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Biodiesel Preparation with Alcohol and Base Catalysed

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Abstract: Refined palm oil was neutralized with CaO (0.017 N) solution and to prepare the transesterification reaction with NaO and methanol. The experimental results: (i) the highest yield (98%), (ii) very low content % FFA (0.05%), (iii) kinematic viscosity was obtained with methanol to oil 3:1, reaction time 30 min and temperature at 60 ºC.

Keywords: biodiesel; calcium oxide; FFA; methanol; catalyses

1. INTRODUCTION

Biodiesel and bimethanol are good for the environment because they add fewer emissions to the atmosphere than petroleum-based fuels. Biodiesel is the perfect fuel for buses and trucks. Biodiesel is a biodegradable and non-toxic diesel fuel substitute that can be used in late-model. Biodiesel is actually good for diesel engines.

Biodiesel obtained from energy crops produces favourable effects on the environment, such as a decrease in acid rain and in the greenhouse effect caused by combustion. Due to these factors and to its biodegradability, the production of biodiesel is considered an advantage to that of fossil fuels. It is also known that emissions from the combustion of these fuels such as carbon dioxide, carbon monoxide, nitrogen oxides and sulphur-containing residues are the principle causes of global warming and many countries have passed legislation to arrest their adverse environmental consequences.

Biodiesel is an alternative fuel for diesel engines that can be produced from renewable feedstocks such as vegetable oil and animal fats. These feedstocks are reacted with an alcohol to produce alkyl monoesters that can be used in conventional diesel engines. Biodiesel is safe to handle and burns at a relatively high temperature.

Biodiesel actually degrades about four times faster than petroleum-based diesel fuel when accidentally released into the environment. Because it is physically similar to petroleum-based diesel fue, biodiesel can be blended with diesel fuel in any proportion. Many vehicles now use biodiesel blends in their diesel engines in United State. The most common blends is a mixture consisting of 20 % biodiesel and 80 % petroleum diesel called B20. The motive for blending the fuels is to gain some of the advantages of biodiesel while avoiding higher costs. Biodiesel is currently higher in price than conventional diesel fuel. Biodiesel is seen not as potentially replacing conventional diesel fuel, but as extending usefulness in situations where workers may be exposed to diesel exhaust for extended periods.

The chemical reaction for base catalyzed biodiesel production is depicted below. The short chain alcohol signified by ROH (usually methanol but sometimes ethanol) is charged in excess to assist in quick conversion. The catalyst is usually sodium or potassium hydroxide that has already been mixed with the methanol. R', R'' and R''' indicate the fatty acid chains associated with the oil or fat which are largely palmitic, stearic, oleic and linoleic acids for naturally occurring oils and fats.

Biodiesel Reaction

$$\begin{array}{lcl}
CH_2\text{-COO-R}' & & CH_2\text{-OH} \quad R'\text{-COOR} \\
| & & | \qquad\qquad | \\
CH_2\text{-COO-R}'' + 3\ \text{ROH} & \xrightarrow{\text{Catalyst}} & \text{CH-OH} + R''\text{-COOR} \\
| & & | \qquad\qquad | \\
CH_2\text{-COO-R}''' & & CH_2\text{-OH} \quad R'''\text{-COOR}
\end{array}$$

Triglyceride Alcohol Glycerol Ester

The National Biodiesel Board does not get involved with commercial biodiesel production or the design and construction of biodiesel facilities, but we have provided an example of a simple production flow chart along with a short explanation of the steps involved to acquaint the reader with the general production process.

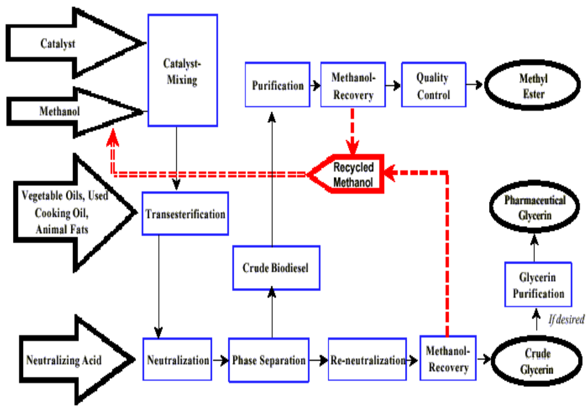

Figure 1.1 Flow Chart of Biodiesel Production Process

The base catalyzed production of biodiesel generally occurs using the following steps:

Mixing of alcohol and catalyst: The catalyst is typically sodium hydroxide (caustic soda) or potassium hydroxide (potash). It is dissolved in the alcohol using a standard agitator or mixer.

Transesterification is the reaction of a liquid with an alcohol to form esters and a by-product and glycerol. It is principle the action of one alcohol displacing another from an ester, the term alcoholysis (cleavage by an alcohol).

Reaction: The alcohol / catalyst mix is then charged into a closed reaction vessel and the oil or fat is added. The system from here on is totally closed to the atmosphere to prevent the loss of alcohol. The reaction mix is kept just above the boiling point of the alcohol (around 60 ºC) to speed up the reaction and the reaction takes place. Recommended reaction time varies from 1 to 8 hours, some systems recommend the reaction take place at room temperature. Excess alcohol is normally used to ensure total conversion of the fat or oil to its esters. Care must be taken to monitor the amount of water and free fatty acids in the incoming oil or fat. If the free fatty acid level or water level is too high it may cause problems with soap formation and the separation of the glycerin by-product downstream.

The present work aim:

To prepare biodiesel from CaO neutralized refined palm oil by transesterification process

Objectives are:

To replace the fossil fuel with biodiesel as an alternative energy

To save the foreign currency expenses in energy sector of our country.

2. EXPERIMENTAL PROCEDURES

2.1 Analysis of Refined Palm Oil

Free Fatty Acid (FFA) content was measured in refined palm oil by titration method. First, refined palm oil, alcohol, 0.02N oxalic acid, phenolphthalein indicator and methyl red indicator were prepared respectively. Then 0.02N NaOH solution was standardized with 10 ml oxalic acid and methyl red indicator. At the equivalent point, the titration was stopped and recorded this NaOH volume. Then calculation of this equation: At the equivalent point;

No of equivalent NaOH = No of equivalent of Oxalic Acid

Then 1 g of refined palm oil and 50 ml of alcohol was titrated NaOH solution. The end point was recorded and calculated with this equation;

No of equivalent FFA = No of equivalent of NaOH

In measuring viscosity, the size of viscometer is 150. Then the sample was filled into the viscometer until its limitation. This viscosity was immerged into the bath heating at the test temperature 40 ºC. Suction was used to adjust the head level of the test sample to the position in the capillary arm of the instrument about 7 mm above the timing mart. With the sample flowing freely, measured, in second to within 0.1s, the time required from the first to the second time mark. This procedure was repeated to make three times measurement of flow time. The average of the time was calculated for kinematic viscosities.

The analysis data of density, viscosity and Free Fatty Acid (FFA) content of refined palm oil was listed in Table 2.1.

Table 2.1 Properties of Refined Palm Oil

Item	Result
Density at 32º C g/cm^3	.88
Viscosity at 32º C cp	80.05
Free Fatty Acid Composition	
Palmitic acid	0.3072
Oleic acid	0.3384
Lauric acid	0.24

2.2 Neutralization Process of Refined Palm Oil with NaOH and CaO

2N NaOH, 20 % NaCL solution and phenolphthalein indicator solution to be used in neutralization process were prepared. First, sodium hydroxide and distilled water (250 ml) were prepared respectively. Then 2N NaOH solution was standardized with 10 ml oxalic acid and methyl red indicator. Then calculation of this equation;

$$N = \frac{\text{Weight of FFA}}{\text{Equivalent weight of NaOH} \times \text{volume}}$$

Finally, distilled water (250 ml) is mixed with 20 g of NaOH, the solution is 2 N NaOH.

100 ml of refined palm oil was measured and put into beaker. Then the beaker was heated in a water bath with temperature controller and the temperature is set at 50 ºC. And then 2 N NaOH solution in the burette was dropped from to the oil while stirring gently. One drop of the neutralized sample was taken in a test tube and put two drops of phenolphthalein indicator and shake well. If the sample change to pink colour, then the neutralization is completed. The mixture is transferred to separating funnel and add 20 % NaCL solution (90 ºC) and shake the separating funnel gently and allow to settle until the two layer appear sharply.

Figure 2.1 Transesterification of NaOH Neutralized oil

The lower layer is drained out. Distilled water (90ºC) is added to the upper layer in the separating funnel and sake vigorously. Settle to be sure that the two layers appear again sharply.

Figure 2.2 NaOH Neutralized Oil after Separating Distilled Water

The lower layer is drained out in a beaker and one drop of phenolphthalein indicator is added to the beaker. If the color do not change to pink, the excess NaOH is washed out of the sample is complete.

Figure 2.3 Neutralized Oil with NaOH

0.017 N CaO, 20% NaCL solution and phenolphthalein indicator solution to be used in neutralization processes were prepared First, distilled water (250 ml) and calcium oxide were prepared respectively. Then 2 N CaO solution was standardized with 10 ml oxalic acid and methyl red indicator. Then calculation of ths equation;

$$N = \frac{\text{Weight of CaO}}{\text{Equivalent weight of CaO} \times \text{volume}}$$

Finally, distilled water (250 ml) is mixed with 14.02 g of CaO, but distilled water (250 ml) is really dissolved with 0.12 g of CaO , the solution is 0.017 N CaO.

100 ml of refined palm oil was measured and put into a beaker. Then the beaker was heated in a water bath with temperature controller and the temperature is set at 50 ºC. And then 0.017 NCaO solution in the burette was dropped from to the oil while stirring gently. One drop of the neutralized sample was taken in a test tube and put two drops of phenolphthalein indicator and shake well. If the sample change to pink colour, then the neutralization is completed. The mixture is transferred to separating funnel and add 20 % NaCL solution (90 ºC) and shake the separating funnel gently and allow to settled until the two layer appear sharply.

Figure 2.4 Transesterification of CaO Neutralized oil

The lower layer is drained out and distilled water (90 ºC) is added to the upper sample layer in the separating funnel and shake vigorously. Settle to be sure that the two layer appear again sharply.

Figure 2.5 CaO Neutralized Oil after Separating Distilled Water

The lower layer is drained out in a beaker and one drop of phenolphthalein indicator is added to the beaker. If the colour do not change to pink, the excess CaO washed out of the sample is complete.

Figure 2.6 Neutralized Oil with CaO

2.3 Transesterification Process of CaO Neutralized Palm Oil

20 ml of CaO neutralized refined palm oil was poured into 250 ml conical flask with glass stopper and stirred and heated at temperature 50 ºC for a short time on a magnetic stirrer with temperature controller. Then required amount of methanol and sodium hydroxide was completely mixed form sodium methoxide solution. The molar ratio of methanol to oil is 3:1. The sodium methoxide solution was added to the heated refined palm oil slowly and stirred it for 30 mm at 60 ºC. And the two layers was observed when the stirring is stopped. The above experiment is conducted with different reaction time (1/2 hr, 1 hr, 2 hr respectively). After transesterification reaction, the product mixture was poured into the separating funnel and allowed to settle for overnight. After separation, the lower glycerol layer was drained out and the upper crude biodiesel layer was washed with warm water.

The preparation of biodiesel by the Batch Reactor is shown in Figure 2.7.

Figure 2.7 Batch Reactor for Preparation of Biodiesel

After separation, the lower glycerol layer was drained out and the upper crude biodiesel layer was washed with warm water. In washing step, warm water was added in crude biodiesel and then stirred gently and settled down until the two layers (oily layer and water layer) were separated. The upper layer was washed biodiesel and the lower layer was water-soap mixture. Then subsequent washings with warm water until the biodiesel was clear and the wash water showed to no pink colour. Washed biodiesel was dried to remove the trace water presention the oil.

3. RESULT AND DISCUSSION

Density was measured using the density bottle (25 ml) and viscosity with viscometer (150). The analysis result are listed in Table 3.1.

Table 3.1 Properties of Refined Palm Oil

Item	Result
Free Fatty Acid, %	1.56
Density at room temperature, g/cm^3	0.905
Viscosity at room temperature, mm^2/s	0.3072

The above experiment is performed with 200 ml refined palm oil also. The results of the neutralization process with NaOH are listed in Table 3.2.

Table 3.2 Neutralization Process Data with NaOH

Volume of oil (ml)	Volume of 2N NaOH (ml)	Volume of 20% NaCL (ml)	Volume of distilled water for washing (ml)	Soap Volume (ml)	Volume of neutral-ized oil (ml)
100	2	20	350	40	60
200	4	40	400	60	140

The above experiment is performed with 200 ml refined palm oil also. The results of the neutralization process with CaO are listed in Table 3.3.

Table 3.3 Neutralization Process Data with CaO

Volume of oil (ml)	Volume of 0.017N CaO (ml)	Volume of 20% NaCL (ml)	Volume of distilled water for washing (ml)	Soap Volume (ml)	Volume of neutral-ized oil (ml)
100	30	20	650	25	75
200	70	40	800	40	160

The analysis data of Free Fatty Acid (FFA) content, density and viscosity of neutralized oil was described in Table 3.4. The neutralized refined palm oil is further used in the transesterification process.

Table 3.4 Comparison Analysis Results of Neutralized Oil

Item	Refined Palm Oil	
	Neutralized with NaOH	Neutralized with CaO
Free Fatty Acid, %	0.456	0.446
Density at room temperature, g/cm^3	0.885	0.875
Viscosity at room temperature, mm^2/s	30.45	30.245

The experimental procedure of transesterification process as same as the except varying the catalyst amount from (0.2 %, ..., 1 %) and the reaction time. The experimental results were mentioned in Table 3.5.

Table 3.5 Transesterification Data with Different Reaction Time and Different % Catalyst

Volume of oil (ml)	Volume of methanol (ml)	Reaction temperature (ºC)	Reaction time	Catalyst wt. %	Amount of methyl ester (% yield)
20	6	60	10 min	0.04 g (0.2%)	15
20	6	60	20 min	0.04 g (0.2%)	17
20	6	60	30 min	0.04 g (0.2%)	19
20	6	60	10 min	0.08 g (0.4%)	14
20	6	60	20 min	0.08 g (0.4%)	16
20	6	60	30 min	0.08 g (0.4%)	17
20	6	60	10 min	0.12 g (0.6%)	15
20	6	60	20 min	0.12 g (0.6%)	16
20	6	60	30 min	0.12 g (0.6%)	18
100	30	60	10 min	0.4 g (0.4%)	85
100	30	60	20 min	0.4 g (0.4%)	92
100	30	60	30 min	0.4 g (0.4%)	98

The analysis data of Free Fatty Acid (FFA) content, viscosity and density of biodiesel was listed in Table 3.6.

Table 3.6 Properties of Product Biodiesel

Item	Result
Free Fatty Acid, %	0.05
Density at room temperature, g/cm^3	0.86
Viscosity at room temperature, mm^2/s	3.6

Free Fatty Acid (FFA) content of refined palm oil was 1.56, density at room temperature 0.905 g/cm^3 and kinematic viscosity at room temperature 80.05 mm^2/s.

The FFA content of neutralized refined palm oil with CaO decrease to 0.446 % and density is also reduce to 0.875 g/cm^3 and kinematic viscosity drop to 30.245 mm^2/s. The same trace is also resulted with neutralized palm oil with NaOH. In this study, although initial FFA content of the refined palm oil was 1.56 % neutralization process was performed before transesterification to get longer storage time of the biodiesel.

Neutralization process of refined palm oil was made with two alkali solution: (1) 2N NaOH solution and (2) 0.017N CaO solution.

Transesterification reaction at different reaction time and using different percent catalyst weight showed that best yield (0.4 %) was obtained with 0.4 % catalyst of CaO neutralized palm oil with transesterification reaction 30 min at 60 ºC using volume of methanol to oil 3:1.

In the transesterification of unneutralized refined palm oil with NaOH and methanol solution higher yield was obtained with (0.6 %) NaOH and reaction time 1 hr at 60 ºC (Transesterification process for the Preparation of Biodiesel).

Analysis data of product biodiesel listed in Table 3.6 showed that FFA content is 0.05 % and the viscosity at room temperature is 3.6 mm^2/s which meets the specification of B100, Biodiesel. Furthermore, the colour of biodiesel prepared from CaO neutralized refined oil is very pale-yellow compared with the product from unneutralized oil. Analysis results of refined palm oil sample and neutralized palm oil sample showed that by neutralizing the purity of refined palm oil is improved.

4. CONCLUSION

This study to obtain very low FFA content (0.05 %) and low kinematic viscosity (3.6 mm^2/s) refined palm oil have to be neutralized. Although the initial FFA content of the refined palm oil from the market is 1.56 %. Neutralization process also provided increase in yield and improve quality of biodiesel. However further scale up works need to be continued from this findings.

5. RECOMMENDATIONS

Recommendations for further research works are outlined as follow.

- Experiment with rapid study in transesterification process must have to be performed to reduce the reaction time.
- Experimental words on boidesel preparation with high fatty acid need to be studied.
- Other base-catalyzed (NaOH, KOH, CaO and $CaCO_3$) should be tested to use for the preparation of biodiesel.

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