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Esterification of Free Fatty Acid in Crude Palm Oil Off Grade

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Abstract

The esterification of free fatty acids (FFA) found in crude palm oil (CPO) off grade with methanol is a promising technique to convert FFA into valuable fatty acid methyl ester (FAME, biodiesel) and obtain a FFA-free oil that can be further transesterified using alkali bases. In this work, the effects of the main 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.

Keywords: CPO off grade, esterification, free fatty acid

1. Introduction

Development of an alternative energy resource to replace traditional fossil fuels has recently become more and more attractive due to the high energy demand, the limited resource of fossil fuel and environmental concerns. Biodiesel fuel derived from vegetable oils or animal fats is one of the promising possible sources to be substituted for conventional diesel fuel and produces favourable effects on the environment. It can be used directly or mixed with conventional fuel for diesel engines or as a heating fuel. 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.

Currently, Indonesia is the world's 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 provinces such as NAD, Banten and Lampung, 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 CPO off grade by simple processing as feedstock for biodiesel production by the farmers to increase its economic value. CPO off grade is one of potential low-cost feedstock for biodiesel production which contained 5-20% of free fatty acids (FFA).

According to several researchers (Freedman *et al*., 1984; Liu, 1994), 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. 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 (Ghadge and Raheman, 2005; Veljkovic *et al*., 2006, Tiwari *et al*., 2007).

The objective of this paper was to evaluate the effect of operational variables on the esterification of FFA in CPO off grade using sulphuric acid as catalyst. This paper discusses the findings of experiments carried out to prepare CPO off grade as low-cost feedstock for biodiesel production.

2. Methodology

The FFA's content of CPO off grade used in this study were 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 a methanol to oil mol ratio of 5:1, 7:1, 9:1 and 11:1.

Experiments were conducted in a laboratory-scale set-up, which consisted of 1-litre glass flasks with mechanic agitation. 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. CPO off grade 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 tempera- ture, the catalyst (H_2SO_4 1% by weight of oil) 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. Samples taken from the reactor were 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:

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

Whereas *A* 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. Using the following definition, the conversion of FAA (X_{FFA}) was calculated:

$$X_{FFA} = \frac{A_i - A_t}{A_i} \qquad (2)$$

Where A_i is the initial acidity of the mixture and A_t is the acidity at a *t* time.

3. Results and Discussion

3.1 Efffect 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:

$$R_1\text{-COOH} + R_2\text{-OH} \leftrightarrow R_1\text{-COO-}R_2 + H_2O \quad (3)$$

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).

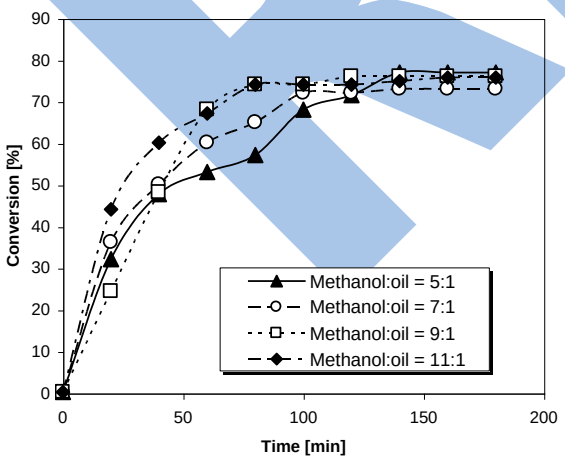

Figure 1. Effect of different amounts of methanol to oil ratio.

The variation of the conversion of FFA for four different methanols to oil molar ratio at a sulphuric acid concentration of 1% is shown in Fig. 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.

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; 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.

3.2 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). Fig. 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 (Chongkhong *et al*., 2007; Berrios *et al*., 2008).

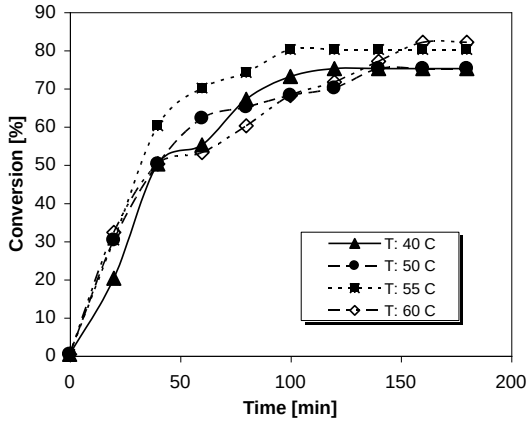

Figure 2. Effect of different reaction temperature.

As expected, raising the temperature increased the esterification rate. The highest rate was obtained at 60^0C, 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 (Chongkhong *et al*., 2007).

3.3 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 Fig. 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.

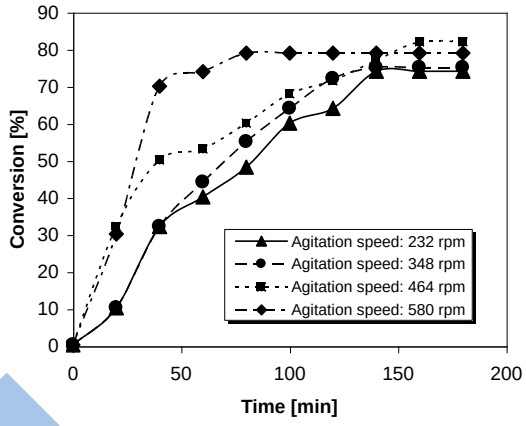

Figure 3. Effect of different agitation speed.

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

$$N_{\mathrm{Re}} = \frac{\eta \times D^2 \times \rho}{\mu} \qquad (4)$$

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 molecules decreased.

3.4 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 60^0Cand

agitation speed of 464 rpm. The conversion as function of time for two different amounts of initial FFA has been shown in Figure 4.

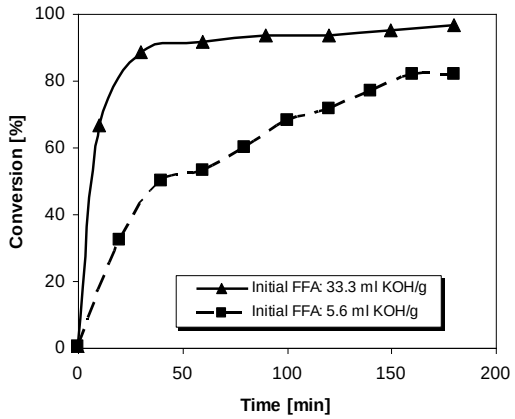

Figure 4. Effect of different amounts of initial FFA

At the first of 50 seconds 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 were also reported by Marchetti and Errazu (2008).

4. Conclusion

Free fatty acids (FFA) in CPO off grade 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 that has been studied shows that the amount of FFA was reduced to values around 1%. These results show that the esterification process is a promising technique to convert FFA in CPO off grade 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.

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