Production of biodiesel from Palm Fatty Acid Distillate

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Abstract

Palm Fatty Acid Distillate (PFAD) is a by-product from palm oil purification process, which contains as high as 90-93% free fatty acid (FFA), or 180-186 mg/g KOH in terms of acid value. The best method of converting PFAD to methyl ester is by esterification reaction, which is the reaction of FFA and methanol to form methyl ester and water. In this study, the variables investigated in the esterification step were the molar ratio of methanol to oil (varied from 16:1 to 24:1) and reaction temperatures (60 and 70 ° C) by using concentrated sulfuric acid catalyst (1 % v/w of oil) with the reaction time of 120 minutes. From experimental results, the esterification process could reduce the acid value of raw material down from 183 mg/g KOH to less than 0.5 mg/g KOH. The purities of biodiesel were between 80-90% and viscosities were between 4-6 mm^2/s. Since PFAD also contains 7-10% of triglyceride, transesterification post-treatment after esterification process was also studied. In the transesterification step, the reactions were carried out with 0.6 wt% of KOH catalysts, methanol to oil ratio of 8:1 and reaction time of 40 minutes. After transesterification post-treatment, the acid value of the biodiesel could be reduced to below 0.8 % with the purity of biodiesel higher than 98%.

Keywords: Palm fatty acid distillate; Biodiesel; Esterification

1. Introduction

Due to the dramatic increase in petroleum oil price, biodiesel has already received widespread attention in Thailand. The popular sources of raw materials are waste vegetable oil and palm stearin, a high melting-point by-product of palm oil refining. In the past 3-4 years, a lot of small and large-scale biodiesel plants have emerged causing the demand for raw material to rise exponentially. This high demand has led to shortages of raw material, as well as an increase in the cost of raw material and related chemicals. This makes biodiesel more expensive than petroleum diesel and forces some plants, especially the ones that do not have a secure source of raw material to close down temporarily. Therefore, alternative raw materials with lower cost are being sought after. One possible alternative is palm fatty acid distillate (PFAD), another less-utilized by-product from palm oil refining. In contrast to palm olein and palm stearin, which consist of almost 100% triglyceride, PFAD contains only about 10% of triglyceride but as high as 90-93% free fatty acid (FFA). The best method of converting PFAD to methyl ester is by an esterification reaction, which is the reaction of FFA and methanol to form methyl ester and water. In the past, the production of biodiesel from high-FFA oil has been done by a two-step process, which is an esterification process to produce biodiesel from FFA followed by the usual transesterification to produce biodiesel from triglyceride [1-7]. Canakci and Van Gerpen [2] investigated biodiesel production from 20% and 40%-FFA oils. In their study, the amount of acid catalyst ranged from 5-25% and the reaction might require multiple esterification steps before transesterification. This amount of acid catalyst is considered high and may result in high corrosion to pilot-scale reactors. The approaches using heterogeneous catalysts like in Marchetti et al. [6] and Wang et al. [7] are interesting alternatives to avoid corrosion problems and will be investigated for PFAD in our further study. In their studies, the surface contact between the active sites of catalyst and reaction mass is the key factor in determining the conversion. Marchetti et al. [6] found that, for raw material with 10% FFA, the conversion of

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FFA to methyl ester using cation-exchanged resin reached only 80%. For a solid Lewis acid catalyst like ferrous sulfate, Wang et al. [7] found a better conversion, but still a long reaction time (4 hrs.) for waste vegetable oil with 38% FFA. Even though there were several studies on production of biodiesel from high-FFA oil, the FFA contents investigated in those studies were less than 50%. In contrast, PFAD, the raw material used in this study, contained more than 90% FFA. We have done a significant number of experimental adjustments to achieve satisfactory conversion of PFAD to biodiesel. For the scope of this paper, a small amount of homogeneous acid catalyst was used. We carried out an investigation into the effects of reaction conditions, including the methanol to oil ratio and reaction temperature on the quality and quantity of biodiesel. Furthermore, the effect of post-treatment by transesterification was also investigated to improve biodiesel quality.

2. Experimental

2.1. Chemicals

Palm Fatty Acid Distillate was supplied by Patum Vegetable Oil Co., Ltd. Sulfuric acid was obtained from Merck. Commercial methanol and potassium hydroxide were obtained from K.D. chemical (Thailand) and Tai-Liang Chemical (Thailand), respectively.

2.2 Procedure

(a) Esterification step

The esterification step was carried out by melting PFAD and maintaining it at the reaction temperature in a refluxed batch reactor. The mixture of methanol and concentrated sulfuric acid were added to the molten PFAD with continuous stirring for 120 minutes. The sulfuric acid was 1% v/w of the PFAD. After the reaction, the mixture was settled in a separatory funnel. The methyl ester in the lower layer was separated out for further purification or post-treatment reaction.

(b) Transesterification post-treatment

In the post-treatment process, the methyl ester obtained from the esterification step was treated by the transesterification reaction. In this process, the mixture of methanol and 0.6 wt% KOH catalyst was added to methyl ester from the esterification step with continuous stirring for 40 minutes at a reaction temperature of 60 °C. The reaction mixture was then settled in a separatory funnel and the methyl ester in the upper layer was separated out.

(c) Washing and Drying (Purification)

The washing process is important for removal of soap, catalyst, methanol and other contaminants. The washing step was carried out by using deionized water. The washing cycles were repeated until the pH of washed water is equal to the pH of the deionized water, which is usually around 6.0-6.8. For methyl ester produced using esterification without post-treatment, the washing was carried out without pH adjustment. However, for methyl ester with tranesterification post-treatment (pH>7), the methyl ester was neutralized prior to washing to avoid slow phase separation due to soap. After washing, the methyl ester was heated up above 100° C to remove excess methanol and water.

2.3 Characterization

The biodiesel produced was characterized for purity, viscosity, acid value and cloud point. Viscosity of biodiesel was tested using a Cannon Fenske No.75 P 573 viscometer at 40 ° C according to ASTM D 445. The cloud point was measured by recording the onset temperature of biodiesel transition from translucent to opaque. The acid value was determined by titration with potassium hydroxide (KOH) according to ASTM D 664. The standard deviations of the acid values measured are within the range of ± 0.03 for all samples. In case that the acidity of oil stemmed from free fatty acid as in biodiesel, free fatty acid content is approximately one half of the acid value. The purity of biodiesel was quantified using a Fisons GC 8000 series gas chromatograph equipped with high temperature column. Methyl heptadecanoate was used as the internal standard. The methyl ester sample was tested with a temperature program ranging from 160 °C up to 240° C with a ramp rate of 5 °C/s.

3. Results and discussion

Biodiesel was produced from PFAD by esterification reaction with various methanol to oil ratios at 60° C and 70° C. After the reaction, part of the biodiesel was washed and dried for further analysis and part of it was further treated by the transesterification post-treatment before washing and drying. The results of the analysis are discussed in two parts. Part I includes the

results of the esterification step and part II illustrates the effect of transesterification post-treatment.

3.1 Esterification step

From extensive adjustment of the reaction conditions, we found that the esterification reaction could be carried out to a sufficient extent at 60 and 70 °C in 2 hours when the methanol:oil ratios were higher than 16:1 and the amount of H_2SO_4 catalyst was 1% v/w. Although the methanol:oil ratios are considered high, the low percentage of acid catalyst used here is considered satisfactory compared to the previous study of Canakci and Van Gerpen [2], where the acid value of raw material with only 40% FFA still cannot be reduced to a sufficient extent by using up to 25% H_2SO_4 catalyst with the molar ratio of methanol to FFA of 9:1. In our study, the ratios of methanol:PFAD investigated were in the range of 16:1 to 24:1. The extent of reaction is indicated by the reduction of acid value, and is represented in terms of % conversion in Table 1. As shown in Table 1, the acid value was reduced from 183 mg KOH/g of oil to below 5 mg KOH/g of oil within 2 hours. This implies that the % conversions of FFA to methyl ester in all cases were above 97.5%. At 60 °C, the conversion was the highest when the ratio of methanol to oil was 20:1, whereas, at 70 °C, the highest conversion occurred at the lower methanol to oil ratio of 18:1. The viscosities of biodiesel produced from these esterification reactions are within the range of 5.0-5.2 mm^2/s, as shown in Table 2.

3.2 Transesterification post-treatment

After esterification, the methyl ester layer was separated. Half of the methyl ester underwent further purification by washing and drying, whereas the other half was post-treated by transesterification reaction with methanol containing KOH catalyst before purification. In the post-treatment process, the ratio of methanol:oil used was 8:1 and the amount of KOH catalyst was 0.6 wt%. The acid values and the viscosities of biodiesel esterified at 60 °C with and without transesterification post-treatment are compared in Figure 1 and 2, respectively. As can be seen, after post-treatment and purification, the remaining FFA in the form of soap was washed out and the acid values were reduced further to below 0.85 for all samples investigated. Figure 2 shows that the viscosities of biodiesel after post-treatment and purification are lower than those without post-treatment and are within the range of 4.4-4.9 mm^2/s for all samples investigated.

The % purity of biodiesel produced from the esterification reaction with and without post-treatment at various methanol:oil ratio are illustrated in Figure 3 for a reaction temperature of 60° C. For the esterification step without post-treatment, the % purity was within the range of 83-90% and after post-treatment, the % purity increased to more than 90%. Significant improvement in biodiesel purity was obtained for the batches esterified using methanol:oil ratios of 20:1 and 22:1 at 60°C. In this study, the maximum purity of 98.5% was achieved at a methanol:oil ratio of 20:1 and a reaction temperature of 60°C with transesterification post-treatment. With post-treatment, the reduction of acid value from 3-4 mg/g KOH down to below 0.8 mg/g KOH indicated that the % FFA was reduced by around 1.0-1.5 %, while the % purity increased by about 10%. Therefore, the increase in % purity of methyl ester after transesterification post-treatment is due mainly to the conversion of triglyceride in PFAD to methyl ester, and, to a lesser extent, the removal of free fatty acid during the washing step. The % yield of methyl ester in this case was 63% w/w. The low % yield was mainly due to the entrainment of fatty acid and methyl ester into the hydrophilic phase in the esterification step, where a large amount of methanol was used. This issue was also raised by Canakci and Van Gerpen [2] when using raw material with 20% and 40% FFA. Another issue related to this 2-step process is the amount of salt produced. As the process uses soluble acid and base catalysts, the amount of salt produced during the pH-adjustment process before washing is quite high. Therefore, the use of heterogeneous catalyst in the esterification step might be useful in this regard. Nevertheless, with such high amounts of FFA in PFAD, good distribution of solid catalyst in FFA would be an important issue in obtaining high conversion of FFA and would be worth further study.

4. Conclusion

The biodiesel production from palm fatty acid by the two-step process provided high quality biodiesel in this study. In the

esterification reaction, the optimum methanol:oil ratios that can reduce the acid value of PFAD to the lowest are 20:1 at 60 °C and 18:1 at 70 °C. After transesterification post-treatment, the % purity of methyl ester can be improved to 98.5% for the batch with a methanol:oil ratio of 20:1 at @ 60 °C with a the % yield of 63 % w/w.

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Table 1: Effects of reaction temperature and molar ratio of methanol:PFAD on the acid value and the corresponding % conversion of PFAD after the esterification step

Methanol:PFAD	Acid Value		% Conversion	
	reaction temp 60 °C	reaction temp 70 °C	reaction temp 60 °C	reaction temp 70 °C
16:1	4.32	3.88	97.6 %	97.9 %
18:1	4.13	3.42	97.7 %	98.1 %
20:1	3.38	3.75	98.2 %	98.0 %
22:1	3.60	3.61	98.0 %	98.0 %
24:1	3.81	3.66	97.9 %	98.0 %

Table 2: Effects of reaction temperature and molar ratio of methanol:PFAD on the viscosity of PFAD after the esterification step

Methanol:PFAD	Kinematic Viscosity at 40 °C (mm^2/s)	
	reaction temp 60 °C	reaction temp 70 °C
16:1	5.12	5.08
18:1	5.08	5.18
20:1	5.02	5.12
22:1	5.10	5.24
24:1	5.18	5.17

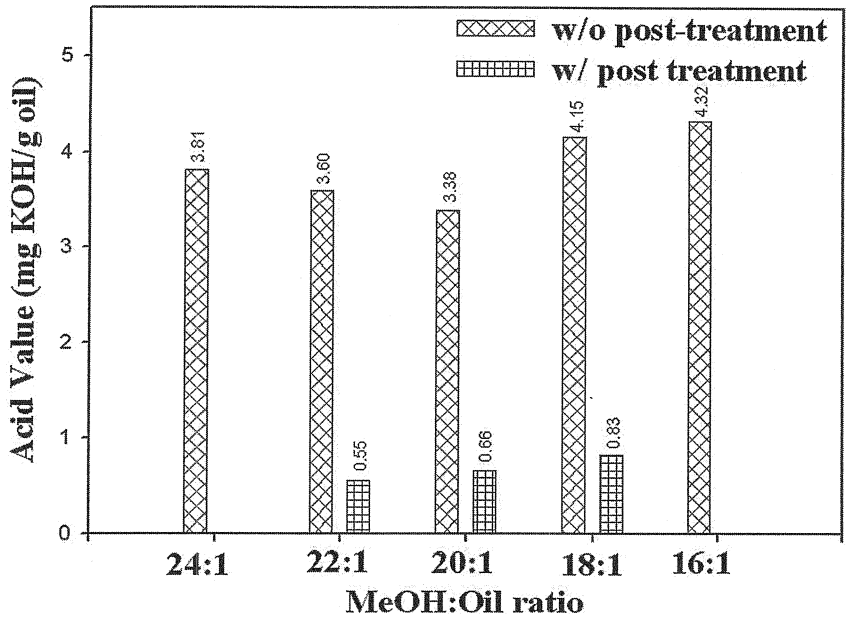

Figure 1. Acid values of biodiesel produced by esterification at 60 °C with and without post-treatment.

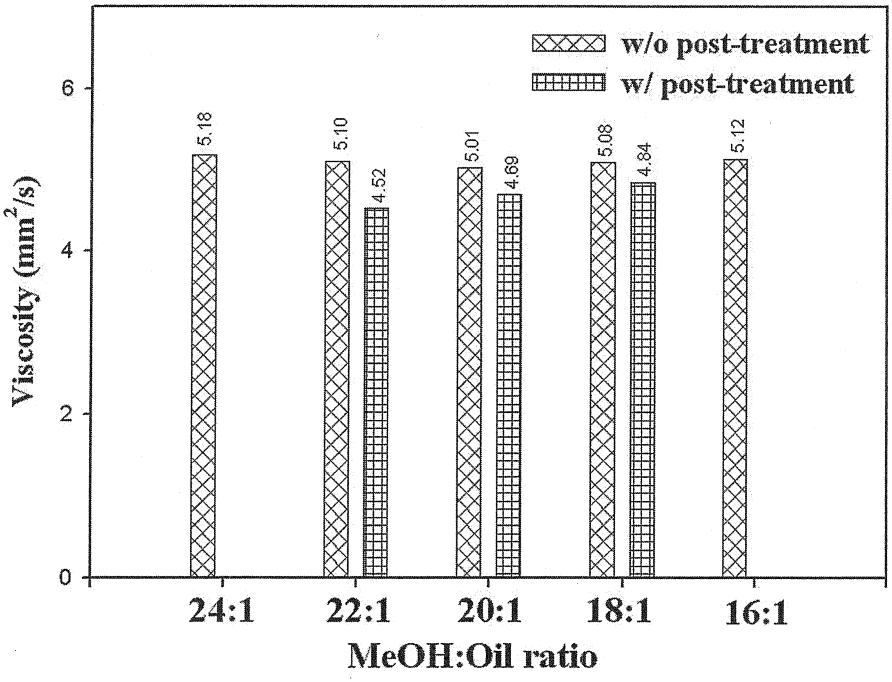

Figure 2. Viscosities of biodiesel produced by esterification at 60 °C with and without post-treatment.

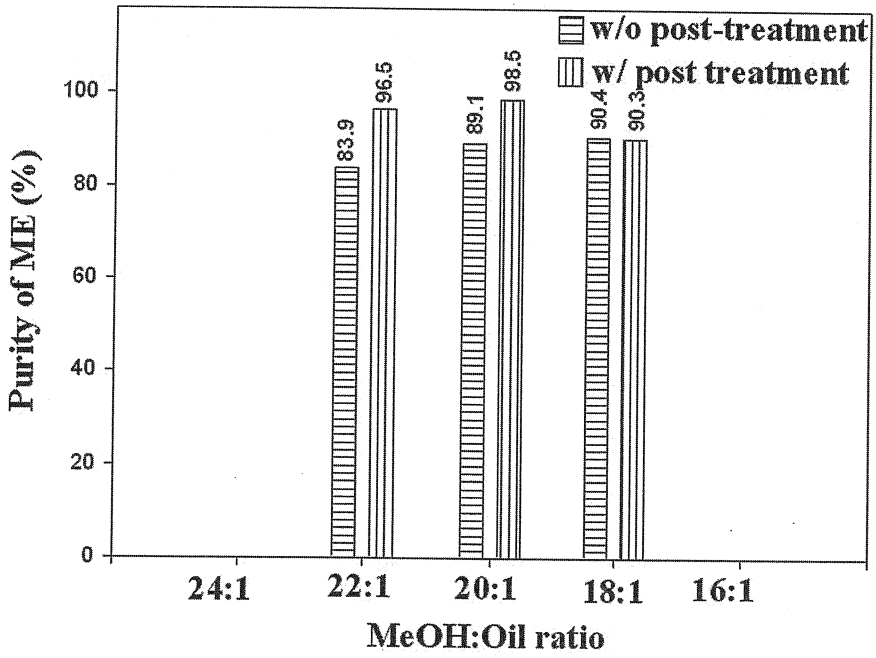

Figure 3. Percent purity of biodiesel produced by esterification at 60 °C with and without post-treatment.