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Biodiesel Production from High Iodine Number Candlenut Oil

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***Abstract*—**Transesterification of candlenut (aleurites moluccana) oil with methanol using potassium hydroxide as catalyst was studied. The objective of the present investigation was to produce the methyl ester for use as biodiesel. The operation variables employed were methanol to oil molar ratio (3:1 – 9:1), catalyst concentration (0.50 – 1.5 %) and temperature (303 – 343K). Oil volume of 150 mL, reaction time of 75 min were fixed as common parameters in all the experiments. The concentration of methyl ester was evaluated by mass balance of free glycerol formed which was analyzed by using periodic acid. The optimal triglyceride conversion was attained by using methanol to oil ratio of 6:1, potassium hydroxide as catalyst was of 1%, at room temperature. Methyl ester formed was characterized by its density, viscosity, cloud and pour points. The biodiesel properties had properties similar to those of diesel oil, except for the viscosity that was higher.

***Keywords*—**biodiesel, candlenut, methyl ester, transestrification

I. Introduction

RECENTLY, biodiesel has been used as an alternative diesel fuel. It is made from renewable resources such as vegetable oil. Many researchers investigated with feedstocks non edible vegetable oil from some seeds such as *Jatropha curcas* [1], rubber *(Hervea brasiliensis)* [2]-[3], jojoba *(Simmondsia chinensis)* [4], mahua *(Madhuca indica)* [5], *Pongamia pinnata* [6], polanga *(Calophyllum inophyllum*) [7]. Candlenut (*Aluerites moluccana)* grows naturally in the east of Indonesia. Candlenut is now cultivated in eastern province of Indonesia as perennial plant. Candlenut seed contains around 30% of candlenut oil which can be obtained by pressing [8] Candlenut oil has a high iodine number that is around 135. It cause the lower of pour point. Crude candlenut oil generally contains about 15% free fatty acids (15% FFA). Vegetable oil contain high free fatty acids, it has significant effects on the transesterification with methanol using alkaline catalyst [8]. It also interfere with the separation of fatty acid ester and glycerols [9]. The high FFA contents was reduce to less than 1% by pretreatment process. Reference [5] has reduced the FFA contents from 19% to less than 1% by using 0,35 v/v methanol to oil ratio, 1% sulfuric acid as catalyst, reaction temperature 65^{o}C in 1 hour reaction. Similar way was also undertaken to reduce FFA in the rubber seed oil to less than 2% [3]. Pretreatment process for crude candlenut oil was undertaken by an esterification with methanol using an acid catalyst. It can reduced the free fatty acid to less than 1% [10].

The main factors affecting transesterification are the alcohol to oil molar ratio, catalyst concentration, reaction temperature and reaction time. The methanol to oil ratio needs to be higher than stoichiometric ratio to drive the equilibrium to a maximum ester yields. The molar ratio is associated with the type of vegetabl oil used. Reference [2] stated thet molar ratio was 6 : 1 for rubber seed oil. It was also undertaken sunflower oil was used [11]. The range of molar ratio from 4,5 : 1 to 9 : 1 were used for methanolysis of used frying oil [12]. Moreover, reference [13] investigated from 10 :1 to 18 : 1 for soybean used frying oil. Catalyst are classified as alkali, acid and alkali-alcoholic. Transesterification of jojoba oil catalysed with sodium metoxide[4]. Potassium hydroxide was most common to be used as catalyst such as jatropha curcas, used frying oil, mahua oil and soybean used frying oil [1]-[6]-[12]-[13]. When rice bran oil was used as feedstock, Reference [14] used a sulfuric acid as catalyst. Sodium hydroxide was also choosen to catalysed the transesterification of rubber seed oil beacause it is cheaper [2]-[3]. A different homogeneous catalyst were used to transesterify a sunflower oil, reference [11] pointed out that near 100% biodiesel yields were only obtained with sodium metxide catalyst.

II. EXPERIMENTAL

A. Materials

Candlenut seeds were obtained from the local market. The seeds were extracted by normal hexane using soxlet extractor. Candlenut oil analyzed that density of 0.9144 g/mL, viscosity of 23.8923 cSt, iodine number of 137.446, free fatty acid, total fatty acid were 1.3879 meqKOH/g oil and 3.3911 meqKOH/g oil respectively. High purity an anhydrous methanol of 99.95% was used, the density of 0.7850 g/mL, water content of 0.04%. Potassium hydroxide as catalyst was purchased from E-Mercks agency.

B. Equipment

The transesterification reaction was carried out in 500 mL three necked reactor equipped with mechanical stirrer, a reflux condenser, thermometer and stopper to remove samples. The reactor was placed in the heating mantle with provided the

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thermostat which was capable for maintaining the constant reaction temperature.

C. Procedure

The reactor was initially charged with the amount of candlenut oil then heated to certain temperature. The potassium hydroxide was dissolve in the methanol and then the solution was fed to the reactor feeder. The solution was also heated to certain temperature (similar to oil temperature in the reactor) then was flowed to the reactor. The reaction was timed as soon as the potassium hydroxide – methanol solution was fed to the reactor. During the reaction, samples were taken at the following reaction time 15, 30, 45, 60 and 75 min. The samples were immediately quenched in water to stop the reaction and two phase were performed. The samples were washed by the distilled water. After formation of two layers, the upper consisted of methyl esters and partial triglycerides and the lower phase contained the glycerol excess methanol and the remaining catalyst together with the soaps formed doing the reaction.

D. Analysis

The analytical methods used to determine the glycerol concentration in the water layer by using periodic acid. The conversion of triglyceride to methyl ester was determined through the material balance of the reaction and for the initial concentration of triglyceride.

III. RESULT AND DISCUSSION

A. Pretreatment process

The candlenut oil used as raw material has high FFA content, it is around 7.77%. It has to be reduced by using 0.30 v/v methanol to oil ratio, 1% sulfuric acid as catalyst, reaction temperature 65^{o}C in 1 hour reaction [10]. It was found that the free fatty acid content was reduced to 0.85% (less than 1%).

B. Effect of temperature

One of the variable affecting the yields of ester is the reaction temperature. Catalytic methanolysis of vegetable oil is normally investigated close to the boiling point of the methanol. Nevertheless, the reaction may be carried out at room temperature which could be very interesting for industrial scale production. It would be very interesting for industrial scale production due to the energy savings that it would imply.[15]-[16]-[17]. In this present work the methanolysis of candlenut oil was undertaken at the room temperature to 70^{o}C. In all experiment ethanol to oil molar ratio of 6 : 1 and 1% potassium hydroxide were used. Figure 1 expresses the effect of reaction temperature on methyl ester formation. After 15 min the ester formed was closed to 96%, showing the effect of temperature on ester formation. However, in the same reaction time (60 min) ester formation was basically identical for these runs (around 98%). As can be observed the increasing conversion was less than 3 % by increasing reaction temperature from 30 to 70^{o}C. It can be observed the effect of temperature on triglyceride conversions were less pronounce. As seen in Figure 1, the final triglycerid conversion were almost reached in 15 min and the curves have an asymptotic tendency with time.

C. *Effect of m ethanol to oil molar ratio*

The methanol to oil molar ratio is one of most important variables affecting the ester yields. In the present investigation molar ratio

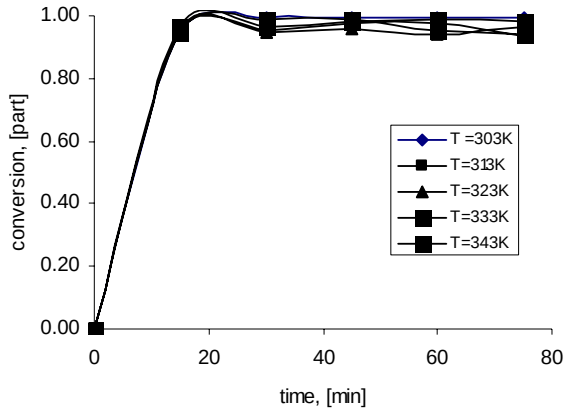

Fig. 1 Effect of temperature

between 3 : 1 and 9 : 1 were used. Figure 2 shows the triglycerides conversion obtained versus the reaction time for the five experiments carried out. It was observed the triglyceride conversion increase as the molar ratio rises. The best result was found on 6 : 1 molar ratio.

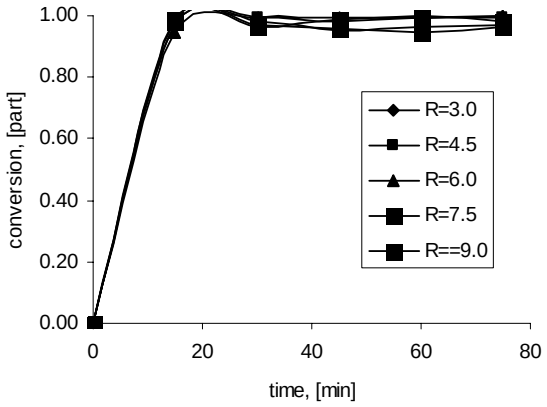

Fig. 2 Effect of methanol to oil molar ratio

This result is similar to those found in the literature [2]-[18]-[19]. At higher molar ratio, more triglyceride will be reacted. However an excess of methanol, it will interfere the separation of glycerin because there is an increase in solubility and the part of glycerin remained in the biodiesel phase. In addition, the glycerin remained in ester phase, it helped drive the equilibrium back to the reverse reaction [16]-[20]. As can be observed at stoichiometric molar ratio, the separation of glycerin layer was fast. In contrast to reaction conducted with an excess of methanol, the separation take time and is also not complete. Therefore the molar ratio of 6 : 1 seems to be the most appropriate.

D. Effect of catalyst concentration

Another important variable affecting the yields of ester is the catalyst concentration. Figure 3 shows the triglyceride conversion obtained are plotted versus reaction time for the concentration of potassium hydroxide was varied. The triglyceride conversion increased with increasing the catalyst concentration. concentration of 1%, for concentration of 1.5% (higher value).

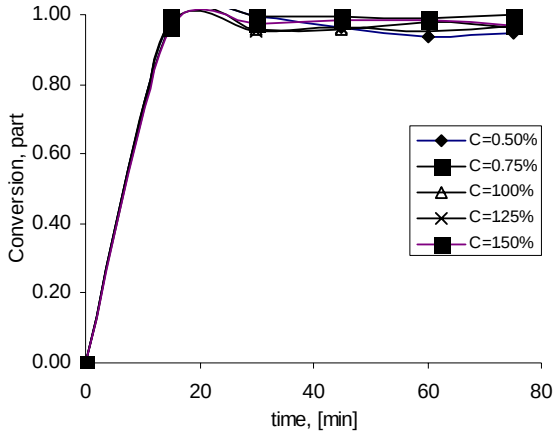

Fig. 3 Effect of catalyat concentration

As can be observed, the best results were achieved for potassium hydroxide concentration of 1%, for concentration of 1.5% (higher value) the yields of methyl ester were lower. Reference [8] found the best results were achieved for potassium hydroxide concentration of 1.25%, for ethanolysis of candlenut oil with higher free fatty acid content. The addition of more potassium hydroxide gives rise to the formation of an emulsion and leads to the formation of gel. There also hinder the glycerin separation as a result there is a dilution of methyl ester and ester yield tend to decrease.

E. Biodiesel physical properties

The physical properties of biodiesel had similar to those of diesel oil, except for the viscosity that was higher (Table II attachment). Table I expressed the kinematics viscosity of various compound of biodiesel and diesel oil. It was shown that for B10 (10% v/v biodiesel to diesel oil) and B20 (20% v/v biodiesel to diesel oil) were close to the diesel oil and for B100 (100% biodiesel) was to higher.

TABLE I
KINEMATIC VISCOSITY ON VARIOUS COMPOUND OF BIODIESEL

Sample	Viscosity (cSt)
Diesel oil	3.743
B10	3.785
B20	3.857
B30	3.945
B40	3.987
B50	4.099

IV. CONCLUSION

The following conclusion can be drawn from this study.

1. Candlenut oil has suitable to produce methyl ester with similar properties to biodiesel. The cultivation of candlenut plant can be considered as potential alternative for renewable energy sources.
2. The ethanol to oil molar ratio is one variable that has most influence on the process. The best result was obtained for a 6/1 molar ratio.
3. Potassium hydroxide can be used as catalyst on methanolysis of candlenut oil. There was an optimal concentration of 1% referred to the initial oil.
4. The effect of temperature was less pronounced. The biodiesel formed was increased with increasing temperature. Nevertheless the transesterifacation can be undertaken at room temperature.
5. Of the variables studied, the triglyceride conversion is almost reached in 15 min and the curves have an asymptotic tendency with the time.

REFERENCES

[1] N. Foidl, G. Foidl, M. Sanchez, M. Mistelbach, S. Hackel, "Jatropha curcas L. as sources for the production of biofuel in Nicaragua," Bioresource Technol, vol 58, pp 77-84, 1996.
[2] O. E. Ikwuagwu, I. C. Ononogbu, O. U. Njoku, "Production of biodiesel using rubber [Hevea Brasiliensis (kunth. Muell.)] seed oil," *Ind. Crops and Product*, vol 12, pp 57-62, 2000
[3] A. S. Ramadhas, S. Jayaraj, C. Muraleedharan, C., "Biodiesel production from high FFA rubber seed oil," *Fuel*, vol 4, pp 335-340, 2005.
[4] L. Canoira, R. Alcantara, M.J. Garcia-Martinez, J. Carrasco, "Biodiesel from Jojoba oil-wax: transesterification with methanol and properties as a fuel," *Biomass and Bioenergy*, vol 30, pp 76 -81, 2006
[5] S. V. Ghadge, H. Raheman, "Biodiesel production from mahua (*Madhuca indica*) oil having high free fatty acids," *Biomass and Bioenergy*, vol 28, pp 601-605, 2005
[6] S. K. Karmee, A. Chadha, "Preparation of biodiesel from crude oil of *Pongamia pinnata*", Bioresource Technol," vol 96, pp 1425-1429. 2005
[7] P. K. Sahoo, L. M. Das, M. K. G. Babu, and S. N. Naik, " Biodiesel development from high acid value polanga seed oil and performance evaluation in a CI engine," *Fuel,* vol 86, pp 448-454, 2007.
[8] H. Sulistyo, I. M. Suardjaja, S. S. Rahayu, " Transesterification of candlenut oil with ethanol to biodiesel" Proceeding on Regional Symposium on Chemical Engineering (RSCE2006) 4-6 December 2006, Singapore, 2006
[9] F. Ma, H. A. Hanna, M.A., 1999,"Biodiesel production: a review," *Bioresource Technol*., vol 70, pp 1-15, 1999
[10] H. Sulistyo, S. S. Rahayu, I. M. Suardjaja, A. P. Sarjono, G. Manshuri, G.,"Proses penyiapan bahan baku pembuatan biodiesel dari minyak kemiri", *Media Teknik,* Oktober 2008.
[11] G. Vicente, M. Martinez, J. Aracil, A. Esteban, "Kinetics of sunflower oil methanolysis," *Ind. Eng. Chem. Res*., vol 44, pp 5447-5454, 2005
[12] A. Tomasevic, S. S Silver-Marinkovic,"Methanolysis of used frying oil," *Fuel. Proc. Technol.*, vol 81, pp 1-6., 2003
[13] K. Lee, J. X. Yu, J. H. Mei, L. Yan, Y. Kim, K. Chung, ,"A kinetic study on the of glyceril monooleate and soybean used frying oil to biodiesel," *J. Ind. Eng. Chem*., vol 13, pp 799-807, 2007
[14] S. Zullaikah, C. Lai,S. R. Vali, Y. Ju, "A two-step acid-catalyzed process for production of biodiesel from rice bran oil", *Bioresouce Technol*., vol 96, pp 1889-1896, 2005
[15] B. Freedman, E.H. Pryde, T. L. Mounts, "Variable affecting the yields of fatty esters from transesterified vegetable oils," *J. Am. Oil. Chem. Soc.,* vol 61, pp 1638-1643, 1984
[16] S. S. Rahayu, I. M. Suardjaja, Sofiyah dan H. Sulistyo, "Biodiesel dari minyak jarak; Proses pembuatan dan uji kinerja mesin diesel," Laporan penelitian Hibah Bersaing XI, DP3M Dikti Jakarta, 2004

[17] J. M. Encinar, J. F. Gonzalez, J. J. Rodriguez, A. Tejedor, " Biodiesel fuels from vegetable oils: Tranesterification of c*ynara carduncul*us L. oils with ethanol," *Energy & Fuels*, vol 16, pp 443 -450, 2002
[18] J. .M. Encinar, J.F. Gonzalez, A. Rodriguez-Reinares, "Biodiesel from used frying oil. variables affecting the yields and characteristics of the biodiesel," *Ind. Eng. Chem.Res.,* vol 44, pp 5491-5499, 2005
[19] B. Freedman, R. O. Butterfield, E. H. Pryde, "Transesterification kinetics of soybean oil," *J. Am. Oil. Chem. Soc.,* vol 63, pp 1375-1380, 1986
[20] K. Krisnamgkura, R. Simamaharnnop,"Continuous transmethylation of palm oil in organic solvent," *J. Am. Oil. Chem. Soc.,* vol 69, pp 166-172. 1992

TABLE II
PHYSICAL PROPERTIES OF METHYL ESTER, DIESEL OIL, FUEL OIL AND BIODIESEL STANDARD

No	Properties		Candlenut ester		Ester	Diesel oil	Fuel oil	Biodiesel standard		
								ASTM	DIN	SNI 04
			B100	B10	BPTP			D6751-02	EN 14214	7182-2006
1	Density	kg/m^3	886.9	839.2	870	820 - 870	840 – 920	-	860 - 900	850 - 890
2	Kinematic viscosity	cSt	4.819	3.785	4.8	5.8	3.6 – 7.2	1.9 - 6	3.5 – 5.0	2.3 - 6
3	Flash point	^oC	160	75.556	182	>65	>65	>130	>120	>100
4	Pour point	^oC	6.667	12.778	12	<18	<18	-	-	-
5	Water content	%	0.32	TRACE	<0.05	<0.05	<0.25	<0.03	<0.05	<0.05
6	Ash content	%	0.006	0.0399	0.007	<0.01	<0.01	<0.02	<0.02	<0.01

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