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Kinetic Study of Esterification of Free Fatty Acid in Low Grade Crude Palm Oil using Sulfuric Acid

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The kinetics of the esterification of free fatty acids (FFA) in low grade crude palm oil (CPO) with methanol was studied. In this work, the effects of operational variables involved in the esterification process i.e. alcohol to oil molar ratio, reaction temperature, agitation speed and the initial amount of FFA of oil, were studied in the presence of sulphuric acid as catalyst at concentration of 1%-w. The experimental results show that the esterification process could lead to a practical and cost effective FFA removal unit in front of typical oil transesterification for biodiesel production. The experimental results were found to fit a first-order kinetic law. The influence of temperature on the kinetic constants was determined by fitting the results to the Arrhenius equation.

***Keywords**:* esterification, free fatty acid, kinetics, low grade CPO

INTRODUCTION

Biodiesel, which consists of long-chain fatty acid methyl ethers (FAME) obtained from renewable lipids such as those in vegetable oils or animal fat, can be used both as an alternative fuel and as an additive for petroleum diesel. The prefix ''bio'' denotes its biological origin and renewable character; by contrast, the better known, non-renewable petroleum diesel is obtained from petroleum distillates. FAME are obtained by reacting triglycerides with lower alcohols such as methanol or ethanol in the presence of a strong base as a catalyst; the reaction yields glycerin as a by-product.

However, in spite of the favourable impact, the economic aspect of biodiesel production is still a barrier for its development, mainly due to the lower price of fossil fuel. The costs of biodiesel production are highly dependent on the costs of feedstock which affect the cost of the finished product up to 60 – 75% (Cetinkaya and Karaosmanoglu, 2004). Currently, partially or fully refined and edible-grade vegetable oils, such as soybean, rapeseed and palm are the predominant feedstock for biodiesel production (Haas, 2005), which obviously results in the high price of biodiesel. Therefore, exploring ways to reduce the cost of raw material is of much interest in recent biodiesel research. At present, Indonesia is the world's second largest producer of palm oil where palm plantation covered about 5.3 million hectares of the country. It is expected that in the near future, Indonesia has the largest palm plantation in the world. Most of palm fruit produced is further processed to produce crude palm oil (CPO) as raw material of palm oil industry. However, in some regions, there was a large number of unprocessing palm fruit due to limitation the number of palm oil industry. Therefore, the excess of unprocessing palm fruit can be converted to low grade CPO by simple processing as feedstock for biodiesel production by the farmers to increase its economic value. Low grade CPO is one of potential low-cost feedstock for biodiesel production which contained 5-20% of free fatty acids (FFA).

In the biodiesel production, the oil or fat used in alkaline transesterification reactions (as typically catalyzed in industrial-scale for biodiesel production) should contain no more than 1% FFA, which is equivalent to 2 mg KOH/g triglycerides (Freedman et al., 1984; Liu, 1994). If the FFA level exceeds this threshold, saponification hinders separation of the ester from glycerine and reduces the yield and formation rate of FAME. The acid catalyzed of high FFA feedstock is an alternative (Crabbe et al., 2001), but it is much slower than the base catalyzed transesterification. An alternative process such as a two-step process of esterification and transesterification was investigated for having high FFA content (Ghadge and Raheman, 2005; Veljkovic et al., 2006). The first step was to esterify the FFA with methanol by acid catalyst until the FFA content was lower than 1%. Then, the acid catalyst was drain and the alkali catalyst was introduced into the system to complete the transesterification. It was reported that the two-step process of acid catalyzed esterification followed by alkaline catalyzed transesterification reaction improved the biodiesel yield (Crabbe et al., 2001; Ghadge and Raheman, 2005; Veljkovic et al., 2006; Tiwari et al., 2007).

In this work, the effect of operational variables (i.e. methanol to oil molar ratio, reaction temperature, agitation speed and initial amount of FFA) on the esterification of FFA in low grade CPO was studied. Sulphuric acid was used as catalyst and methanol was used as alcohol. This paper discusses the findings of experiments carried out to prepare low grade CPO as low-cost feedstock for biodiesel production. The influence of operational variables on the kinetics of esterification of FFA in low grade CPO was also studied in order to optimize the reactor design.

EXPERIMENTAL

The raw material used in the esterification was low grade CPO with FFA's content of 5.6% and 33.3%, i.e. acid value of 11.6 and 67.3 mg KOH/g triglycerides, respectively, which is far above the 1% limit for satisfactory transesterification reaction using alkaline catalyst for biodiesel production. The FFA content was determined by a standard titrimetry method.

First, the gumming in the oil, such as phospholipids, was removed by addition of H_3PO_4 0.6%. The mixture was stirred at a speed of 400 rpm for 15 minutes. The colloidal formed was removed from the oil by filter paper. Then, the oil was esterified with methanol using methanol. Experiments were conducted in a laboratory-scale setup, which consisted of 1-litre glass flasks. Mechanic agitation was provided with different level. Airtight caps were used to retain any vaporized methanol from the reacting mixture. The flask was kept in a water bath maintained at a fixed temperature. Low grade CPO was taken in a sufficient amount and added to the reactor. The oil fed into the reactor was preheated before the catalyst and the alcohol was added. After reaching the reaction temperature, the catalyst and the alcohol were adjoined in the reactor to start the experiment. The excess methanol was used to overcome the equilibrium limitations. The progress of the reaction was monitored by measuring the acid value at every 20-minute interval. The acid value is defined as the amount of KOH necessary to neutralize the 1 g of the oil sample. The decrease in the acid value showed the forward progress of the esterification process. The influence of methanol to oil molar ratio, reaction temperature, agitation speed and the amounts of initial FFA on the esterification rate was studied at a fixed catalyst concentration (H_2SO_4) of 1% by weight of oil.

At various time, a sample was withdrawn quickly from the reactor. The sample was washed with water to stop the reaction and to separate the catalyst and the alcohol from the oil phase. A weighted amount of the samples was prepared to make titration analyses, which will determine the remaining FFA. Phenolphthalein was used as indicator. The titration was done with a 0.1 N alkaline solution of KOH. The amount of KOH consumed was registered and acid value (*A)* was calculated using the following equation:

$$A = \frac{V \times 1000 \times M \times C}{W} \qquad (1)$$

where <u>*A*</u> is the acid value; *C* is the concentration KOH, mol/l; *W* is the weight of the sample, mg; *M* is the molecular weight of the solution, g/mol; *V* is the volume of solution employed for titration, ml. By using the acid value at specific time and the initial acidity of the mixture, one can obtained the conversion of FAA (X_{FFA}).

RESULTS AND DISCUSSION

Effect of The Methanol to Oil Molar Ratio

Acid-catalyzed esterification is an equilibrium reaction, much more methanol than that given by the stoichiometric 1:1 mole ratio of methanol to oil is required to drive the reaction to completion, i.e., to form 1 mole of FAME from 1 mole of oil. In addition, excess methanol was used since the water being formed during the esterification reaction gets dissolved in the excess methanol. Thus, equilibrium limitation due to the reversibility of the reaction can be shifted towards right side of the reaction. The esterification reaction can be written as follows:

$$R_1\text{-COOH} + R_2\text{-OH} \leftrightarrow R_1\text{-COO-}R_2 + H_2O \qquad (2)$$

which is catalysed by acids. In this work, R_1 was a linier chain of 11-17 carbon atoms containing a variable number of unsaturation depending on the particular origin of the raw material, and R_2 was a methyl radical. The reaction was found to proceed up to 90% conversion levels at appreciable rate beyond which the rate of progress of the reaction was substantially slower (Tiwari et al., 2007).

The variation of the conversion of FFA for four different methanol to oil molar ratio at a sulphuric acid concentration of 1% is shown in Figure 1. The reaction temperature was set at 55^0C and the agitation speed at 464 rpm. The reaction rate increased with increasing the quantity of methanol and reaction time. This can be attributed to the fact due to higher concentration of methanol in the system will reduce the equilibrium limitation due to a large excess of methanol.

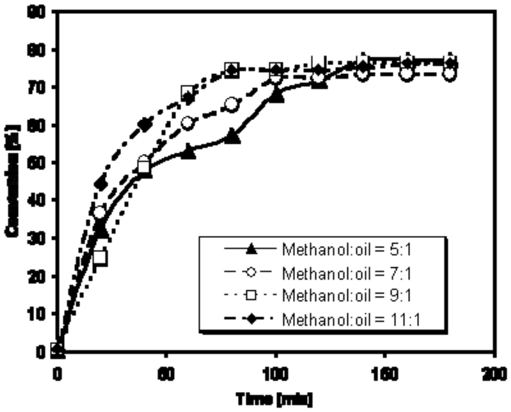

Figure 1. Effect of Different Amounts of Methanol to Oil Ratio

The reaction progressed rapidly during the first 100 min showing over 70% conversion of FFA for methanol to oil molar ratio of 9:1 and 11:1 and over 65% for methanol to oil molar ratio of 5:1 and 7:1. After 100 min, there was no significant improvement in the FFA conversion for all of methanol to oil molar ratio used. This might be due to the effect of water produced during the esterification of FFA, which prevented further reaction (Ghadge and Raheman, 2005; Veljkovic et al., 2006; Tiwari et al., 2007). The dilution of the acid catalyst with the water formed in the reaction reducing its catalytic activity. Almost in all of experiment conducted, the reaction approved to equilibrium after 100 min, prolonging the reaction time did not efficiently increase conversion of FFA.

Effect of The Reaction Temperature

Since the reaction temperature was also expected to affect the conversion of FFA, four different reaction temperatures were evaluated, keeping the remaining reactions parameters constant (methanol to oil molar ratio of 1:7 and agitation speed of 464 rpm). Figure 2 shows the variation of the FFA conversion with the reaction temperature. From this figure, it can be seen that the rate of reaction was greatly influenced by both the reaction temperature and reaction time. The results showed that the reaction was typically endothermic; when the temperature increased, the final conversion increases as well. This result corroborates those obtained by previous reported (Chonghong et al., 2007; Berrios et al., 2008).

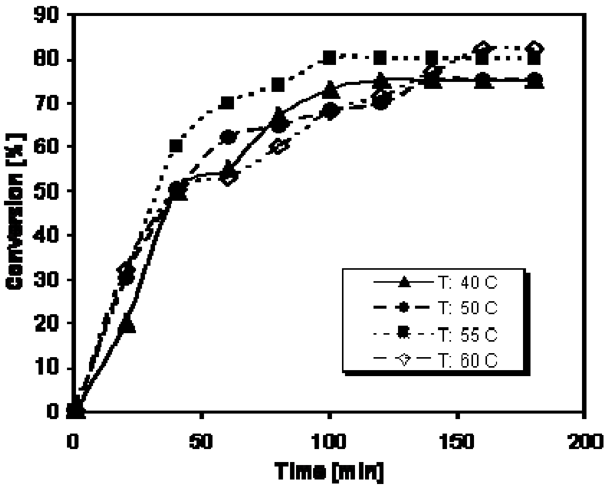

Figure 2. Effect of Different Reaction Temperature

As expected, raising the temperature increased the esterification rate. The highest rate was obtained at 60^{0}C, which is close to the boiling point of methanol at atmospheric pressure. A higher temperature obviously increased the rate further, but required using a pressure above atmospheric level or a more sophisticated experimental set-up such as that employed by Kocsisova et al. (2005). In addition, a higher temperature will provide a higher possibility of methanol losing and produced darker product (Chonghong et al., 2007).

Effect of The Agitation Speed

The main reason for low rates of reaction is the mass transfer limitations since the oil and alcohol form immiscible phases in the system. So, it requires agitation in order to avoid mass transfer taking control over the process and to increase the rates of chemical reactions (Ma et al., 1999). The effect of variation in the agitation speed on the FFA conversion has been studied at four different levels (232, 348, 464 and 580 rpm). The results obtained have been shown in Figure 3. These results revealed that mixing significantly affected the reaction rate in which insufficient mixing could lead to a very slow reaction rate. Increase of agitation speed (as well as mixing intensity) provided a higher FFA conversion. However, Noureddini and Zhu (1997) observed in their experiments that further increase of agitation speed did not provide a better result due to a small decrease of FFA conversion was observed.

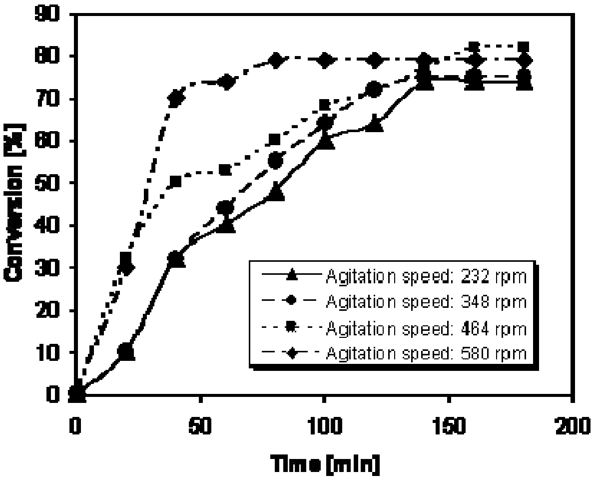

Figure 3. Effect of Different Agitation Speed

The mixing intensity of an impeller can be expressed by the Reynolds number:

$$N_{\text{Re}} = \frac{\eta \times D^2 \times \rho}{\mu} \qquad (3)$$

Where η is the rotational speed of the impeller, D is the diameter of the impeller, ρ is the fluid density and μ is the fluid viscosity. With the rotational speed of the impeller set at 232, 348, 464 and 580 rpm, the Reynolds numbers are estimated to be in the range 6000 to 10000, indicating that the flow in the reactor was turbulent in the above range of impeller speeds. After 140 min, no significant difference in the esterification rate or the yield of FAME was found within the above range of mixing intensities, so that an agitation speed in the range 100-600 rpm was adequate (Zheng et al., 2006). Routinely, a speed of 464 rpm was used almost in all subsequent experiments. As recommended by Zheng et al. (2006), if the agitation speed further increased (such as the Reynolds number above 12000) the FFA conversion will decreased due to contact between molecule decreased.

Effect of The Initial Amount of FFA

Effects of varying the initial amount of FFA were also studied at the methanol to oil ratio of 5:1, the reaction temperature of 60^{0}Cand agitation speed of 464 rpm. The conversion as function of time for two different amounts of initial FFA has been shown in Figure 4.

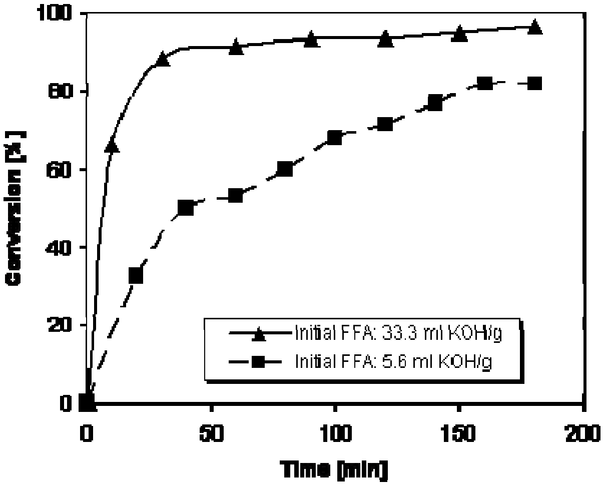

Figure 4. Effect of Different Amounts of Initial FFA

At the first of 50 sec of reaction time, the reaction rate of the initial FFA of 33.3 ml KOH/g was twice compared to the reaction rate of the initial FFA of 5.6 ml KOH/g. The experimental results show that when the initial amount of FFA was increased, the reaction reached a higher final conversion. Furthermore, the reaction rate also increased with increasing amount of FFA. These results were to be expected since the reaction is an equilibrium reaction and increasing one of the reactants would displace the equilibrium towards the product. The same trend results was also reported by Marchetti and Errazu (2008).

Reaction Kinetics

The kinetic model used based on the following assumptions (Berrios et al., 2008): (a) esterification reaction was a reversible heterogeneous process the rate of which under the operating conditions used was controlled by that of the chemical reaction; (b) rate of non-catalysed reaction was negligible relative to the catalysed reaction; (c) chemical reaction occurred in the oil phase; and (d) methanol to oil molar ratio used was high enough for the methanol concentration to remain constant throughout the process. Under these conditions, the reaction was assumed to be pseudo-homogeneous, first-order in the forward direction and second-order in the reverse direction, and hence to conform to the following kinetic law:

$$\frac{-d[FFA]}{dt} = K_1[FFA] - K_2[FAME][water] \qquad (4)$$

where [FFA] denotes the concentration of FFA in mg KOH/g oil (i.e. the acid value); [FAME] and [water] are the concentrations of FAME and water, respectively, formed during the reaction, both also referred to 1 g of oil; and K_1 and K_2 are the kinetic constants for the forward and reverse reaction, respectively. If [FAME] and [water] are assumed to be zero at the start (t = 0), and [FFA] = A_0 - Er (A_0 and Er being the initial concentration of FFA and the acidity removed, respectively), then, according to Carberry (1976):

$$\frac{dEr}{dt} = K_1(A_0 - Er) - K_2 Er^2 \qquad (5)$$

Integration of Eq. (5) yields

$$2K_2 \alpha t = \ln \frac{[A_0 + Er(\beta - 0,5)]}{[A_0 - Er(\beta + 0,5)]} \qquad (6)$$

where

$$\alpha = \sqrt{\frac{K^2}{4} + KA_0} \qquad (7)$$

K_1 and K_2 were determined by trial and error, using variable β values until a plot of the right-hand side of Eq. (6) consisting of a straight line with a negligible intercept was obtained. By way of example, Figure 5 shows the fitting of the experimental data obtained at a methanol to oil molar ratio of 5:1, agitation speed 464 rpm and a temperature of 55^{0}C. Similar plots were constructed under all other experimental conditions.

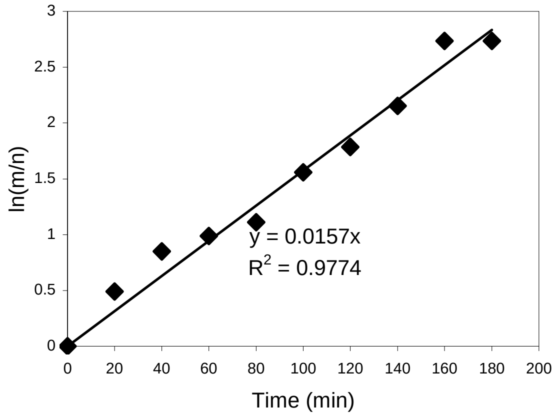

Figure 5. Determination of The Kinetic Constants (m = A_0+Er(β-0.5) and n = A_0-E(β+0.5))

Table 1 shows the kinetic constants obtained from the experiments. Based on the K_1 to K_2 ratio, it indicates that the esterification reaction of FFA in low grade CPO is irreversible in forward direction. Meanwhile, the hydrolysis reaction in reverse direction hardly took place. Berrios et al. (2008), Noureddini and Zhu (1997) and Marchetti and Errazu (2008) have proposed fitting experimental data to a first-order kinetic law based on the small value of K_2.

Tabel 1. Kinetic Constant of Esterification of Free Fatty Acid in Low Grade CPO.

	K_1	K_2	K_1 / K_2
Methanol to oil molar ratio*			
5:1	0.0070	0.0002	35
7:1	0.0071	0.0002	30.8696
9:1	0.0076	0.0005	13.818
11:1	0.0075	0.0004	16.67
Temperature **			
40^{0}C	0.0027	0.0001	27
50^{0}C	0.0030	0.0002	12.5
55^{0}C	0.0052	0.0002	26
60^{0}C	0.0050	0.0001	50
Agitation speed ***			
232 rpm	0.0045	0.00001	580
348 rpm	0.0049	0.00005	98
464 rpm	0.0050	0.00015	33.33
580 rpm	0.0061	0.0003	20

Note:

* Temperature: 55^{0}C and agitation speed: 464 rpm

** Methanol to oil molar ratio: 5:1 and agitation speed 464 rpm

*** Methanol to oil molar ratio: 5:1 and temperature 55^{0}C.

The effect of temperature on the specific reaction rate was determined by fitting K_1 and K_2 to the Arrhenius equation,

$$K = A \bullet \exp\left(\frac{-\Delta E}{RT}\right) \quad (9)$$

using plots of ln K as a function of the reciprocal temperature. Both the frequency factor, A, and the energy of activation (ΔE), were obtained by nonlinear regression. The energy of activation and frequency factor for the forward reaction was found to be 30.4 kJ/mol and 305, respectively.

CONCLUSION

Free fatty acids (FFA) in low grade CPO can be effectively removed by esterification with methanol using sulphuric acid as catalyst. FFA is a strong poison and also lead to the formation of soap with the resulting separation difficulties for base catalyst as typically catalyzed in industrial unit for biodiesel production. The esterification process is a promising technique to convert FFA in Low grade CPO into valuable fatty acid methyl ester (FAME, biodiesel) and obtain a FFA-free oil that can be further transesterified using base catalyst for biodiesel production. The present result indicates that the esterification reaction of FFA in low grade CPO is irreversible and fitting experimental data to a first-order kinetic law.

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