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Study of Esterification Reaction between Ethanol and Acetic Acid Using Homogeneous and Heterogeneous Catalyst

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ABSTRACT

The Ethyl acetate is the final product of esterification reaction between ethanol and acetate acid which usually used as a solvent. Catalysts are used to boost the esterification reaction rate, mostly the homogenous catalyst (acid liquid catalyst) is used. The use of homogeneous catalyst needs quite long process to separate, that is the reason why using the heterogeneous catalyst is the alternate way. The purpose of this research is to compare the performance of homogeneous catalyst (sulphuric acid) and heterogeneous catalyst (natural zeolite from Bayah) by varying the factors that has an impact on reaction such as agitation speed and particle size (for heterogeneous Catalyst). The reaction was performed in batch reactor by varying the speed of agitation speed in range 500-700 rpm and the catalyst particle size 60 mesh and 100 mesh for the solid catalysts. The goal of the variation is to maximize the reactant mass transfer to the active site of the catalyst. The result of this research shows that on the agitation speed of 700 rpm and 100 mesh Bayah natural zeolite is able to yield higher conversion of acetate acid compared to using the sulphuric acid catalyst, which are 45.03% and 15.19% .

Keywords: *ethyl acetate, zeolite, sulphuric acid, ethanol, acetic acid*

1. INTRODUCTION

Ethyl acetate is one of the most material that often use in printing ink industry, paint, glue, PVC film, luquid polymer in paper industry, and also pharmacy industry (McKetta and Cunningham, 1994). But recently, ethyl acetate is on trial for using it as an alternative fuel of motorcycle or well known as green premium (Heuser et.al, 2019). Ethyl acetate mostly resulted through esterification process between acetate acid and ethanol, with the help of catalyst. The catalyst that often used is homogenous catalyst as sulfate acid (Ding et al., 2012; Arbain and Salimon , ed. 2011; and Nurhayati et al., 2017). But the use of homogeneous catalyst needs a separation process that take more time and causing corrosion to the equipment (The Martin Companies, 2009). On the other hand, the use of solid catalyst on esterification reaction is much easier than separating them, but the active sites that the catalyst has are limited compared to the homogeneous catalyst (liquid catalyst). That is the reason why the solid catalyst needs a pre-treatment before use it with its maximum work (wang et. al.,2016). This research try to observe the esterification process using homogenous (liquid) and heterogenous (solid) catalysts with the same condition operation. The purpose of this research is to compare the performance between homogenous (sulphuric acid) and heterogenous (natural zeolite from Bayah) catalysts in esterification process by variating factors that has an impact to the chemical reaction. The use of Bayah natural zeolite has a purpose, which is to maximizing the use of local natural resources, which haven't been maximally used. Basically, The esterification reaction between ethanol and acetate acid happen as equation (1).

$$C_2H_5OH + CH_3COOH \rightarrow CH_3COOC_2H_5 + H_2O \quad (1)$$

The correlated research about esterification reaction on the producing ethyl acetate has been done by other researcher before, those are Hua et.al. (2015) and Unlu et. al. (2017), whether using liquid catalyst or solid catalyst. But most of the researchers using synthetic catalysts and the reactant with reagent grade material.

This research try to use activated solid catalyst (Bayah natural zeolite) and liquid catalyst (sulfuric acid), with the technical grade raw material. The performance of the used catalysts (Bayah natural zeolite and sulfuric acid) measured based on how much acetate acid converted by using the catalyst. To maximize the performance of both catalysts especially the solid catalyst, so the internal and external resistance on the mass transfer must be reduced as least as possible. Reducing the resistance by minimizing the size of the catalyst particles and speeding up the agitation speed. The research that has been done by Idrus et. al (2020) on producing high oleic pentaerythritol tetraester that has been done on 300-600 rpm of agitation speed, yield PE ester increasing as the increase of agitation speed. The observation that has been done by Ramadhan et.al (2019) on the different research shows the same result, which is the conversion of oleic acid increase as the increase of the agitation speed to the reaction system. Meanwhile, the observation of the size of catalyst particles that has been done by Mekala and Goli ((2015) and Ramadhan et.al (2019), both giving the same result, which is the smaller the size of catalyst particles, the bigger the conversion of the reactant.

Basically, reducing the size of solid catalyst if the size is suitable with the operation condition of the on-going reaction, so it will give a good impact to the resulted reactant conversion. However, if it doesn't suitable with the operation condition (between the size of catalyst particles-agitation speed), it will cause a decrease to the reaction rate. Those phenomenon happened to Gangadwala et. al. (2003). The result of the research that has been done by Gangadwala et. al. (2003) with the size range of catalyst 25 – 100 mesh (0,0707 – 0.0125 cm) and agitation speed of 1000 rpm shows that the best size of catalyst particles resulted by 25 mesh (0,0707 cm), with quite good decrease of mole fraction acetate acid which is from 0,5 to 0,21 (56% acetate acid converted). Based on Fogler (2006), the smaller the size of the catalyst particles the weaker the internal resistance, and vice versa. However, if the size of the catalyst particles are too small on certain agitation speed will cause a stagnant movement of the particles in the fluid (the particles will move along the fluid movement). In that condition, the reactant mass transfer to the outer surface of catalyst will get smaller and as a result the reactant that diffuses into the outer surface of catalyst will less and of course the amount of reactant that diffuse into the active site of catalyst will less too causing a decrease of reaction rate. Based on the phenomenon from the reference, so this research try to do particles size of catalyst (Bayah natural zeolite) variation and get the agitation speed higher.

2. METHODS

2.1. Raw material

The raw material that used in this research are the technical grade acetate acid with the concentration of 98% bought from Rofa Laboratorium Center via Shopee, technical grade ethanol with the concentration of 96% bought from *Toko Indojay Sehat* via Shopee, analysis grade sulfate acid (Merck) with the concentration of 95-97% bought from CV. Trijaya Dinamika, Tangerang, and also the Natural Zeolite from Bayah-Banten, Indonesia which has been activated with 6 N H_2SO_4 on the size of 60 and 100 mesh.

2.2 Equipment of Experimental

This research has been done by using Three-neck Flask as reactor batch. More detail, look at the equipment scheme in Figure 1.

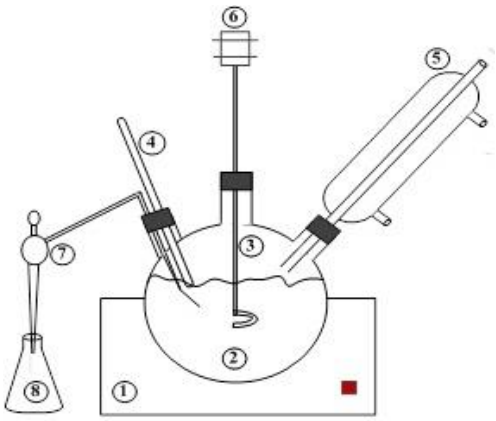


Fig. 1. Schema of esterification reaction between ethanol and acetic acid

Legends: 1. Heater Jacket, 2. Three-neck flask, 3. Mercury Mixer, 4. Thermometer, 5. Cooler, 6. Mixer Motor, 7. Sample Taker, 8. Sample Container

2.3. Bayah Natural Zeolite Activation

First, Bayah natural zeolite crushed, then sifted by using screener to get 60 mesh and 100 mesh of zeolite particles size. The the zeolite was put inside of 6N sulfate acid solution with the ratio of 1 g zeolite : 10 ml solution for the activation. The zeolite activation condition was done at 110^{o}C for 2 hours. After done with the activation, then it washed by using aquadest (neutral pH), after that, it drained by putting the zeolite into the oven at 200 ^{o}C for 2 hours. The next step is cooling the zeolite at ambient temperature, and the zeolite ready to use. The activation procedure is based on the latest research (Nuryoto et.al, 2015 and Nindya et. al., 2020 and Shadrikov dan Petukhov, 2014).

2.4. Experimental Procedure

Heating up the ethanol and acetate acid with certain volume (based on the ratio reactant 3 mole ethanol: 1 mole acetate acid) at 70^{o}C in the separate place. When each liquid has reached 70 ^{o}C, both of the liquid was put into the reactor alongside the agitation with agitation

speed of 500-700 rpm (based on research of Nuryoto et. al, 2015 dan Ramadhan et. al, 2019). When the reactant has already considered fully mixed and the temperature has reached at 70°C, then the sample was taken to analyze the initial concentration of acetate acid (Ao) using acid-base titration with 1 N NaOH. The next step is injecting the catalyst (for the liquid catalyst with amount of 1 ml and for the solid catalyst with amount of 1 gram) with particle size of 60 and 100 mesh (based on the research of Ramadhan et. al, 2019). For the next sample was taken every 15 minutes for 60 minutes (until final reaction) to analyze the concentration of acetate acid (A_S) with the same method.

To calculate how many acetate acid that converted into a product, calculated by equation (2):

$$x_A = \frac{A_o - A_S}{A_o} \times 100\% \qquad (2)$$

where,
$x_A =$ Acetate acid conversion, %
$A_o =$ Initial concentration of acetate acid, N
$A_s =$ Residual concentration of acetate acid, N

3. RESULTS AND DISCUSSION

3.1. Without Catalyst

In the esterification reaction between acetate acid and ethanol was done without the existence of catalyst, shown in figure 2 only resulting low conversion of acetate acid, which is only 12.15% for 60 minutes reaction. How high the conversion that resulted for the reaction time (60 minutes) and reaction temperature (70°C) is not equal as the result of conversion that gained in this research. It means that if the esterification process between ethanol and acetate acid is done without the catalyst, the reaction will be not efficient and effective. For that, in the esterification process between ethanol and acetate acid, the existence of catalyst to boost the reaction rate is very necessary and to maximize the result of acetate acid conversion.

3.2. Effect of Particle Sizes

The result of the research that has been done (see Fig 3), The acetate acid conversion on 100 mesh is higher than 60 mesh which are 45.03% compared to 36.46% for the reaction time of 60 minutes. This shows that reducing the size of Bayah natural zeolite particles is done to lower the internal resistance that inhibits the reactant to the active site of Bayah natural zeolite catalyst is succeed. Other than that, That result also shows that the decrease of zeolite particle size to 100 mesh with the 700 rpm speed of agitation to increase the obtained reaction product that wanted still able to achieve. The phenomenon on this research is similar with the research that has been done by Ramadhan et. al (2019), which observe the production of glycerol oleic with the 40, 50, and 60 mesh sized of catalyst with the 700 rpm speed of agitation, that increased the result of glycerol conversion which are 63.5, 72.99 and 73.65%.

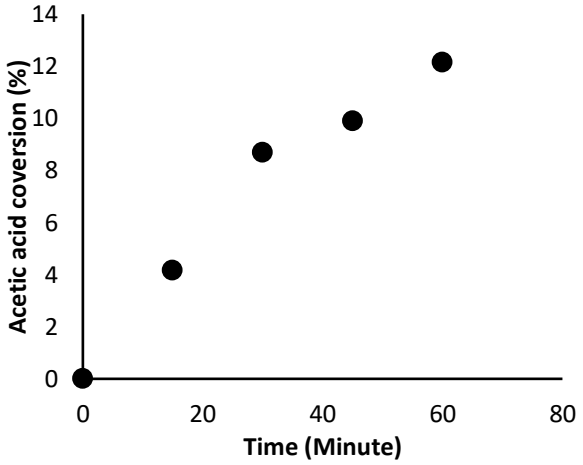


Fig.2. Acetic acid conversion in esterification without catalyst at 700 rpm speed of agitation

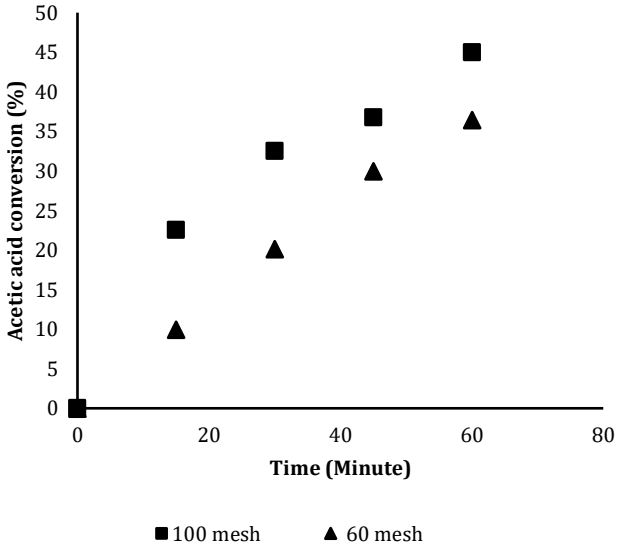
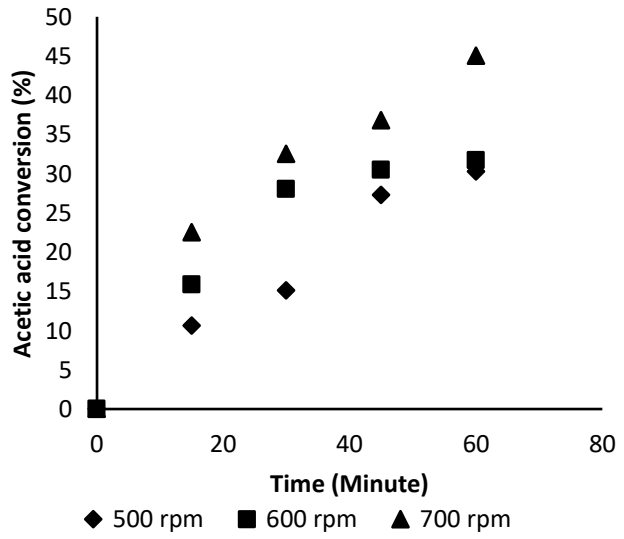


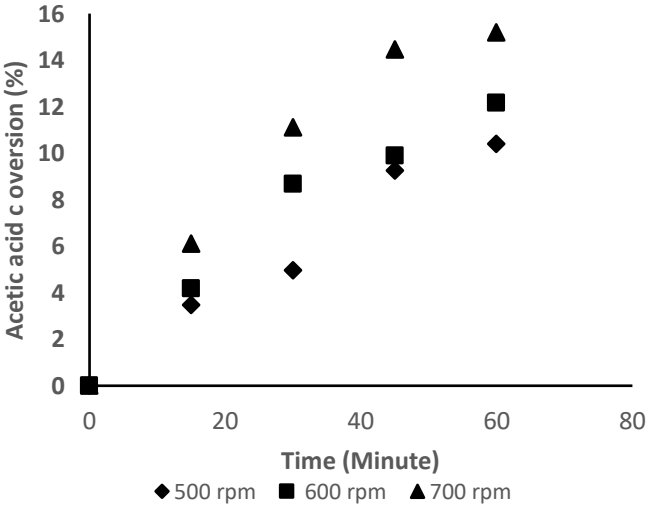
Fig. 3. Effect of catalyst size to acetic acid conversion at 700 rpm speed of agitation

3.3. Effect of Agitation Speed

To compare the performance of heterogeneous (Bayah natural zeolite) and homogenous (sulfuric acid) catalyst, Bayah natural zeolite that used in size of 100 mesh, because it is able to resulting a high acetate acid conversion (see Fig 3). In Fig 4.a shows that Bayah natural zeolite catalyst in the reaction time of 60 minutes, in particular order gives the amount of acetate acid conversion of 30.30% (500 rpm), 31.71 %(600 rpm), and 45.02% (700 rpm). For the H2SO4 catalyst (Fig 4.b), the resulted conversion on the same operation condition is way lower which is only 10.40% (500 rpm), 12,15% (600 rpm) and 15.19% (700 rpm). But, overall in Fig 4.a and b, the agitation speed that given in the reaction process, cause a positive impact to the increase of acetate acid conversion that resulted. This means that the increase of agitation speed that given is able to boost the contact between the reacting substances, and to boost the reaction rate.



(a) Zeolite catalyst (1 g/ 70 ml reactant)



(b) Sulfuric acid catalyst (1 ml / 70 ml reactant)

Fig. 4. Effect of agitation speed to acetic acid conversion: (a) Bayah natural zeolite)catalyst and (b) Sulfuric acid (H_2SO_4) Catalyst.

The conversion of acetate acid that has been resulted by the sulfate acid catalyst is way lower than Bayah natural zeolite catalyst (see Fig 4.a and b), it happened because the amount of excess sulfate acid catalyst (above 0.923%), so there is possibility that will cause the ethanol (alcohol) reacted with sulfate acid and creating monosulphate (Setyawardhani et al., 2005). This condition will cause the decrease of ethanol-acetic acid contact and also affect the resulted acetate acid conversion.

3.4. Mathematical model to approximate the happening phenomenon of the reaction.

Study of mathematical models is just done to Bayah natural zeolite, which able to resulting the higher conversion of acetate acid compared to sulfate acid catalyst. Besides, it only done to the agitation speed variation. The mathematical model approach that has been done is using pseudo-homogeneous model. This is based on the size of Bayah natural zeolite particles which is relatively small (100 mesh). The assumption that used is the reaction leads to the left (backwards) is ignored. Because the reactant is made 3 times more than the stoichiometric calculation (3 mole of ethanol/mole of acetate acid). The reaction equation that shown in equation (1) can be simplify to :

$$A + B \rightleftharpoons C + D \qquad (3)$$

With, A : acetate acid; B: ethanol; C : ethyl acetate and D: water

The explanation of chemical reaction rate in equation (3) with considering the assumptions that used, so resulting equation (4).

$$(-r_A) = -\frac{dC_A}{dt} = -\frac{dC_B}{dt} = kC_AC_B \qquad (4)$$

If the acetate acid conversion + XA, and the initial concentration of acetate acid and initial ethanol concentration are CAO and CBO, also M is ratio of CB_0/CA_0, the obtained:

$$\ln\frac{C_B}{C_A} = (C_B - C_{Ao})k\,t + \ln M \qquad (5)$$

By connecting ln CB/CA versus time, so the calculation in equation (5) can be drawn like in Fig. 5

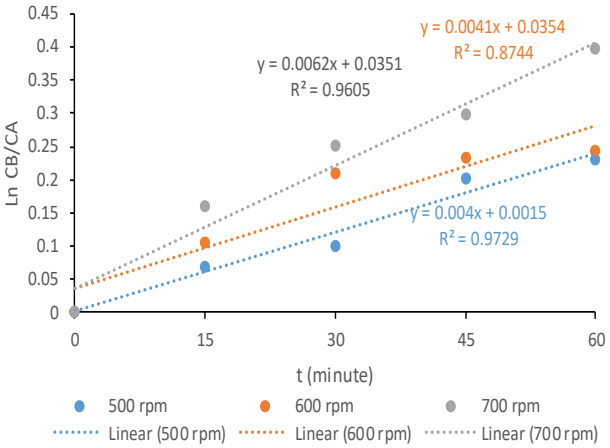


Fig.5. ln CB/CA versus time

The result of trendline linearization that has been done shows that the value of R^2 is approaching 1 (see in Fig 5). This result shows that the pseudo-homogeneous model approach second order is quite valid to describe the phenomenon that happened in esterification reaction between ethanol and acetate acid with Bayah natural zeolite catalyst size 100 mesh. For the value of constant reaction rate (k) on 500-700 rpm are shown in Table 1.

The tendency of constant reaction rate value to the agitation speed is available in Fig. 6. In the increase of agitation speed from 500 – 600 rpm, affect the increase of the Value of k that resulted a small tendency (almost similar), but from 600 rpm to 700 rpm, the value of k is increasing quite significant (see **Fig.** 6). Graphic in Fig 6 shows that the increase of agitation speed from 600 to 700 rpm has a quite significant impact to the decrease of

mass transfer external resistance compared to 500 to 600 rpm. It is causing a significant increase of the constant reaction rate value.

Table 1. The value of k on every agitation speed

Agitation speed (rpm)	CBo (mole/ml)	CAo (mole/ml)	Slope	k ($mole^{-1}s^{-1}$)
500	16.47	6.67	0.004	0.000408
600	16.47	6.833	0.0041	0.000425
700	16.47	5.5	0.0062	0.000565

The correlation between (k) and agitation speed (v), In this case, it can be put in mathematical equation which is by doing trend line using polynomial to Fig 6. The result of the trend line that has been done is equation (7):

$$k = 6 . 10^{-6} v^2 - 7.10^{-6} v + 0{,}0022 \quad (7)$$

The equation that obtained (equation (7)) can use to approximate the impact of agitation speed (v) to the constant reaction rate (k) in range of 500-700 rpm. This equation will be enough to help the operational approach and scale up. Even though, the possibility of a deviation to the real condition. But as long as the deviation is still forgiven (below 10%), so the deviation still can be tolerated.

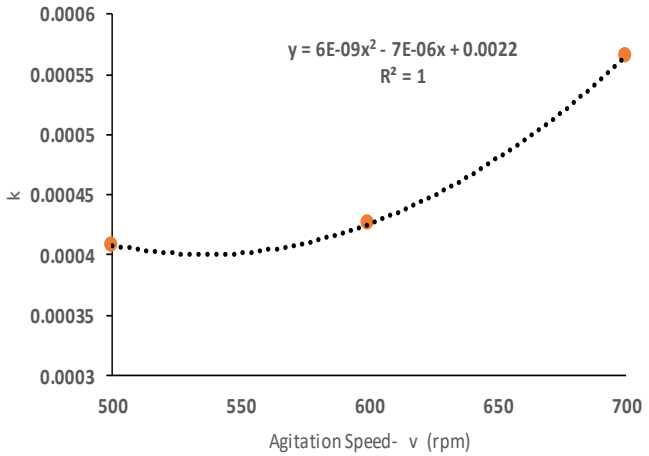


Fig. 6. k versus agitation speed (v)

4. CONCLUSION

From the research, can concluded that the performance of Bayah natural zeolite catalyst (1 g zeolite/70 ml reactant) has a better performance compared to sulphuric acid catalyst (1 ml/70 ml reactant) with the same operation condition (70°C and 500-700 rpm). The highest acetate acid conversion obtained for the Bayah natural zeolite catalyst is at particle size of 100 mesh, agitation speed of 700 rpm, and reaction time of 60 minutes, which is 45.02%. The mathematical model approach that has been done to describe the phenomenon that happened, with the value of R^2 resulting near of 1.

5. REFERENCES

Ding J., Xia Z., Lu J. 2012. Esterification and Deacidification of a Waste Cooking Oil (TAN 68.81 mg KOH/g) for Biodiesel Production. Energies. Vol. 5, pp. 2683-2691.

Fogler S.H. 2006. Elements of Chemical Reaction Engineering. 4 Edition Prentice Hall International Series in the Physical and Chemical Engineering Sciences.

Heuser K., Liao V., Narain N. 2019. Ethanol to Ethyl Acetate. University of Pennsylvania-ScholarlyCommons.

Hua Y, Xiaozhen F., Shaoqing Z. 2015. Synthesis of ethyl acetate catalyzed by (NH4)6[MnMo9O32].8H2O with Waugh structure. Journal of Chemical and Pharmaceutical Research. Vol.7. No.10., pp. 445-448.

Gangadwala, J., Mankar,S., and Mahajani,S., 2003. Esterification of Acetic Acid with Butanol in the Presence of Ion-Exchange Resins as Catalysts. Ind. Eng. Chem. Res., 42, pp. 2146-2155.

Idrus N.F., Yunus R., Abidin Z.Z., Rashid U., Rahman N.A. 2020. Hidh Oleic Pentaerythritiol Tetraester Formation via Transesterification : Effect of Reaction Condition. Indones. Jur. Chem. Vol. 20. No.4. pp.887-898.

McKetta J.J. Cunningham W.A. 1994. Enclyclopedia of Chemical Processing and Desig. Vol. 49. M Dekker. Inc. New York., USA

Mekala M., Goli V.R. 2015. Kinetics of esterification of acetic acid and methanol using Amberlyst 36 cation-exchanger resin solid catalyst. Progress in Reaction Kinetics and Mechanism. Vol. 40. No.4., pp. 367-382

Nindya C.C.S., Ramadhan A.D., Nuryoto, Kurniawan T. 2020. Esterifaication Glycerol (By product in Biodiesel Production) with Oleic Acid Using Mordenite Natural Zeolite as Catalyst: Study of Reaction temperature and Catalyst Loading Effect. International Conference on Advanced Mechanical and Industrial Engineering 2020 (ICAMIE 2020), Cilegon-Banten, Indonesia, 8th January 2020.

Nuryoto N, Sulistyo H., Sediawan W.B., Perdana I. 2015.. Preliminary Study of Bayah Natural Zeoliteas Catalyst at the Ketalization of Glycerol. The 10th International Forum on Strategic Technology 2015 June 3 - June 5, 2015, Universitas Gadjah Mada, Bali-Indonesia

*

Nurhayati, Anita S, Amri T.A., Linggawati A. 2017. Esterification of Crude Palm Oil Using H2SO4 and Transesterification Using CaO Catalyst Derived from Anadara granosa. Indones. Jur. Chem.. Vol. 17 No. 2, pp. 309 - 315

Ramadhan A.D., Nindya C. C. S., Nuryoto, Kurniawan T. 2019. The Use of Natural Zeolite as A Catalyst for Esterification Reaction Between Glycerol and Oleic Acid. Jurnal Reaktor., Vol19, No.4., pp. 172-179.

Shadrikov, A.S. and Petukhov, A.D. 2014, Natural Zeolite Clinoptlolite Characteristics Determination and Modification. National Technical University ofUkraine - Kyiv Polytechnic Institute, pp 162-167.

Setyawardhani D.A., Yoenitasari, Wahyuningsih S. 2005. Kinetika Reaksi Esterifikasi Asam Formiat Dengan Etanol Pada Variasi Suhu Dan Konsentrasi Katalis. E K U I L I B R I U M Vol. 4. No. 2., pp. 64 – 70

The Martin Companies. 2019. Material Safety Data Sheet-MSDS. Sulfuric Acid.

Unlu D., Hacioglu A., Hilmioglu N. 2017. Ethyl Acetate Synthesis By Chitosan / Poly (VinylPyrrolidone) Blend Menbrane in Pervaporation Menbrane reactor Journal of The Tuskish Chemical Society. Vol1. No.1, pp. 25-28.

Wang Y, Yokoi T, Namba S., Tatsumi T. 2016. Effects of Dealumination and Desilication of Beta Zeolite on Catalytic Performance in n-Hexane Cracking. Catalysts . Vol. 6. No. 8.pp. 75-99