Crude Candlenut Oil Ethanolysis to Produce Renewable Energy at Ambient Condition

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Abstract - Transesterification reaction of crude candlenut (aleurites moluccana) oil with ethanol to form fatty acid ethyl ester by using a potassium hydroxide as catalyst was studied. Experiments were performed at ambient condition. The operation variables employed for transesterification were ethanol to oil molar ratio and catalyst concentration. The objective of the present investigation was to produce a renewable energy that the ethyl ester formed was used as biodiesel. Pretreatment process was undertaken to reduce the free fatty acid to less than 2% by esterification with ethanol. The optimal triglyceride conversion was attained by using ethanol to oil ratio of 7.5:1, potassium hydroxide as catalyst was of 1.50%. Ethyl ester formed was characterized by its density, viscosity, cloud and pour points. The ethyl ester viscosity of 5.593 cSt was close to the viscosity of diesel oil of 5.8 cSt, and other properties have also similar to those of diesel oil.

Index Terms— Transeterification, candlenut oil, biodiesel

I. Introduction

Tranesterification of triglycerides and esterification of free fatty acid with ethanol are the main chemical pathways for synthesis of biodiesel. Biodiesel, a biofuel that can substitute petroleum diesel. It has gained much attention because its clean burning and renewable. In conventional of biodiesel production, methanol is used as alcohol resources. To make biodiesel a renewable energy, methanol can be replaced with ethanol such as bioethanol. Many researchers investigated with feed stocks from several kinds of seed. Candlenut (*aleurites moluccana*) is one of the seed which is now cultivated in eastern area of Indonesia. Candlenut oil has a high iodine number that is more than 125. It cause a lower of pour point. Crude candlenut oil contain more than 7% free fatty acids (FFA). It has significant effects on transesterificatioan with alcohols using alkaline catalyst [4], [7], [9], [10]. An acid catalyzed pre-treatment process with subsequent water separation steps is necessary to reduce the FFA and water concentration below the treshold limit. It can be investigated by esterification with ethanol using an acid catalyst. Crude mahua oil can be reduced from 19% to less than 1%, crude rubber seed oil reducing FFA content to less than 2% while crude candlenut oil can be reduced to 0.85% [4], [9], [11]. In addition, the acid catalyst can also be used triglyceride transesterification [6]. The acid transesterification catalyzed is much slower than alkali catalyzed and also need higher temperature and pressure condition, but the soap formation can be avoided [3]. In the absence of catalyst as in [2], they found the ester conversion was of 0% after 120 minutes reaction. Reference [1] investigated transesterification of canola oil at ambient conditions. They pointed out that one method to improve performance will be obtained by maximizing interfacial surface area. It is to enhance tha mass transfer rate. Reference [13] expressed that the initial mass transfer controlled region was not significant using an impeller speed of 600 rpm. Solid acid catalyst was used for transesterification of *Pongamia pinnata* oil . The maximum conversion of 92% was achieved. Tetrahydrofuran (THF) was used as co-solvent, the conversion enhanced to 95% [5]. A two step acid catalyzed methanolysis process was employed for production of biodiesel from rice bran oil. By two step process, more than 98% fatty acis methyl ester in the product can be obtained [14]. Reference [12] pointed out that simultaneous free fatty acid esterification and triglyceride transesterification using a solid acid catalyst has been undertaken with removal of water and unreacted methanol. Crude candlenut oil contains more than 7% of FFA. This paper discussed the findings of experiments carried out to pretreatment process for reducing the FFA content of candlenut oil below of 2% for maximum biodiesel production at ambient temperature.

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II. EXPERIMENTAL

A.. Materials

Candlenut oil is obtained from the kernel of candlenut seeds which is a medium to large tree found in most of part of eastern Indonesia. The unrefined crude candlenut oil is brown in colour. The density and viscosity were 0.9145 g/mL and 25.8940 cSt respectively. This oil had an iodine number of 137 and initial acid value of 1.5972 mgek KOH/g oil coressponding to FFA level of 7.77 % and saponification number of 3.3843

mgekKOH/g oil. The absolut ethanol of 99.61% was used , the density of 0.7836 g/mL. E-mercks potassium hydroxide is used as catalyst.

B. Equipment

Three necked of 500 mL was used a laboratory scale reactor for these experiment purposes. This reactor was equipped with mechanical stirrer, a reflux condenser, thermometer and stopper to removed samples. This reactor was also placed in the heating mantle with provided the thermostat and maintain the constant temperature, for pre-treatment process (esterification of FFA). Meanwhile for transesterification process, the heating mantle was not operated due to ambient conditions.

C. Procedure

1. Pretreatment process

A half litre of crude candlenut oil was poured into the flask and heated to about 70^{o}C, ethanol was added with the preheated crude candlenut oil and stirrer for a few minutes. Sulfuric acid was also added with the mixture to form of 0.25% by oil weight. Heating and stirring are continued for 60 minutes at atmospheric pressure. The product is then poured into separating funnel to separate the excess ethanol and sulfuric acid. Top layer was removed and the lower layer was separated for further processing (alkaline transesterification).

2. Alkaline transesterification

Alkaline catalyzed transesterification process used the experimental set-up of acid catalyzed pretreatment process. The product of pretreatment process was charged into a reactor. The potassium hydroxide was dissolved in the ethanol and the solution was fed to the reactor. It is assumed that the reaction was started as soon as all reactants and catalyst were fed into reactor. Samples were taken at following reaction time 15, 30, 45, 60 and 75 minutes. The samples were immediately quenched in water to stop reaction and two phases were performed. Samples were washed with the distilled water. After formation of two layers, the upper layer consist of ethyl esters and remaining triglyceride.

3. Analysis

The analytical methods used to calculate the glycerol concentration in the water layer (lower phase) by using periodic acid. Triglycerides conversion to ethyl esters was determined through material balance of the reaction and the initial triglycerid concentration.

III. RESULT AND DISCUSSION

A. Pretreatment process

Crude candlenut oil had a FFA content of 1.5972 mgek/g oil. It was equivalent to 7.77% of FFA. Esterification was investigated by using 4.8 mgek ethanol/mgek oil, 0.25% of sulfuric acid as catalyst, reaction temperature 70^{o}C in 1 hour raction at atsmospheric pressure. The product is then poured into separating funnel to separate the excess ethanol and sulfuric acid. It was found that the FFA content was reduced to 1.46% (less than 2%). Reference [11] has found that esterification of crude candlenut oil with methanol can reduce a FFA content from 9.78% to 0.85%.

B. Transesterification

Most of alkaline catalytic alcoholysis of vegetable oil is commonly investigated close to boiling point of the alcohol. Reference [11] investigated the methanolysis of cundlenut oil by using potassium hydroxid as catalyst. They observed the increasing conversion wass less than 3% by increasing reaction temperature from 30 to 70^{o}C. This present investigation tried to carried out at ambient condition. It could be interesting for industrial scale production because the energy consumption will be minimized. The impeller speed was set at 600 rpm, then mass transfer was negligible and the chemical reaction step was supposed to control the reaction rate.

1. Effect of ethanol to oil molar ratio

One of the most important variables affecting the ester yields is the ethanol to oil molar ratio. Stoichiometrically, the ethanol to triglycerides molar ratio required is 3: 1. In practice this is not enough to complete the reaction. Higher molar ratio is required to drive the reaction to completion at a faster rate. It is observed that lower molar ratio requires longer reaction time and lower conversion of triglycerides. In the present investigation molar ratio was chosen between 3: 1 and 9: 1. The effect of molar ratio on conversion of triglycerides is shown Fig. 1. It has been seen that conversion increases with increase in molar ratio. Fig. 1 represents the triglyceride conversion was very fast during the beginning reaction, which involved a high ethyl ester production rate at this stage. The final triglyceride conversion were almost reached in 15 minutes and the conversion then kept constant as equilibrium was approached. The optimum ester yield is obtained for the molar ratio of 7.5: 1. If further increase in molar ratio the conversion of triglycerides more or less remains the same. The excess of ethanol will move over the ester layer. The Excess of ethanol in the ester can cause decrease the flash point of the biodiesel as in [9]. It will also 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 excess of ethanol will increase the glycerin formed. It will help the direction of the equilibrium back to the reverse reaction, as in [8]. The excess of ethanol can be removed by washing with the distilled water.

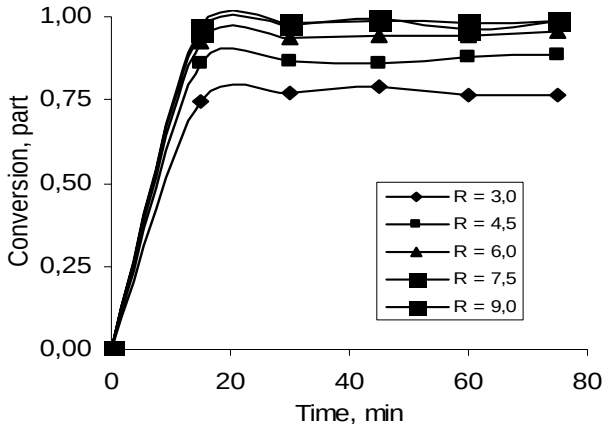

Fig. 1. Effect of ethanol to oil molar ratio

2. Effect of catalyst concentration

The potassium hydroxide concentration in the range of 0.5 – 1.5% (weight of KOH/weight of oil) is used in the present experimental. The effect of catalyst concentration on the ester yield is shown in Fig 2. The triglyceride conversion increased with increasing the catalyst concentration. Similar results were found that the triglyceride conversion reached a constant after 15 min reaction. The maximum conversion of triglyceride is achieved at 1.50% of KOH. From the results shown in Fig. 1, it can be seen by the fact that ethyl ester are significantly less viscous than candlenut oil. This lower viscosity allows a higher oxygen diffusion rate which increases contact between oxygen and the ethyl ester. These results show that the oxidative stability of the ethyl ester was retrogressive compared to that of candlenut oil and diesel fuel. However, commercial diesel fuel contains anti-oxidants and dispersants as additives for oxidative stability.

These observations suggest that transesterification of candlenut oil with ethanol to produce ethyl ester, has a high potential to be used in alternative diesel fuel production. The oxidative instability for a vegetable oil based antioxidant additive as well as other additives. However, work on production of vegetable oil based anti-oxidants and dispersants is being pursued in many laboratories.

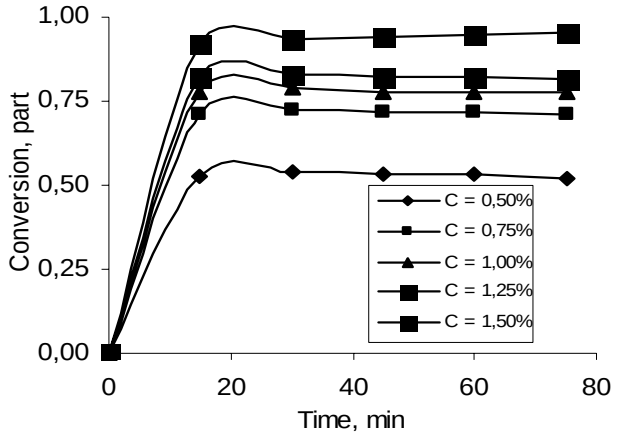

Fig. 2. Effect of catalyst concentration

C. Comparasion with previous work.

This present investigation has found that the maximum triglycerides conversion was 98.77% by pretreatment process. The FFA content in triglyceride was 1.46%. Reference [10] has found the maximum triglycerides conversion was 53.46% with FFA content in triglycerides of 9.78%. The present work has significantly improved the triglycerides conversion.

D. Biodiesel physical properties

One of most important properties of biodiesel is kinematics viscosity. Table I expressed the ethyl ester kinematics viscosity for various catalyst concentration and ethanol to oil molar ratio. Results were shown that ethyl ester kinematics viscosity depends on triglycerides conversion. The kinematics viscosity was 9.200 cSt when catalyst concentration used was 0.50% whereas the kinematics viscosity was 5.097 cSt at catalyst concentration of 1.50%

Similar result has been found for ethanol to oil molar ratio. The kinematics viscosity were 5.456 cSt and 4.916 cSt when molar ratio were 3 and 9 respectively.

Table I. Kinematics viscosity for various catalyst concentration, C and ethanol to oil molar ratio, R

C, %	μ, cSt	R	μ, cSt
0.50	9.200	3,0	5.456
0.75	6.799	4,5	5.180
1.00	5.607	6,0	5.097
1.25	5.395	7,5	5.376
1.50	5.097	9,0	4.916

Table II presented the kinematics viscosity of various compound of biodiesel and diesel oil. It was shown that all of biodiesel mixture with diesel oil have a kinematics viscosity less than 5.8 cSt (maximum value of diesel oil kinematics viscosity).The physical properties of biodiesel had similar to those of diesel oil, (Table III in an attachment).

Table II. Kinematics viscosity on various mixture of Biodiesel

Sample	Viscosity, cSt
Diesel oil	3.743
B10	3.875
B20	3.973
B30	4.466
B40	4.471
B50	4.800
B100	5.593

IV. CONCLUSION

The production of fuel quality biodiesel from high iodine number and high FFA feed stocks at ambient condition is investigated in the present study. It is found that the feed stocks with high FFA could not directly be transesterified with KOH as catalyst. The reason for this is because KOH catalyst reacts with the FFA to form soap that prevents the separation of the glycerin and ester. The high FFA level of crude candlenut oil can be reduced to less than 2% in pretreatment process of esterification using acid catalyst at 70^{o}C temperature and 1 hour reaction time. The FFA content can be reduced from 7.77% to 1.46%. The alkaline catalyst transesterification process converts the product of pretreatment process to ethyl ester and glycerol. The effects of ethanol to oil molar ratio, catalyst amount are analyzed in each step. It has been found that the triglycerides conversion is strongly affected by molar ratio of ethanol to oil. The molar ratio of 7.5:1 and 1.50% KOH as catalyst favor the completion of transesterification process with in 1 hour, at ambient conditions. This process gives a yield of

98.77% candlenut biodiesel. It was concluded that biodiesel production by ethanolysis of candlenut oil can be undertaken at ambient conditions. It would be interesting due to the energy savings and would be reduced the operating cost of production.

The biodiesel product has comparable fuel properties with that of diesel oil. The viscosity of biodiesel is nearer to that diesel oil. The flash point of biodiesel is greater than that of biodiesel standard. The present analysis reveals that biodiesel from crude candlenut oil is quite suitable as an alternative to diesel oil. However, further research and development on additional fuel property measures, long-term run and wear analysis of biodiesel fueled engine is also necessary.

The biodiesel will in the medium term find the energy supply in countries with agricultural over production or with sufficient resources of land.

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Table III. Physical properties of methyl ester, diesel oil, fuel oil and biodiesel standard

Properties		Candlenut ethyl ester B100	Candlenut ethyl ester B10	Diesel oil	Fuel oil	Biodiesel Standard (**)		
						ASTM D 6751-02	DIN EN 14214	SNI 04-7182-2006
Densities	(kg/m^3)	877.5	849.5	820 - 870	840 - 920	-	860 - 900	850 – 890
Viscosities Kinematics	(cSt)	5.593	3,875	5,8	3,6 - 7,2	1,9 – 6	3,5 - 5,0	2,3 – 6
Flash Point	(^oC)	194	80.556	> 65	> 65	>130	>120	>100
Pour Point	(^oC)	-10	6	< 18	< 18	-	-	-
Water Content	(%)	0,30	TRACE	< 0,05	< 0,25	< 0,03	< 0,05	< 0,05
Ash Content	(%)	0,0062	0,0046	< 0,01	< 0,02	< 0,02	< 0,02	< 0,01

**(Ghadge and Raheman, 2005)