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Biodiesel with Decreased Viscosity Produced from Crude Palm Oil

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ABSTRACT

Studies were carried out on transesterification of crude palm oil with methanol for biodiesel production. The reaction parameters such as alcohol/oil molar ratio, catalyst concentration, temperature, degumming and washing processes were optimized for crude palm oil. The fatty acid methyl ester contents in the reaction mixture were quantified by Cannon Automatic Viscometer (CAV-2000), and the Automatic Flash Point and Inductive Coupled Plasma Spectrometer (ICPS-9000). The optimum alcohol/oil molar ratio was 9:1. The flash point value of the product was more than 120°C. The catalyst concentration at 1% $NaOCH_3$ (v/v) and degumming of crude palm oil by 5% (v/v) phosphoric acid at 80°C for 1 hour decreased the viscosity of methyl ester from crude palm oil to 4.72 mm^2/s which is lower than the standard viscosity set by the Energy Business Department.

Key words: biodiesel-crude palm oil, methyl ester, transesterification, viscosity, degumming

INTRODUCTION

In recent years, biodiesel has become more attractive as an alternative fuel for diesel engines because of its environmental benefits and it is made from renewable resources. Biodiesel fuel production now exceeds 100,1000 tonnes per year in several countries, including Belgium, France, Germany, Italy and the United States. (Krawczyk, 1996). For the production of low-viscosity biodiesel fuel produced from crude palm oil, an alkali-catalysis process has been established. Fatty acid methyl esters derived from renewable sources such as vegetable oils has gained importance as alternative fuels for diesel engines. The edible oils such as soybean oil in USA and palm oil in countries with tropical climate such as Malaysia are being used for biodiesel production (Karaosmanoglu *et al*., 1996).

Vegetable oils and animal fats are chemically triglyceride molecules, in which three fatty acid chains are ester-bound to one glycerol molecule. Problems encountered in substituting triglycerides for diesel fuels are mostly associated with their high viscosity, low volatility and polyunsaturated character (Srivastava and Prasad, 2000). Three main processes, pyrolysis, micro-emulsification and transesterification have been investigated in attempts to overcome these drawbacks and allow vegetable oils and wastes to be used as viable alternative fuels. Transesterication, also call alcoholysis, is the process of reacting triglyceride such as vegetable oils with alcohol in the presence of catalyst to produce fatty acid ester and glycerol. Methanol is utilized more frequently than ethanol, propanol, butanol and amyl alcohol because of its low cost and its physical and chemical advantages. The

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molecular weight of ester molecule is roughly one-third of straight vegetable oil molecule and has viscosity approximately as twice as that of diesel fuel.

Alkalis used for transesterification include NaOH, KOH, carbonates and alkoxides such as sodium methoxide, sodium ethoxide, sodium propoxide. Sodium methoxide has been found to be more effective than sodium hydroxide, presumably because a small amount of water is produced upon mixing NaOH and MeOH (Alcantra *et al.*, 2000). Alkali-catalyzed transesterification proceeds approximately 4000 times faster than that catalyzed by the same amount of an acidic catalyst (Formo, 1954).

There is also a decrease in viscosity and improvement of fatty acid methyl esters in the process of transesterification. The standard viscosity of biodiesel (B 100) set by the Energy Business Department ranges from 3.5 to 5.0 mm^2/s to align with EN 14214, ASTM D445. Attempts have been made for the conversion of crude palm oil to fatty acid methyl esters. In this study, the influence of the variables such as alcohol to oil molar ratio, catalyst concentration, reaction temperature, degumming and washing on transesterification were investigated.

MATERIALS AND METHODS

Crude palm oil was obtained from Chumporn Industrial Palm Oil Co., Ltd. The crude palm oil was filtered by using muslin cloth with 10-15 μm pore size(Meher *et al.*, 2006).

Absolute methanol was purchased from Lab. Supplies. Sodium methoxide was purchased from Fluka. Phosphoric acid was purchased from J. T. Baker and petroleum ether was purchased from Malinckrodt.

The apparatus used for transesterification was consisted of an oil bath and a 250 ml round-bottom reaction flask equipped with a magnetic stirrer and a water-cooled condenser. A temperature indicator was used to measure the reaction temperature. Crude palm oil was preheated to the desired temperature before starting the reaction. The sodium methoxide-methanol solution was freshly prepared in order to maintain the catalytic activity and to prevent moisture absorbancy. The measurement was started after adding methanolic solution to crude palm oil in the reaction flask.

The variables affecting transesterification such as catalyst concentration (0.3, 0.5 and 1%(V,V) $NaOCH_3$), alcohol/oil molar ratio (7:1 to 9:1), degumming (5%(V,V) H_3PO_4 at 80°C for 1 hr) were studied in order to have optimal reaction condition.

The influence of the variables such as alcohol to oil molar ratio, catalyst concentration, reaction temperature, degumming, washing and viscosity of methyl esters in the product of crude palm oil transesterification were studied. Three replications were carried out for each experimental variables. The viscosity, flash point and phosphorus residual were quantified by Cannon Automatic Viscometer (CAV-2000), Automatic Flash Point, and Inductive Coupled Plasma Spectrometer (ICPS-9000), respectively.

After the completion of the reaction, the product was kept overnight for the separation of biodiesel and glycerol layers. The catalyst and unused methanol were in the lower glycerol layer whereas fewer amounts of catalysts, methanol and glycerol were in the upper biodiesel layer. The upper layer was collected for further purification. To obtain pure biodiesel, method of washing with hot distilled water and dissolving in petroleum ether (1:1) were performed in the refining process. The biodiesel after separation was washed using same amount of hot water (60°C) to remove the remained catalysts and glycerol. The moisture from washed biodiesel was removed by boiling at 120°C for 1 hour.

RESULTS AND DISCUSSIONS

Characterization of crude palm oil

The viscosity of crude palm oil quantified by CAV-2000 was 39.33 mm^2/s This viscosity is about ten times higher than that of diesel, with consequent poor fuel atomization, incomplete combustion, carbon deposition on the injectors and valve seats, and fuel build-up in the lubricant oils. This can, therefore, cause serious engine deterioration, hence, it is absolutely necessary to subject the crude palm oil to treatments that diminish the viscosity.

Influence of methanol/oil molar ratio

The alcohol to oil molar ratio is one of the important factors that affects the reaction. The average molecular weight of crude palm oil was calculated as 858 and the alcohol to oil molar ratio was varied from 7:1 to 9:1. The viscosities of methyl ester versus alcohol to oil molar ratio are shown in **Table 1**. The viscosity of methyl esters for methanol/oil molar ratio of 9:1 was 4.72 ± 0.01 mm^2/s. It was found that the reaction was faster with higher molar ratio of methanol to oil whereas longer time was required for lower molar ratio (7:1) to get the same conversion. Krisnangkura and Simamaharnnop (1992) transesterified palm oil at 70°C in an organic solvent with sodium methoxide as a catalyst and found that the conversion increased with increasing molar ratios of methanol to palm oil.

Influence of catalyst concentration

Methanolysis of crude palm oil was carried out with $NaOCH_3$ as a catalyst at concentration of 0.3,0.5 and 1% (v/v) of oil at 65°C (1.5 hr.) with MeOH/oil molar ratio of 9:1. **Table 2** showed the viscosity of methyl ester versus catalytic concentrations. The transesterification reaction was strongly dependent upon the concentration amount of catalyst applied. The lower catalytic concentration i.e. 0.3% $NaOCH_3$ was insignificant to catalyze the reaction to completion. However, 1% $NaOCH_3$ really increased the reaction rate to the optimum in the

Table 1 Methanol/oil molar ratio and viscosity of methyl esters.

Molar ratios	Viscosity (mm^2/s)[a]		
	After degumming	After washing	After moisture removal
7:1	4.57 ± 0.01[c]	2.18 ± 0.02[a]	4.84 ± 0.11[a]
8:1	4.39 ± 0.04[a]	2.27 ± 0.04[b]	5.33 ± 0.07[b]
9:1	4.47 ± 0.06[b]	2.27 ± 0.01[b]	4.72 ± 0.01[a]

[a] Each measurement is an average of three replications ± standard deviation. Means within a column with different letters(a,b,c) are significantly different at $P < 0.05$

[a,b,c] Dependent variables : viscosity ; different letters mean significantly different viscosity at 95 % confident interval; same letters mean no significantly different viscosity at 95 % confident interval

Table 2 Viscosity of methyl ester versus catalytic concentrations.

Concentrations(%v/v)	Viscosity(mm^2/s)[a]		
	After degumming	After washing	After moisture removal
0.3%$NaOCH_3$	32.77 ± 0.08[c]	7.42 ± 0.04[c]	44.39 ± 0.33[b]
0.5%$NaOCH_3$	30.68 ± 0.44[b]	6.64 ± 0.50[b]	47.29 ± 1.70[c]
1%$NaOCH_3$	4.48 ± 0.06[a]	2.27 ± 0.01[a]	4.72 ± 0.01[a]

[a] Each measurement is an average of three replications ± standard deviation. Means within a column with different letters(a,b,c) are significantly different at $P < 0.05$

[a,b,c] Dependent variables : viscosity ; different letters mean significantly different viscosity at 95 % confident interval; same letters mean no significantly different viscosity at 95 % confident interval

reaction with 4.72 ± 0.01 mm^2/s viscosity. With the increase in catalytic concentration, there was a decrease in the yield of methyl ester due to the formation of soap which increased the viscosity of the reactants.

Influence of degumming

Studied were carried out with and without 5% H_3PO_4 added. It was observed that without 5% H_3PO_4 added, the saponification of glycerides tended to be accelerated before the completion of alcoholysis. The soap consumes the catalyst and reduces the catalytic efficiency, as well as causing an increase in viscosity,the formation of gels and difficulty in achieving separation of glycerol.The viscosity of degumming methyl ester with and without 5% H_3PO_4 added were shown in **Table 3**. This is in accordance with the result of Dorado *et al*., (2004).

Physical property of methyl ester

The viscosity, flash point values and phosphorus residual of methyl ester in the product were quantified by Cannon Automatic Viscometer (CAV-2000), Automatic Flash Point and Inductive Coupled Plasma Spectrometer (ICPS-9000), respectively. The viscosity of methyl ester was 4.72 mm^2/s.Flash point values was more than 120°C and phosphorus residual was 8.895 mg/kg (0.00008 %). The resulted showed that the viscosity and phosphorus residual were lower than the standard values set by the Energy Business Department. As a consequence of its advantages, there is considerable interest in developing the use of biodiesel fuel.

CONCLUSION

The present experimental study revealed that the reaction conditions for methanolysis of crude palm oil was 1% $NaOCH_3$, MeOH/oil molar ratio 9:1 at the reaction temperature 65°C (1.5 hr). The viscosity of methyl ester was 4.72 ± 0.01 mm^2/s which is lower than the standard viscosity set by the Energy Business Department. With 9:1 molar ratio of MeOH/oil or higher, free fatty acids contained in crude palm oils and fats could also be converted efficiently to methyl esters in supercritical methanol, leading to increase of the total yield of methyl esters from used oils. The reaction was completed within 1.5 hr. The viscosity of methyl ester is lower with higher catalyst concentration and higher molar ratio of methanol to oil. The flash point of methyl ester from crude palm oil was more than 120°C and phosphorus residual of methyl ester in the product was 0.00008% wt. However, this experiments had some drawbacks,including the difficulty of recycling glycerol and the need for either removal of the catalyst. In particular, several steps such as the evaporation of methanol, removal of saponified products, neutralization are needed to recover glycerol as a by-product.

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Table 3 Viscosity of methyl ester with and without 5% H_3PO_4 added.

5% H_3PO_4	Viscosity(mm^2/s)[a]		
	After degumming	After washing	After moisture removal
Added	4.47±0.06[a]	2.27±0.01[a]	4.72± 0.01[a]

[a] Each measurement is an average of three replications ± standard deviation. Means within a column with same letters(a) are no significantly different at $P < 0.05$

[a,b,c] Dependent variables : viscosity ; different letters mean significantly different viscosity at 95 % confident interval; same letters mean no significantly different viscosity at 95 % confident interval

LITERATURE CITED

Alcantra, R., J. Amores, L. Canoira, O.E.Fidalg, M.J.Franco and A. Navarro. 2000. Catalytic production of biodiesel from soy-bean oil, used frying oil and tallow. **Biomass Bioeng.** 18: 515-527.

Dorado,M.P., E. Ballesteros, F.J. Lopez and M. Mittelbach. 2004. Optimization of alkali-catalyzed transesterification of *Brassica carinata* oil for biodiesel production. **Energ. Fuel.** 18(1): 77-83.

Formo, M.W. Ester reactions of fatty material. 1954. **J.. Am. Oil Chem. Soc.** 31: 548-559.

Karaosmanoglu, F., K.B. CigizogluK, M. Tute and S. Ertekin. 1996 Investigation of refining steps of biodiesel production. **Energy Fue.l** 10: 890-895.

Krawczyk, T. 1996. Biodiesel-alternative fuel maks inroads but hurdle remin. **Inform** 7: 800-815

Krisnangura, K. and R. Simamaharnnop. 1992. Continuous transmethylation of palm oil in an organic solvent. **J. Am. Oil Chem. Soc.** 69: 166-169

Meher, L.C., V.S. Dharmagadda and S.N. Naik. 2006. Optimization of alkali-catalyzed transesterification of *Pongamia pinnata* oil for production of biodiesel. **Bioresource Tech.** 97: 1392-1397.

Srivastava, A. and R. Prasad. 2000. Triglycerides-based diesel fuels. **Renew. Sust. Energ. Rev.** 4: 111-133.