and petrochemicals *Turkish J. Chem.* **31** 5551–67
[8] Abbott H C, Smith J M and Van Ness. 2001 Introduction to Chemical Engineering Thermodynamics 6th Edition: *New York McGraw Hill*

.