The Properties of Biodiesel Using Ultrasonic Continues Process

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INTRODUCTION

Biodiesel is a fatty acid methyl ester. Biodiesel or fatty acid methyl ester is a clean burning alternative fuel. Biodiesel can be made from any vegetable oil including oils pressed straight from the seed such as soybeans, sunflower, canola, olive oil, and coconut. Biodiesel also can be made from waste cooking oil, animal fats and non-edible oils such jatropha curcas oil (JCO). The concept of using vegetable oil for fuel has been around, as long as the diesel engine. Most vegetable oil can be converted into biodiesel but the cost of the vegetable oil feedstock is now a factor. However, one of non-edible oil is JCO have potential to become biodiesel fuel compared with vegetable oil have would disturb the food market.

In facts, JCO cannot be used for nutritional purposes without detoxification this makes its use as energy or fuel source very attractive especially biodiesel. In Madagascar, Cape Verde and Benin, JCO was used as mineral diesel substitute during the Second World War.[1] JCO is a multipurpose bush and small tree belonging to the family of Euphorbiaceae. It is a plant with many attributes; multiple uses and has considerable potential. The plant can be used to prevent and control erosion, to reclaim land, grown as a live fence, especially to contain or exclude farm animals and be planted as a commercial crop. It is a native of tropical America, but now thrives in many parts of the tropics and sub-tropics in Africa and Asia. The wood and fruit of Jatropha can be used for numerous purposes including fuel. The seeds of Jatropha contain viscous oil, which can be used to manufacture candles and soap, in cosmetics industry, as a diesel and paraffin substitute or extender. This latter use has important implications for meeting the demand for rural energy services and also exploring practical substitutes for fossil fuels to counter greenhouse gas accumulation in the atmosphere. These characteristics along with its versatility make it of vital importance to developing countries. [2]

In view of these, the jatropha curcas is suitable and more advantages to be converted biodiesel. These vegetable oils are more suitable source for biodiesel production compared to animal fats and waste cooking oil since they are renewable in nature. However, there are concern that biodiesel from vegetable oil would disturb the food chain. Oil from jatropha is an acceptable choice for biodiesel production because it is non-edible and can easily grow in harsh environment. [3] Moreover, alkyl ester of JCO meets the biodiesel standard in many countries.
**Experimentation:**
In the experiment of biodiesel production process in the optimal stages consist of preparation of sample, acid catalyse esterification, followed by base catalysed transesterification and purification.[4] On the other hand in the applied stage in order to ensure the project will satisfy the application in small medium industry, the optimum parameter transesterification process from optimal stages was use to run a small biodiesel pilot plant. The experimental procedure is shown in the flow chart Figure 1.

**Preparation of sample:**
Jatropha curcas oil must be filtered to remove residues by vacuum filter. After this, the filtered jatropha curcas oil was tested for free fatty acid (FFA) content. Free fatty Acid value was determined by method AOCS Ca5a-40 to estimate the free fatty acid content. If FFA content above 1% it must be processed with acid catalysed esterification to remove FFA.[4]

**Acid catalysed esterification:**
Acid catalysed esterification is to reduce the free fatty acid (FFA) by converting it into esters. After titration was performed and the feedstock is more than 2%, esterification process will be performed. Theoretically, esterification also will increase the yield of biodiesel. In this process methanol and sulphuric acid (H2 SO4) was used. This process used alcohol and acid catalyst based on the ratio that been referred to previous study which is methanol to oil ratio is 18:1 and the catalyst is 0.5%. The experiment was carried out using ultrasonic in line reactor which include ultrasonic generator to control ultrasonic parameter. Ultrasonic in line reactor with frequency of 20kHz.[5][6] The fixed output power selected at 600Watt. The 600 watt is the power limit for this reactor. Increasing the power over this limit would mechanically over-stress the reactor tube and could cause damage. 1000g of JCO per batch was heated at 65°C. Firstly, powder NaOH was dissolved completely in methanol (MeOH) and then the mixture of MeOH- NaOH was added with JCO and heated together at 65°C.

Fig. 1: Flowchart of methodology.
around 20 minutes. After this, all the mixture is added to the in line reactor. As soon as the mixture NaOH-MeOH was added to JCO, the time was noted and the reaction was carried out for 15 minutes. After the reaction completed, the mixture was allowed to settle down for one hour and the methanol water fraction at the top layer was removed refer Figure 2.

**Fig. 2:** Shows the layers of methanol water fraction and the JCO.

**Alkaline base catalyzed transesterification:**

In alkaline base catalyzed transesterification, the reaction mixture consisted of esterification of jatropha oil with methanol and alkaline catalyst sodium hydroxide (NaOH) were investigated for methanol to oil molar ratio and catalyst to oil ratio. Furthermore, it focused on the reduction of reaction time. The alkaline base catalyzed transesterification ultrasonic process was carried out to study the effect of reaction time from 3, 5 and 7 minutes and molar ratios of methanol to oil 6:1, 7:1 and 9:1. These optimal reaction parameters in methanol to oil molar ratios were used in additional experiment to investigate the quantity of NaOH as a catalyst. The quantity of NaOH was 1wt% to the weight of jatropha oil. The mixture was left two hours to separate the glycerol and the methyl ester of fatty acids layer.[7][8] The in line ultrasonic reactor was adjusted to 20 kHz. The fixed output power selected at 600 watt. In this experiment methanol was used because of its lower cost and easily available compared to other alcohol like ethanol and butanol propanol. For the catalyst, sodium hydroxide (NaOH) will be used. This catalyst have been chosen because it is safe to use and of its fast reaction. Figure 3 show the transesterification reaction.

**Fig. 3:** Transesterification result.

**Purification:**

Investigation on the purification process was done to evaluate the effect of water concentration at 5, 10 and 20 v/v with output power of ultrasound in line reactor 600w. The ultrasonic in line frequency adjusted to 20 kHz. The optimal parameters in water concentration without output power were used in additional experiment to verify the influence of processing at 3, 5 and 7 minutes. The sample oil after purification was analyzed using physical properties test and chemical properties test. Biodiesel purification is an important process because to remove glycerin, soap excess of alcohol and residual of catalyst.[9][10] PH paper is used in this process to determine the soap content of biodiesel. This process was repeated for several times to ensure the value of biodiesel is in neutral condition (pH7). Figure 4 shows the separation in purification process.
**Fig. 4:** Separation in purification process.

**Physical Properties of Biodiesel:**

The standard properties for biodiesel are important so that they meet ASTM D 6751 or EN 14214 standard. The properties of biodiesel depend very much on the nature of raw material as well as the technology or process used for its production. In this respect, the requirement standard has specified relevant parameters to govern the quality of biodiesel fuel. In the physical properties by ASTM D6751 and EN14214 list all the important physical properties like density, flash point, acid value, water content and kinematic viscosity.[11]

**RESULT AND DISCUSSION**

**Jatropha Curcas Oil (JCO) before Esterification Process:**

Physical properties can be observed or measured without changing the composition of matter. Table 1 shows the properties of jatropha curcas oil (JCO) before esterification process. It shows the high free fatty acid, kinematic viscosity, water content, acid value and density.

<table>
<thead>
<tr>
<th>Water content (%)</th>
<th>Kinematic viscosity (mm²/s)</th>
<th>Acid Value %</th>
<th>FFA (%)</th>
<th>Density (g/cm³)</th>
<th>Flash point (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.256</td>
<td>25.6</td>
<td>&gt; 12.4</td>
<td>&gt;10.1</td>
<td>0.92</td>
<td>240</td>
</tr>
</tbody>
</table>

**Esterification Process:**

In this study, the pre-treatment step was carried out by following the esterification reaction. Firstly, the jatropha curcas oil (JCO) was heated at 65°C. After this add mixture acid sulphuric and methanol into the reactor containing the heated JCO mixing together. The ratio of methanol to JCO ratio was 18:1 and the time of reaction at 65°C.

After the reaction was completed, the mixture was allowed to settle down for one hours and the methanol water fraction at the top layer was removed. After that, the free fatty acids (FFA) content of the sample was determined using acid base titration technique. A standard solution of 0.1N sodium hydroxide (NaOH) solution was used. Others properties like kinematic viscosity, density, acid value and water content was obtained as in Table 2. The important physical property need to identify before transesterification process is FFA. Without prior removal of FFA, large quantity of fatty soap was formed in the reaction and the entire products become gel-like materials. Table 4.3 shows the properties test after the esterified process.

<table>
<thead>
<tr>
<th>Water content (%)</th>
<th>Kinematic viscosity (mm²/s)</th>
<th>Acid Value (Mg KOH/g)</th>
<th>FFA (%)</th>
<th>Density (g/cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.164</td>
<td>4.5</td>
<td>0.402</td>
<td>0.402</td>
<td>0.9036</td>
</tr>
</tbody>
</table>

**Transesterification Process:**

The result of all the tests done on each of biodiesel samples from 3, 5 and 7 minutes reaction time with different molar ratio are brought fort into table form. The result included the kinematic viscosity, density, yield of biodiesel, flash point, water content and acid value. The results of all testing for each biodiesel samples are shown in Table 3.

**Graph analysis:**

All the data is analysed, this data will be presented in graphical form so that it is better understood and more easily analysed. In this study the graphs of biodiesel yield, kinematic viscosity, water content, density and flash point.
Table 3: Result of all testing for each biodiesel sample.

<table>
<thead>
<tr>
<th>Molar ratio</th>
<th>Reaction time (minute)</th>
<th>Biodiesel yield (%)</th>
<th>Kinematic viscosity (mm²/sec)</th>
<th>Acid value (mg KOH/g)</th>
<th>Density (g/cm³)</th>
<th>Flash point (°C)</th>
<th>Water content (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6:1</td>
<td>3</td>
<td>85</td>
<td>4.4</td>
<td>0.28</td>
<td>0.890</td>
<td>160</td>
<td>0.050</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>87</td>
<td>4.15</td>
<td>0.28</td>
<td>0.886</td>
<td>168</td>
<td>0.048</td>
</tr>
<tr>
<td></td>
<td>7</td>
<td>89</td>
<td>4.10</td>
<td>0.28</td>
<td>0.893</td>
<td>175</td>
<td>0.045</td>
</tr>
<tr>
<td>9:1</td>
<td>3</td>
<td>83</td>
<td>3.9</td>
<td>0.28</td>
<td>0.903</td>
<td>178</td>
<td>0.050</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>85</td>
<td>4.0</td>
<td>0.28</td>
<td>0.895*</td>
<td>180</td>
<td>0.043</td>
</tr>
<tr>
<td></td>
<td>7</td>
<td>87</td>
<td>3.9</td>
<td>0.28</td>
<td>0.895*</td>
<td>200</td>
<td>0.039</td>
</tr>
<tr>
<td>12:1</td>
<td>3</td>
<td>82</td>
<td>3.8</td>
<td>0.28</td>
<td>0.881</td>
<td>170</td>
<td>0.046</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>84</td>
<td>4.86</td>
<td>0.28</td>
<td>0.854</td>
<td>184</td>
<td>0.040</td>
</tr>
<tr>
<td></td>
<td>7</td>
<td>86</td>
<td>4.73</td>
<td>0.28</td>
<td>0.849</td>
<td>190</td>
<td>0.042</td>
</tr>
</tbody>
</table>

Biodiesel yield analysis:

There are many factors that could affect the yield of biodiesel. The factor such as types of feedstock, content of free fatty acid, the amount of alcohol, molar ratio and reaction time. In this study, the molar ratio and reaction time was used as a constraint on JCO to produce the biodiesel.

Figure 5 shows the graph of biodiesel yield against reaction time. The graph shows three different lines representing three types of molar ratio. All three lines showed an increase, where the line molar ratio 6:1 shows the high yield production while molar ratio 12:1 shows the lowest production. The line molar ratio 9:1 is located midway between the line molar ratio 6:1 concentration and molar ratio 12:1. From the graph, it has been observed the three-lines at the inception are different. It can observe that the production yield increasing with increasing the reaction time and decrease with molar ratio.

Fig. 5:

Acid value analysis:

The acid number or acid value indicated the quantity of free fatty acid and mineral acids present in the biodiesel sample. The acid value also affects the significant role in the quantity control of feedstock. The acid value is defined as the miligrams of sodium hydroxide required to neutralize the free acids in 1g of sample. The acid value of this biodiesel varied from low 0.301 to 0.455mg NaOH/g and there were less than the 0.5 mg NaOH/g specified as the maximum value according to ASTM standard.

In figure 6, the graph of acid value against reaction time shows three lines from different amount of catalyst. The graph show the acid value were increased with the increasing of reaction time. The acid numbers of biodiesel were influenced by reaction times, in which increasing reaction time would increase in the value of acid number.[12]

Fig. 6: Graph of acid value against reaction time.
Based on Figure 6, it is relatively high acid value and close to the limit ASTM standard. From the observation, the high acid value mainly depends on the kinds of oil used as raw material. The acid value can increase during storage period because of hydrolysis of fatty acid.

**Flash point analysis:**
The flash point temperature of biodiesel fuel is the minimum temperature at which the fuel will ignite flash on application of an ignition source. Flash point varies inversely with the fuel’s volatility. Minimum flash point temperatures are required for proper safety and handling of biodiesel fuel. This will be relatively consistent for all feedstock presuming reaction completion and if the alcohol is distilled or washed out. According to the ASTM standard, the minimum flash point reading for biodiesel is 93°C. Flash point and fire point are important temperatures specified for safety during transport, storage, and handling.

The results obtained showed in Figure 7 that all the biodiesel produced in this study had a flash point in the range 160°C to 200°C. The higher value occurred at the 5 minutes reaction time in which the molar ratio 9:1. Meanwhile, the lower flash point value occurred at 3 minutes reaction time in the line molar ratio 6:1. The value of flash point increased when time reaction increased. Figure 7 show the flash point against reaction time.

For these studies, it obtained high value for the flash point and shows the higher than the minimum point in ASTM standard. The higher value of flash point is better because a liquid with a higher flash point is less likely to auto ignite and is thus less of a fire hazard and making its safer to transport, use, and store.

**Conclusion:**
Biodiesel is primarily produced in batch reactors. Ultrasonic biodiesel processing allows for the continuous in line processing. Ultrasonication increased the biodiesel yield to about 82% until 89%. Ultrasonic reactors reduce the esterification process from 2 hours using conventional to 20 minutes with Figure 7: Flash point against reaction time.

The flash point temperature of the JCO biodiesel is higher than that of conventional diesel, because the JCO biodiesel do not have the light fractions. [13] The safety of the JCO biodiesel is ensured due to higher flash point temperature. The low flash point reading might have been caused by the incomplete reaction during the transesterification process due to the short period of reaction time given. The higher content of excess methanol in biodiesel samples could affect the measure of the flash point. [14]

For these studies, it obtained high value for the flash point and shows the higher than the minimum point in ASTM standard. The higher value of flash point is better because a liquid with a higher flash point is less likely to auto ignite and is thus less of a fire hazard and making its safer to transport, use, and store. [15]
saves energy and effort to process the biodiesel. Another benefit is the resulting increase in the purity of the glycerin. The process can be converted from batch to continuous, substantially increasing the production scale.

In conclusion, free fatty acid (FFA) contents in the JCO were found to be high about >10%, the FFA content in the oil was reduced via esterification of JCO with methanol and sulphuric acid as a catalyst. In this study, the effects of esterification parameters namely the time of reaction, temperature, catalyst-to-JCO oil ratio and methanol-to-JCO oil ratio on the final free fatty acid content of JCO were studied.[16] The final FFA content of JCO was successfully lowered to 0.402 % at 65°C reaction temperature, using 1% of catalyst-to-JCO ratio, 18:1 of methanol-to-JCO oil ratio, and 20 minutes of reaction time. Without prior removal of FFA, a large quantity of fatty soap was formed in the reaction and the entire products become gel-like materials. However, after using two-steps reaction consisting of the esterification followed by transesterification, the yield and quality of product are markedly enhanced.

In the transesterification process, JCO was carried out using methanol as excess reactant in the presence of sodium hydroxide (NaOH) as alkaline catalyst. The experimental works were carried out at reaction temperature 65°C, at various reaction times of 3 minutes, 5 minutes and 9 minutes, at 6:1, 9:1 and 12:1 at molar ratio and 1% catalyst concentration. From the transesterification process the optimum condition was achieved when molar ratio methanol to oil 6:1 and 1% catalyst concentration in 7 minutes. All samples of JCO biodiesel then have been tested for several properties which were acid value, density, water content, flash point and kinematic viscosity. The biodiesel was characterized for its physical properties using ASTM standard methods for JCO biodiesel.[17]

Biodiesel purification is an important process because to remove glycerine, soap excess of alcohol and residual of catalyst. The pH paper is used in this process to determine the soap content of biodiesel. This process was repeated for several times to ensure the value of biodiesel is in neutral condition (pH7).

As the conclusion, Jatropha curcas oil represents the potential substance as new source energy to yield the ester methyl (biodiesel) as substitution of diesel oil. Furthermore, all the physical properties of biodiesel from jatropha oil were meets the standard of biodiesel in many countries. That shows the jatropha curcas is suitable and more advantages to converted biodiesel.[18]

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REFERENCES


Amin Talebian-Kiakalaieh, Nor Aishah Saidina Amin, Hossein Mazaher, 2013. A review on novel processes of biodiesel from waste cooking oil, applied energy, 104.


