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KINETICS STUDY OF FREE FATTY ACIDS ESTERIFICATION FOR BIODIESEL PRODUCTION FROM PALM FATTY ACID DISTILLATE CATALYSED BY SULFATED ZIRCONIA

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ABSTRACT

Kinetic study of free fatty acids (FFAs) esterification for biodiesel production from palm fatty acid distillate (PFAD) using sulfated zirconia (S-ZrO$_2$) prepared by solvent-free method calcined at low temperature as the heterogeneous catalyst was studied. The reaction was performed in a batch-stirred reactor at the different temperature to obtain the kinetic data. The effect of reaction condition such as methanol to PFAD molar ratio, stirring rate and catalyst concentration on FFA conversion were also investigated. The experimental data was interpreted with the second-order heterogeneous kinetic model involving the rate of mass transfer and the rate of reaction. The proposed kinetic model and the experimental data are in good agreement.

Keywords: biodiesel, palm fatty acid distillate, esterification, sulfated zirconia.

INTRODUCTION

Biodiesel as an alternative diesel fuel has several advantages as compared to petroleum based diesel fuel and has been industrialized in many countries. Several studies reveal that continuous process of reactive distillation column for biodiesel production is more popular due to low energy cost [1-3]. However, the price of produced biodiesel is still more expensive than fossil diesel due to high price of virgin vegetable oil feedstocks. It has been revealed that the cost of feedstocks is account for 60–75% of the total cost of biodiesel production [4]. The low cost feedstocks are those feedstocks which usually have a high level of Free Fatty Acid (FFA) value such as animal fats, grease, waste cooking oil, and some non-edible oils. Employing a low-cost feedstocks can be expected to gain the economic attractiveness for biodiesel production [5-7].

Palm Fatty Acid Distillate (PFAD) is by-product of palm oil refining process which contains 85-95% FFA and 5-15% triglycerides. Therefore, PFAD can be used as low-cost feedstock for biodiesel production [8]. The conventional process used to produce biodiesel from feedstocks containing high FFA such as PFAD is two-step process [7-9]. The first step is esterification reaction of FFA with methanol using homogeneous acid catalyst to form Fatty Acid Methyl Ester (FAME) and water. The second step is transesterification between triglycerides and methanol using homogeneous base catalyst to form FAME and glycerol. This two-step process, however, lead to longer step of product purification than one step process used when employing highly refined vegetable oil as feedstock. The product purification includes the removal of catalysts and by product, and also methanol recovery. This complicity can cause environmental effect since the spent catalyst cannot be reuse. Moreover, corrosion problem can also be resulted from use of homogeneous acid catalyst such as sulfuric acid [10,11]. There are a number of alternative methods that have been developed to overcome those problems such as supercritical process [12,13] and heterogeneous solid catalytic process [13-19].

Biodiesel production using heterogeneous solid catalytic process is considered as potential method to overcome those problems associated with homogeneous process. It is environmental friendly, less corrosive, reusable, and the catalyst can be easily removed from the reaction mixture [20]. Among the heterogeneous solid catalysts, solid acid catalysts have been considered to be use on biodiesel production from low-cost feedstocks due to its special properties that can promote esterification as well as transesterification reaction [22].

Sulfated zirconia is a solid super acid catalyst that widely used in many process due to its strong acid properties [23]. Biodiesel production using sulfated zirconia as solid acid catalyst has been reported by several authors. Furuta *et al*. studied transesterification of soybean oil with methanol and esterification of n-octanoic acid with methanol using solid superacid catalysts of sulfated tin and zirconium oxides and tungstated zirconia [22]. The reaction was conducted in fixed bed reactor under atmospheric pressure. They found that the catalysts show a high activity for the transesterification as well as the esterification. The yield of methyl ester close to 100% at temperatures over 175 ^{0}C, reaction time 20 hr, molar ratio of methanol to oil 40 for transesterification reaction (flow rate of methanol 4.4 g h^{-1}; soybean oil 3.0 g h^{-1}), molar ratio of methanol to acid 4:5 for esterification reaction. Other research on the simultaneous transesterification and esterification reaction using sulfated zirconia were also reported by Lopez *et al*. whereby tricaprylin and caprylic acid were used to simulate the compositions of TGs and FFAs typically present in vegetable oils and animal fats [24]. Others research that focused on biodiesel production using different solid acid catalysts including sulfated zirconia were also reported by Jitputti *et al*. for

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transesterification of crude palm kernel oil and crude coconut oil [25]; Muthu *et al*., for synthesis of biodiesel from neem oil [19]; Li *et al*. for biodiesel production from acid oil containing about 60 %wt of free fatty acids [26]; and Kansedo *et al*. for transesterification of palm oil and crude sea mango [23].

There are several methods for the preparation of sulfated zirconia that have been reported [23]. Sulfated zirconia used in this study was prepared by a simple calcination in the absence of any solvent developed by Sun *et al*. [27] with modification on calcination temperature. The solvent-free preparation of sulfated zirconia was used as catalysts in the alcoholysis of soybean oil and in the esterification of oleic acid [28]. The conversion of soybean oil was 98% under optimized reaction condition at the temperature of 120 ºC, reaction time 1 hr, and 5% (w/w) of catalyst. The comparative test shows that the catalyst was also active for the esterification of FFA and with an overall yield of 98%. Other study on sulfated zirconia prepared by the solvent-free method was reported by Rattanaphra *et al*. for the simultaneous transesterification and esterification of rapeseed oil with methanol in the presence of myristic acid [29]. The ester yield close to 86% with initial FFA of 10%, reaction time 1 hr, alcohol to oil molar ratio of 20, catalyst loading 3%, and temperature of 170 ºC. Another research was also conducted on biodiesel production from neem oil [19] resulting an optimized FFA conversion to 94% using 1 wt% sulfated zirconia with methanol-to-oil molar ratio of 9:1, temperature of 65°C and reaction time of 2 h.

The kinetic study on esterification reaction using heterogeneous solid acid catalyst has been reported in literature and can be categorized into four main applied kinetic models depends on the system involved in the reaction: the pseudo-homogeneous model (P-H), the Langmuir–Hinshelwood(L–H) model, the Eley–Rideal (E–R) model and the Popken (P–P) model [30]. Among those four models, P-H model is widely used to describe the esterification of FFA in the present of triglyceride. However, the heterogeneous kinetic studies for biodiesel production using sulfated zirconia are very limited. Rattanaphra *et al*. have been developed the kinetic model for esterification reaction of 10% myristic acid mixed with refined rapeseed oil using sulfated zirconia by means of pseudohomogeneous model [31]. The previous work for production of biodiesel from high FFA content feedstock using sulfated zirconia were limited to the amount of FFA less than 60 wt% without any detailed description on kinetic study. This research is focused on the development of kinetic study of FFA esterification for biodiesel production from PFAD using sulfated zirconia as solid acid catalyst. The reaction was performed in a batch-stirred reactor at the different temperature to obtain the kinetic data. The effect of reaction condition such as methanol to PFAD molar ratio, stirring rate and catalyst concentration on FFA conversion were also investigated. The experimental data was interpreted with the second-order heterogeneous kinetic model involving the rate of mass transfer and the rate of reaction.

EXPERIMENTAL SECTION

Materials
PFAD with FFA content 95% (w/w) was obtained from PT. Smart Tbk, Surabaya, Indonesia. Methanol (99,9%), Zirconium (IV) oxide chloride octahydrate (≥99%), ammonium sulfate (≥99%), and Sodium Hydroxide (99%) were purchased from Merck.

Catalyst preparation
Sulfated zirconia was prepared by solvent-free method calcined at low temperature, modified from previous method described by Sun *et al*. [27]. Zirconium (IV) oxide chloride octahydrate (ZrOCl$_2$.8H$_2$O) and ammonium sulfate ((NH$_4$)$_2$SO$_4$) in a molar ratio of 1:6 were ground in carnelian mortar for 20 min at room temperature. After placement in air for 18 h at room temperature, the sample was calcined at 400 ºC for 5 h.

Esterification reaction
Catalytic activity of sulfated zirconia was tested for esterification reaction of PFAD with methanol. Esterification raction was conducted in a batch stirred reactor using two necks flat-bottomed flask equipped with magnetic stirrer, oil bath, temperature controller, reflux and sampling system. Prior to the reaction, PFAD was preheated and poured into the reactor following by methanol and sulfated zirconia at the designed reaction condition. Reaction was investigated for 180 minutes with the temperatures in range of 50-65 ºC, catalyst concentration in the range of 1-5 %, and methanol to PFAD molar ratios in the range of 5-15. The sample was withdrawn every 20 minute to analyze the acidity of reaction mixture and separated from the catalyst with filtering.

Analysis
The withdrawn samples were analyzed by a standard acid–base titration procedure modified from those previously described by Tesser *et al*. [32]. The samples were firstly heated in the oven at 110 ºC in order to remove the excess of methanol and water formed during reaction. The samples was then weighted and dissolved in ethanol containing some droplets of phenolphtalein as indicator. NaOH solution 0.3 M were used as alkaline solution for the titration. The volume of alkaline solution consumed was recorded and the acidity (a) of the sample can be calculated by means of this following equation:

$$a = \frac{V_t C_t M}{1000\,m} \tag{1}$$

where V_t is the volume of titrating solution, C_t is the concentration of titrant, m is the weight of sample, and M is the average molecular weight of FFA.

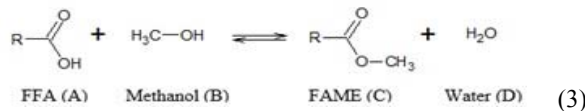The conversion of FFA was calculated as follows:

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$$x = \frac{a_i - a_t}{a_r} \tag{2}$$

where x is conversion of free fatty acid, a_i is initial acidity index, and a_t is *acidity index* at specified time t.

Kinetic model

The esterification reaction of FFAs with methanol is given in the following form:

FFA (A)   Methanol (B)   FAME (C)   Water (D)   (3)

The kinetic model was proposed by using these following assumptions: (1) The overall rate is controlled by both external mass transfer rate and reaction rate. (2) The reaction rate is the first order to the concentration of FFA and the first order to the concentration of methanol on the catalyst surface. (3) Since methanol is used in excess, the reverse reaction rate is neglected and the methanol concentration in the liquid phase remain constant, and (4) FFA consist of several fatty acids, mainly palmitic acid and oleic acid, and all of fatty acid have the same rate of mass transfer and rate of reaction. Based on those assumptions, the differential equation of the overall rate can be written as follows:

▪ Mass balance of FFA in the liquid phase

$$\frac{dx_A}{dt} = k_A a_c m \left(1 - x_A - \frac{C_{As}}{C_{A0}}\right) \tag{4}$$

Where C_{As} and C_{A0} denotes the concentration of FFAs on the catalyst surface and the initial concentration of FFAs in the liquid phase, respectively. While k_A is mass transfer rate coefficient of FFAs, $a_c m$ is the external surface area per unit volume of liquid and x_A is the conversion of FFAs.

▪ Mass balance of methanol in the liquid phase

$$\frac{dC_B}{dt} \approx 0 \tag{5}$$

▪ Mass balance of FFA on the catalyst surface

$$\frac{dC_{As}}{dt} = k_A a_c m [C_{A0}(1 - x_A) - C_{As}] - \eta k_r m C_{As} C_{Bs} \tag{6}$$

C_{Bs} and ηk_r refer to the concentration of methanol on the catalyst surface and the reaction rate constant.

▪ Mass balance of methanol on the catalyst surface

$$\frac{dC_{Bs}}{dt} = k_B a_c m (C_{B0} - C_{Bs}) - \eta k_r m C_{As} C_{Bs} \tag{7}$$

Where C_{B0} is the initial concentration of methanol in the liquid phase and k_B is the mass transfer rate coefficient of methanol.

Boundary conditions for the proposed kinetic model are: t=0; $x_A = x_{A0}$; $C_{As} = C_{As0}$ and $C_{Bs} = C_{Bs0}$. The kinetic parameters (k_A, k_B, and ηk_r) are optimized by a nonlinear regression program, which adjusted these parameters iteratively until a predefined criterion is satisfied. The criterion is the minimization of the Sum of Square Error (SSE) as an objective function:

$$SSE = \sum ((x_A)_{calc} - (x_A)_{dat})^2$$
$$= f(k_A, k_B, \eta k_r, C_{As0}, C_{Bs0}) \tag{8}$$

▪ Arrhenius Equation

$$k_r^c = A_r \exp\left(-\frac{E_r}{RT}\right) \tag{9}$$

Where A_r is the pre-exponential factor, E_r is the activation energy, R is the universal molar gas constant, and T is the absolute temperature.

RESULTS AND DISCUSSIONS

Estimation of kinetic parameter

The optimization using nonlinear regression program, describe previously, was used to determine whether the proposed kinetic model was reasonable. The inputs were the FFAs conversion versus time at the difference reaction temperature. By adjusting the kinetic parameters, the calculated FFAs conversion will be compared to the experimental data. The program will also draw the plot of calculated FFAs conversion versus time. A close fit between the plots indicates an adequate scheme of kinetic model. On the other hand, a poor fit between the plots indicates an incorrect scheme. Figure-1 shows the relationship between FFAs conversion versus time at the different temperatures. The goodness fit in Figure-1 shows that the agreement between the calculated plot and experimental data was good (average SSE of 0.004919).
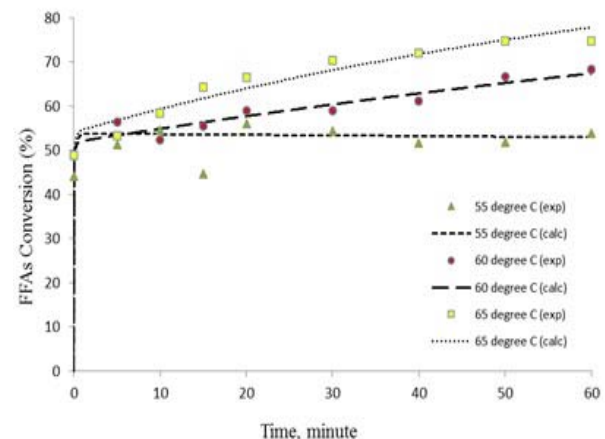

Figure-1. Kinetic modeling plot and experimental data for FFAs conversion versus time.

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The calculated results for the reaction kinetic parameters including the reaction rate constant and the mass transfer rate coefficient are summarized in Table-1. From this table, it can be seen that reaction rate constant (k_r'), mass transfer coefficient of FFA (k_A), and mass transfer coefficient of methanol (k_B) rise as the temperature increase. The reaction rate constant increases significantly (almost ten times every increase in temperature of 5 ^{0}C, approximately). However, mass transfer coefficient of FFA and methanol rise insignificantly. k_A is smaller than k_B at all the reaction temperature studied, which mean that methanol is easier to be adsorbed onto the surface of catalyst than that of FFAs.

Table-1. Kinetic parameters and SSE.

Temp, ^oC	k_A x10^6 dm.s^{-1}	k_Bx10^6 dm.s^{-1}	k_r'x10^6 dm^{6}gcat^{-1}.mol^{-1}.s^{-1}	SSE
55	274.19	845.12	9.3576	0.00823
60	326.00	1004.80	98.845	0.00257
65	362.77	1118.10	186.080	0.00395

According to kinetic theory of heterogeneous reaction, Mears' Criterion can be used to determine whether the external mass transfer is the limiting step [33]. Modified Mears' Criterion for heterogeneous liquid-solid catalytic reaction can be written as follows:

$$C_{MA} = \frac{k_r^t \cdot m C_{AB} R n}{k_A} \tag{10}$$

$$C_{MB} = \frac{k_r^t \cdot m C_{BB} R n}{k_B} \tag{11}$$

Where C_{MA} is the criterion for FFAs, C_{MB} is the criterion for methanol, R is the catalyst particle radius, and n is the reaction order. When the value of Mears' Criterion is less than 0.15, the external mass transfer effect can be neglected. Then, by using the kinetic parameters obtained from kinetic model and the experimental data, C_{MA} and C_{MB} are calculated and tabulated in Table-2.

Table-2. Mears' criterion.

Temperature, ^oC	C_{MA}	C_{MB}
55	0.00027	0.00060
60	0.00222	0.00519
65	0.00369	0.00872
Average	0.00206	0.00484

From the average value of C_{MA} and C_{MB} shown in Table-2, it can be concluded that external mass transfer effect can be neglected and the overall rate is then controlled by the rate of chemical reaction. This result also means that all the experimental runs have been performed in conditions in which the external mass transfer

phenomena can be neglected. The effect of the external mass transfer on the overall rate has been verified by doing experiment at different stirring rates (700, 800, 950 rpm) and a constant rate has been observed above the threshold value of about 700 rpm. Although the reaction system was different, this result was similar with another result reported by Tesser [14,34]

The parameters of the Arrhenius equation were estimated by curve fitting method (Figure-2). The pre-exponential factor and the activation energy were estimated to be 5.14 x 10^{18} dm^6.gkat^{-1}.mol^{-1}.s^{-1} and 144.9194 kJ/mol. The value of activation energy is much higher than that found by Rattanaphra and co-workers in the kinetic study of myristic esterification with methanol in the presence of triglycerides catalysed sulfated zirconia [31]. The reaction temperature used in the work of Rattanaphra was higher than that employed in this experiment. They found the activation energy value of 22.5 kJ/mol by using the temperature range of 393-443 K, respectively. The high value of activation energy indicates that the reaction is kinetically controlled [35-37].
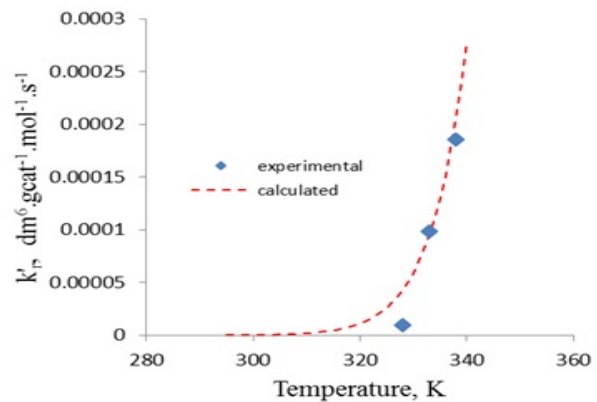
Figure-2. Curve fitting result of Arrhenius equation.

The profile of FFAs conversion at the different reaction parameters are represented in Figure 3-6. It can be seen that all figure have the same trend. There is a dramatic increase in the FFAs conversion shortly after catalyst was added to the reaction mixture. This may be due to high activity of sulfated zirconia as catalyst which promotes instantaneous esterification reaction. As the reaction progressed, the concentration of water formed also increased with the same tendency and this resulted in slower FFAs conversion. Water has the ability to deactivate solid acidic catalysts due to its high affinity to the active site of acidic catalysts, especially the sulfate groups [15]. Thus it can be understood that after the spike high enough conversion, the reaction rate decreased due to decreased activity of the catalyst.

Effect of catalyst concentration

Effect of catalyst concentration was studied by varying catalyst concentrations of 1, 3, and 5%. With the methanol to PFAD molar ratio, stirring rate, and

temperature were set to constant values (10, 800 rpm, and 60 ^{0}C respectively), conversion data of FFA versus time in various catalyst concentration can be seen in Figure-3. By increasing the catalyst concentration, it will increase the frequency of contact between reactants and the catalyst so that the reaction rate will increase. It can be observed that the higher catalyst concentration, the higher FFA conversion achieved. Significant increase occurred when the catalyst concentration rose from 1 to 3%. Furthermore, insignificant increase of conversion occurs when the catalyst concentration rose from 3 to 5%, although the resulting graph fluctuated. It can be concluded that the catalyst concentration of 3% is the optimum one.
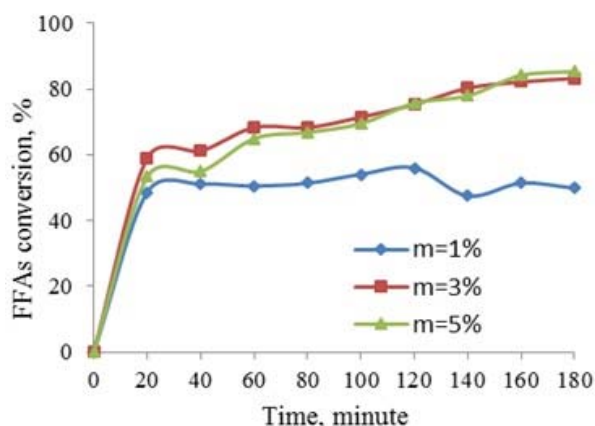

Figure-3. FFAs conversion versus catalyst concentration.

Effect of methanol to PFAD molar ratio
        Effect of the molar ratio of reactants was studied with the ratio of 5, 10, and 15. Conversion data of FFA versus time on the different methanol to PFAD molar ratio can be seen in Figure-4.
        From Figure-4 it can be observed that the higher the ratio of methanol/PFAD, the higher the FFA conversion achieved. Theoretically, increasing the methanol to PFAD molar ratio will increase the FFA conversion. The equilibrium of the esterification reaction will shift towards to the products by the increase of methanol concentration. With the increase in the ratio of 5 into 10, there is a fairly high conversion increases. However, an increase from 10 towards 15 produces graphs coincide. The possible cause is the side reaction may occur during the reaction. As the increase of FFA conversion, water was also formed. Water formed can reacts with triglyceride via hydrolysis reaction to form FFA [31]. From these results it can be concluded that the ratio of 10 is the optimum ratio. The same result was also reported by Song *et al*. [17].
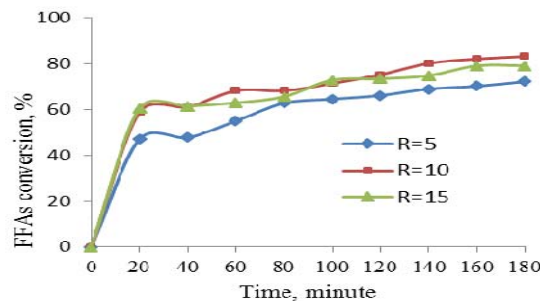

Figure-4. FFAs conversion versus methanol to PFAD molar ratio.

Effect of stirring rate
        Effect of stirring rate upon conversion of free fatty acid was studied by varying stirring rate by 700, 800, and 950 rpm. Conversion data of FFA versus time at various stirring rate can be seen in Figure-5. According to the figure, it can be concluded that stirring rate has slight effect upon conversion of FFA. However, the highest conversion was observed at stirring rate of 800 rpm. These results support the proposed model of the reaction kinetics, which states that the overall rate is controlled by the rate of chemical reaction. From the variations, it can be concluded that at speed above 700 rpm, the condition required for perfect mixing is achieved so that external mass transfer resistance is negligible.
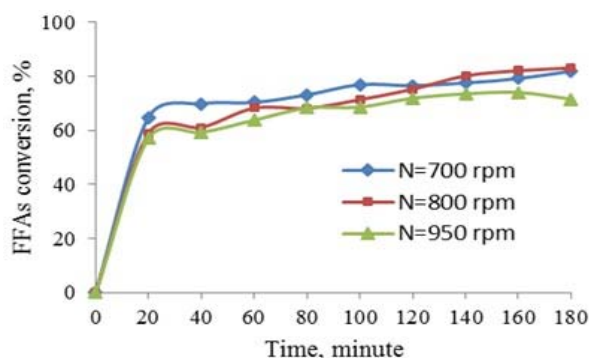

Figure-5. FFAs conversion versus stirring rate.

Effect of temperature
        Effect of reaction temperature on the conversion of free fatty acid was studied in the temperature variation of 55, 60, and 65 ^{0}C. Conversion data of free fatty acids versus time at various reaction temperatures can be seen in Figure 6. Esterification reaction is an endothermic reaction [14]. Based on thermodynamic, an increase in temperature of endothermic reaction will result to increase of maximum conversion. Maximum conversion of reaction is nearly constant with the increase of temperature from 50 to 55 ^{0}C. Yet, the maximum conversion increases with the increase of temperature from 55 to 60 ^{0}C. In the other hand, the maximum conversion decreases with the increase of temperature from 60 to 65 ^{0}C. These results reveal that the reaction temperature has an insignificant

effect on the esterification reaction of FFAs. The same results have been reported by Gan and co-workers [38].
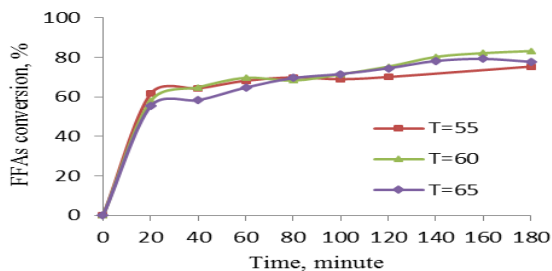

Figure-6. FFAs conversion versus reaction temperature.

CONCLUSIONS

The esterification reaction of FFAs in the biodiesel production from PFAD in batch reactor system employing sulfated zirconia as the catalyst has been studied. The optimum condition was observed at 180 minutes reaction time, molar ratio of methanol/PFAD of 10, catalyst concentration of 3% (w/w), stirring rate of 800 rpm, and at reaction temperature of 600 ^{0}C. At the optimum condition, the achieved conversion of FFAs is 83.2215 %.

A kinetic model for the esterification of FFAs was established using the second-order heterogeneous kinetic model involving the rate of mass transfer and the rate of reaction. By fitting the experimental data and the kinetic model, the pre-exponential factor 5.14 x 10^{18} and the activation energy 144.9194 kJ/mol were obtained.

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REFERENCES

[1] Budiman, A., Ishida, M. 1997. Relationship between distillation column and distribution of exergy losses and driving forces", J. Chem. Eng. Japan. 30(5), 966-969.

[2] Budiman, A., Sutijan, Sawitri, D.R. 2011. Graphical exergy analysis of retrofitted distillation column. Int.J.Exergy. 8(4), 477-493.

[3] Kusumaningtyas, R.D., Rochmadi, Purwono, S., Budiman, A. 2014. Graphical exergy analysis of reactive distillation column for biodiesel production. Int. J. Exergy. 1 (4), 447-467.

[4] Atadashi, I.M., Aroua, M.K., Abdul Aziz, A.R., Sulaiman N.M.N. 2012. Production of biodiesel using

[5] Chongkong, S., Tongurai, C., Chetpattananondh, P. 2009. Continuous esterification for biodiesel production from fatty acid distillate using economical process. Renew. Energ. 34, 1059-1063.

[6] Kawentar, W.A., Budiman, A. 2013. Synthesis of biodiesel from second-used cooking oil. Energy Proc. 32, 190-199.

[7] Canakci, M., Van, G.J. 1999. Biodiesel production via acid catalysis. TASAE. 42, 1203–1210.

[8] Chongkhong, S., Tongurai, C., Chetpattananondh, P., Bunyakan, C. 2007. Biodiesel production by esterification of palm fatty acid distillate. Biomass Bioenergy. 31, 563–568.

[9] Berchmans, H.J., Hirata, S. 2008. Biodiesel production from crude Jatropha curcas L. seed oil with a high content of free fatty acids. Bioresour. Technol. 99, 1716–1721.

[10] Marchetti, J.M., Errazu, A.F. 2008. Comparison of different heterogeneous catalysts and different alcohols for the esterification reaction of oleic acid. Fuel. 87, 3477–3480.

[11] Zhang, H., Ding, J., Qiu, Y., Zhao, Z. 2012. Kinetics of esterification of acidified oil with different alcohols by a cation ion-exchange resin/ polyethersulfone hybrid catalytic membrane. Bioresour. Technol. 112, 28–33.

[12] Yujaroen, D., Goto, M., Sasaki, M., Shotipruk, A. 2009. Esterification of palm fatty acid distillate (PFAD) in supercritical methanol: Effect of hydrolysis on reaction reactivity. Fuel. 88, 2011–2016.

[13] Alenezi, R., Leeke, G.A., Winterbottom, J.M., Santos, R.C.D., Khan, A.R. 2010. Esterification kinetics of free fatty acids with supercritical methanol for biodiesel production. Energy Convers. Manag. 51, 1055–1059.

[14] Tesser, R., Di Serio, M., Guida, M., Nastasi, M., Santacesaria, E. 2005. Kinetics of oleic acid esterification with methanol in the presence of triglycerides. Ind. Eng. Chem. Res. 44, 7978–7982.

[15] Liu, Y., Lotero, E., Goodwin, J.G. 2006. A comparison of the esterification of acetic acid with methanol using heterogeneous versus homogeneous acid catalysis. J. Catal. 242, 278–286.

high free fatty acid feedstocks. Renew. Sust. Energ. Rev. 16, 3275-3285.

[16] Gan, M., Pan, D., Ma, L., Yue, E., Hon, J. 2009. The Kinetics of the Esterification of Free Fatty Acids in Waste Cooking Oil Using Fe2(SO4)3/C Catalyst. Chinese J. Chem. Eng. 17(1), 83-87.

[17] Song, C., Qi, Y., Deng, T., Hou, X., Qin, Z. 2010. Kinetic model for the esterification of oleic acid catalyzed by zinc acetate in subcritical methanol. Renew. Energ. 35, 625–628.

[18] Hidayat, A., Rochmadi, Wijaya, K., Hinode, H., Budiman, A. 2013. Comparison of activated carbons prepared from Indonesian forest and agricultural residues. Asian J Chem. 25 (3), 1569-1575.

[19] Muthu, H., Selvabalal, V.S., Varathachary, T.K., Selvaraj, D.K., Nandagopal, J., Subramanian, S. 2010. Synthesis of biodiesel from neem oil using sulfated zirconia via tranesterification.Braz. J. Chem. Eng. 27(04), 601 – 608.

[20] Chin, L.H., Abdullah, A.Z., Hameed, B.H. 2012. Sugar cane bagasse as solid catalyst for synthesis of methyl esters from palm fatty acid distillate. Chem. Eng. J. 183, 104–107.

[21] Sharma, Y.C., Singh, B., Korstad, J. 2011. Latest developments on application of heterogenous basic catalysts for an efficient and eco friendly synthesis of biodiesel: A review. Fuel. 90, 1309–1324.

[22] Furuta, S., Matsuhashi, H., Arata, K. 2004. Biodiesel fuel production with solid superacid catalysis in fixed bed reactor under atmospheric pressure. Catal. Commun. 5, 721–723.

[23] Kansedo, J., Lee, K.T. 2012. Transesterification of palm oil and crude sea mango (Cerbera odollam) oil: The active role of simplified sulfated zirconia catalyst. Biomass Bioenergy. 40, 96-104.

[24] López, D.E., Goodwin Jr., J.G., Bruce, D.A., Furuta, S. 2008. Esterification and transesterification using modified-zirconia catalysts. Appl. Catal. A: Gen. 339, 76-83.

[25] Jitputti, J., Kitiyanan, B., Rangsunvigit, P., Bunyakiat, K., Attanatho, L., Jenvanitpanjakul, P. 2006. Transesterification of crude palm kernel oil and crude coconut oil by different solid catalysts. Chem. Eng. J. 116, 61–66.

[26] Li, Y., Zhang, X.D., Sun, L., Xu, M., Zhou, W.G., Liang, X.H. 2010. Solid superacid catalyzed fatty acid methyl esters production from acid oil. Appl. Energy. 87, 2369–2373.

[27] Sun, Y., Ma, S., Du, Y., Yuan, L., Wang, S., Yang, J. 2005. Solvent-free preparation of nanosized sulfated zirconia with Bronsted acidic sites from a simple calcination. J. Phys. Chem. B. 109, 2567–2572.

[28] Garcia, C.M., Teixeira, S., Marciniuk L.L., Schuchardt, U. 2008. Transesterification of soybean oil catalyzed by sulfated zirconia. Bioresour. Technol. 99, 6608–6613.

[29] Rattanaphra, D., Harvey, A.P., Srinophakun, P. 2010. Simultaneous conversion of triglyceride/free fatty acid mixture into biodiesel using sulfated zirconia. Top Catal. 53, 773–782.

[30] Cheng, Y., Feng, Y., Ren, Y., Liu, X., Gao, A., He, B., Yan, F., Li, J. 2012. Comprehensive kinetic studies of acidic oil continuous esterification by cation-exchange resin in fixed bed reactors. Bioresour. Technol. 113, 65–72.

[31] Rattanaphra, D., Harvey, A.P., Thanapimmetha, A., Srinophakun, P. 2011. Kinetic of myristic acid esterification with methanol in the presence of triglycerides over sulfated zirconia. Renew. Energ. 36, 2679-2686.

[32] Tesser, R., Casale, L., Verde, D., Di Serio, M., Santacesaria, E. 2010. Kinetics and modeling of fatty acids esterification on acid exchange resins. Chem. Eng. J. 157, 539–550.

[33] Foggler, H.S. 1999. Element of chemical reaction engineering, 3rd ed. Prentice Hall International Series, New Jersey.

[34] Tesser, R., Casale, L., Verde, D., Di Serio, M., Santacesaria, E. 2009. Kinetics of free fatty acids esterification: batch and loop reactor modeling. Chem. Eng. J. 154, 25-33.

[35] Shi, W., He, B., Li, J. 2011. Esterification of acidified oil with methanol by SPES/PES catalytic membrane. Bioresour. Technol. 102, 5389–5393.

[36] Berrios, M., Siles, J., Martìn, M.A., Martìn, A. 2007. A kinetic study of the esterification of free fatty acids (FFA) in sunflower oil. Fuel 86, 2383–2388.

[37] Anjali, P., Varsha, B. 2013. Kineticstudy of oleic acid esterification over 12-tungstophosphoric acidcatalyst anchored to different mesoporous silica supports. Fuel Process. Technol. 102, 141–149.

[38] Gan, S., Ng, H.K., Chan, P.H., Leong, F.L. 2012. Heterogeneous free fatty acids esterification in waste cooking oil using ion-exchange resins. Fuel Process. Technol. 102, 67–72.