A Study of Biodiesel Production from Crude Jatropha Oil (CJO) with High Level of Free Fatty Acids

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Abstract

A two step-transesterification process was adopted to produce biodiesel from crude jatropha oil in lab scale and pilot plant. The crude jatropha oil used was sourced with high different level of free fatty acids. The first sample (FFA=4.5%) was subjected to pretreatment step under reaction condition of 0.225 v/v sulfuric acid (H2SO4), 6:1 w/w methanol (MeOH) to oil mole ratio, reaction temperature of 65°C, and 180 min of reaction time. Meanwhile, the second jatropha oil sample (FFA=8%) was subjected to pretreatment process in pilot plant under reaction condition of 0.225 v/v sulfuric acid (H2SO4), 4.5:1 w/w methanol (MeOH) to oil mole ratio, reaction temperature of 65°C, and 180 min of reaction time. Moreover, the esterifies oil from both jatropha oil samples was subjected to alkaline base step using base-catalyst process parameters of 1.2 w/w potassium hydroxide (KOH), 4.5:1 w/w methanol to oil mole ratio, reaction temperature of 60°C, and 120 min of reaction time. The final biodiesel yield obtained was 82% and 90% from the first and the second jatropha oil sample respectively. The basic physiochemical properties of the jatropha methyl ester produced from both jatropha oil samples were found to be within the ASTM D6751 specified limits.

Keywords: Transesterification; biodiesel; jatropha oil; free fatty acid (FFA)

1.0 INTRODUCTION

Interest in production of biodiesel from crude jatropha oil is growing in many countries. It is driven by the fact that jatropha can grow and produce on land that is marginal for agriculture, and that the production of biodiesel from crude jatropha oil can reduce imports of petroleum products, can stimulate rural and regional economies, and that the plantings can be as a combination of industrial-scale plantings and small-holder plantings, and because there is potential for a number of different products from the oil and by-products.
For the large scale biodiesel production from crude jatropha oil (CJO), the price of CJO has the largest input cost. However, the costs of other chemicals are also significant. Optimizing the amounts of these chemicals along with other parameters such as reaction temperature and time indicates that real savings can be made in time and chemical cost, which significantly improves operating economics.

### 2.0 TRANSESTERIFICATION PROCESS

Transesterification is the chemical reaction between triglycerides and alcohol to form an ester and glycerol with or without the presence of catalyst [1]. This process is also known as alcoholysis. Generally, the yield of transesterification can be enhanced by adding catalyst. The reaction is represented in Figure 1, where the mechanism of transesterification consists of three reversible reactions, in which the triglycerides are converted into diglycerides followed by conversion to monoglycerides, and then lastly converted into glycerol, producing one ester at each conversion stage [1-3]. Transesterification is regarded as the best method among other biodiesel production methods, due to its low cost and simplicity [1].

![Figure 1 Stoichiometric transesterification of triglycerides [1-3]](image)

Transesterification can be categorized into two main types, which are the catalytic and non-catalytic methods. Catalytic transesterification includes alkaline-catalyzed reaction, acid-catalyzed reaction and enzyme-catalyzed reaction. Non-catalytic transesterification is commonly referred to as supercritical methanol (SCM) transesterification. At present, conversion of vegetable oils into biodiesel is usually performed using alkaline-catalyzed transesterification. This is due to its effectiveness of alkaline catalyst. Moreover, the process is less corrosive compared to the use of acid and enzyme-based catalysts [3].

The transesterification reaction is affected by various parameters depending on the reaction conditions. If the parameters are not optimized, either the reaction is incomplete or the yield is reduced to a significant extent. Each parameter is equally important in order to achieve a high quality biodiesel which meets the regulatory standards [4]. The maximum yield of biodiesel should be reached when the values of these variables are optimized. Some of these variables are molar ratio of alcohol to oil, concentration of catalyst, reaction time and reaction temperature.

#### 2.1 Molar Ratio of Alcohol to Oil

One of the most important variables affecting the conversion to methyl esters is the molar ratio of methanol to vegetable oil. Stoichiometric transesterification of triglycerides requires ratio of three moles of alcohol and one mole of triglyceride to produce three moles of fatty acid alkyl ester and one mole of glycerol [4]. Normally, excess alcohol is used to transesterify the oil completely to the ester. Base-catalyzed transesterification of oil with FFA less than 1% requires molar ratio of methanol to oil of 6:1. Nevertheless, transesterification of oil with high FFA content by using acid catalyst will require molar ratio up to 24:1 [3].

#### 2.2 Concentration of Catalyst

Catalyst has an optimum range of concentration that will produce highest yield in transesterification process. Sulphuric acid is a common catalyst that works best in the range of 1.5-2.25 M concentration [4]. Base catalysts, on the other hand, are more effective than acid catalyst as they react faster. High conversion rate of above 90 % for sodium hydroxide occurs at 1.0 to 1.4 % (w/w), whereas that for potassium hydroxide occurs at 0.55 to 2.0 % (w/w) [3]. Further increase in catalyst concentration does not affect the conversion but adds extra cost, as the catalyst needs to be removed from the reaction mixture after completion of the reaction. Moreover, the yield of biodiesel was reduced if the alkali catalysts were used at above their optimum concentration as this causes more soap formation [5].

#### 2.3 Reaction Temperature

The rate of reaction is strongly affected by the reaction temperature. However, the reaction temperature is limited by the boiling point of the alcohol, as temperature above the boiling point of the alcohol will vaporize the alcohol, causing lower transesterification yield [4]. For instance, a base-catalyzed transesterification by using methanol (boiling point: 60 – 70 °C at atmospheric pressure) is conducted at temperatures of 40 to 100°C. However, the optimum temperature is 60°C and increase in temperature above this point will result in a reduction in yield [3].

#### 2.4 Reaction Time

The methylester conversion rate increases with the reaction time. The reaction starts slowly due to the mixing and dispersion of alcohol into the oil, then, the reaction proceeds faster until maximum yield is reached [6]. For its higher reactivity base-catalysed transesterification requires less time than acid-catalysed. The maximum biodiesel yield can be reached in a reaction time of 120 minutes or less in case of base-catalyzed transesterification [7], while it can go for up to 180 minutes for acid-catalysed transesterification.

Moreover, prolonged reaction time will cause backward reaction of transesterification, forming soap [3,4]. Besides, there are other variables affecting transesterification process such as free fatty acids, moisture and water content, rate and mode of stirring, purification of the final product, mixing intensity, and effect of using organic co-solvents [8].

### 3.0 RESEARCH BACKGROUND

Jatropha oil is a triglyceride type of non-edible vegetable oil. Its biodiesel is considered as a potential alternative to fossil diesel fuel. This is due to the fact that its methyl ester properties are similar to diesel fuel and also because the plant has the ability of absorb CO₂ from the atmosphere [2]. However, direct burning of jatropha oil in diesel engine faces many problems...
because of its high viscosity. This high viscosity is due to the oil’s high molecular weight which is around ten times higher than the diesel ones. Therefore, reduction in viscosity is very important to make Jatropha oil a suitable alternative fuel to diesel. This can be achieved by the transesterification process [1, 2].

Crude jatropha oil has a wide range of FFA contents with different composition range as shown in Table 1 and Table 2, and the FFA are usually beyond the optimum level for alkaline transesterification to occur [9]. Alkaline-catalyzed transesterification of high-FFA oils will lead to soap formation which makes separation of the products difficult. Despite acid catalyst not having this issue; it is also not practical due to its long reaction time. Thus, a two-step transesterification is introduced as the best approach where the CJO is pretreated with acid-catalyzed esterification to reduce the FFA content to less than 1%, followed by base-catalyzed transesterification of the CJO to fatty acid methyl ester (FAME) [10,11].

### Table 1 Free fatty acid content of crude jatropha oil

<table>
<thead>
<tr>
<th>Free fatty acid content (FFA %)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.23 ± 0.02</td>
<td>[12]</td>
</tr>
<tr>
<td>2.71</td>
<td>[13]</td>
</tr>
<tr>
<td>3.4</td>
<td>[14]</td>
</tr>
<tr>
<td>7.3</td>
<td>[11]</td>
</tr>
<tr>
<td>14.9</td>
<td>[15]</td>
</tr>
<tr>
<td>21.5</td>
<td>[16]</td>
</tr>
<tr>
<td>22.6</td>
<td>[17]</td>
</tr>
</tbody>
</table>

### Table 2 Fatty acid composition of crude jatropha oil

<table>
<thead>
<tr>
<th>Fatty acid</th>
<th>Composition (%)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lauric (C12:0)</td>
<td>Range a Range b</td>
<td>0.1</td>
</tr>
<tr>
<td>Myristic (C14:0)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Palmitic acid (C16:0)</td>
<td>14.2</td>
<td>11.3</td>
</tr>
<tr>
<td>Palmitoleic (C16:1)</td>
<td>1.4</td>
<td>-</td>
</tr>
<tr>
<td>Stearic acid (C18:0)</td>
<td>6.9</td>
<td>17</td>
</tr>
<tr>
<td>Oleic acid (C18:1)</td>
<td>43.1</td>
<td>12.8</td>
</tr>
<tr>
<td>Linoleic (C18:2)</td>
<td>34.4</td>
<td>47.3</td>
</tr>
<tr>
<td>Linolenic acid (18:3)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Arachidic (C20:0)</td>
<td>-</td>
<td>4.7</td>
</tr>
<tr>
<td>Behenic (C22:0)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Saturates (%)</td>
<td>21.1</td>
<td>-</td>
</tr>
<tr>
<td>Unsaturates (%)</td>
<td>78.9</td>
<td>-</td>
</tr>
</tbody>
</table>

**a,b,c,d,e** Data obtained from ref [3,18,19,20,21] respectively.

1 Data provided by Biofuel Biomass Sdn. Bhd.

### 3.1 Acid-Base Catalyst

Improper handling and storage of CJO leads to increase in FFA as a result of chemical reactions such as hydrolysis and polymerization. It has been reported that complete transesterification will not occur if the oil contains a high percentage of FFA [2]. Among the many proposed pretreatment methods, the esterification of FFA with methanol in the presence of acidic catalysts is the most commonly applied method. The acid catalysts will utilize the free fatty acids in the oil and convert them into biodiesel [1]. The successful pretreatment of the high FFA of jatropha oil to less than 1% has been reported by many researchers. Berchmaus and Hirata [15] reported reduction of the FFA of Jatropha oil from 14.9% to less than 1%, in combination of 1% w/w of H2SO4, 60% w/w methanol to oil ratio and reaction time of 1 hour at 50°C. The FFA content of crude Jatropha oil was also reduced successfully from 21.5% to less than 1% by Siddharth Jain and M.P. Sharma [22]. They used optimum parameter values of 1% w/w H2SO4, 3:7 w/w of methanol to oil ratio, reaction temperature of 65°C and 180 min of reaction time. Azhari [23] found that using of 1%w/w H2SO4, 60%w/w of methanol to oil ratio, reaction temperature of 60°C and 180 min of reaction time can decrease the FFA of jatropha oil from 25.3% to 0.5%. Patil and Deng [24] have achieved a high yield of biodiesel from Jatropha curcas oil by decreasing the FFA from 14% to less than 1%. They used pretreatment conditions of 6:1 methanol to oil ratio, 0.5% (v/v) of H2SO4 at 40°C and 120 min. A summary of these approaches is reported in Table 3.
3.2 Alkaline-Based Catalyst

The primary parameters relevant to biodiesel production by transesterification of vegetable oils by alcohol using a base catalyst are the FFA content and moisture content. The FFA content of CJO is vary and depends on the quality of the feed stock [24]. High number of this fatty acid will result incomplete reaction and low yield of biodiesel due to soap formation. However, the main alkaline base catalysts used are NaOH and KOH. High production yield of 99% has been achieved by using KOH catalyst in concentration of 1 w/w, 6:1 mol of methanol to oil ratio, reaction temperature of 65°C and 60 min of reaction time [30]. Many others researchers reported high production yield in different process parameters. Some of their works are listed in Table 4.

<table>
<thead>
<tr>
<th>Initial FFA (%)</th>
<th>Process parameters</th>
<th>Reaction condition</th>
<th>MeOH to oil ratio</th>
<th>Final FFA (%)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>14.9</td>
<td>H₂SO₄ (1.0% w/w)</td>
<td>60 min, 50°C</td>
<td>60% w/w</td>
<td>1</td>
<td>[15]</td>
</tr>
<tr>
<td>21.5</td>
<td>H₂SO₄ (1.0% w/w)</td>
<td>180 min, 65°C</td>
<td>30% v/v</td>
<td>1</td>
<td>[22]</td>
</tr>
<tr>
<td>25.3</td>
<td>H₂SO₄ (1.0% w/w)</td>
<td>180 min, 60°C</td>
<td>60% w/w</td>
<td>0.5</td>
<td>[23]</td>
</tr>
<tr>
<td>14</td>
<td>H₂SO₄ (0.5wt %)</td>
<td>120 min, 45±5°C</td>
<td>6:1 mol</td>
<td>1</td>
<td>[24]</td>
</tr>
<tr>
<td>14</td>
<td>H₂SO₄ (1.43%v/v)</td>
<td>88 min, 60°C</td>
<td>28% v/v</td>
<td>1</td>
<td>[25]</td>
</tr>
<tr>
<td>6.85</td>
<td>H₂SO₄ (0.5% w/w)</td>
<td>60 min, 50°C</td>
<td>9:1 mol</td>
<td>1.12</td>
<td>[26]</td>
</tr>
<tr>
<td>12.5</td>
<td>H₂SO₄ (3.0 %w/w)</td>
<td>20 min, 30°C</td>
<td>15% w/w</td>
<td>&lt; 3</td>
<td>[27]</td>
</tr>
<tr>
<td>-</td>
<td>H₂SO₄ (0.5 %w/w)</td>
<td>90 min, 55-57°C</td>
<td>13% w/w</td>
<td>1</td>
<td>[28]</td>
</tr>
<tr>
<td>14</td>
<td>H₂SO₄ (1.0% w/w)</td>
<td>120 min, 70°C</td>
<td>12% w/w</td>
<td>1%</td>
<td>[29]</td>
</tr>
</tbody>
</table>

### 4.0 MATERIALS AND METHODS

In this work, two different types of crude jatropha oil (CJO) were used. For lab scale, CJO sourced from the Republic of Sudan was used to produce biodiesel in optimum process parameters. The jatropha curcas seeds were provided from a jatropha plantation located at Kosti in the centre of Sudan. After extraction using a mechanical expeller, the oil was processed for experimentation in the Laboratory of Oils and Fats, Department of Chemical Engineering, Institute of Technology, Bandung. For the pilot plant, the crude jatropha oil (CJO) was purchased from Bionas SDN Bhd Company in Kuala Lumpur and processed for experimentation in a pilot plant located in FKKSA, Universiti Malaysia Pahang. All chemicals used in the production processes and analysis methods were obtained in their analytical grade. Sulfuric acid (H₂SO₄) was used as catalyst with methanol for the esterification process, while potassium hydroxide (KOH) was the base catalyst selected over sodium hydroxide (NaOH) to enhance the reaction for the second step of the transesterification process. The main physiochemical properties of each CJO sample were determined as per standard methods and reported in Table 5.

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**Table 3** Optimized conditions for esterification of crude jatropha oil

**Table 4** Optimized conditions for Transesterification of Jatropha curcas oil

**Table 5** Physiochemical properties of crude jatropha oil (CJO) from different sources
5.0 EXPERIMENTAL PROCEDURE

The following experimental procedure was adopted for the production of biodiesel in lab scale and pilot plant. Due to the high fatty acid number of the selected jatropha samples, the transesterification process is conducted in two steps. H$_2$SO$_4$ is used as acid catalyst to reduce the FFA to less than 1% in the esterification step, while KOH was used as base catalyst to produce the methyl ester from the esterified oil. The detail procedure is described for both lab scale and pilot plant.

5.1 Production of Biodiesel from Jatropha Oil in Lab Scale

5.1.1 Acid Pretreatment Step

At the lab scale, experiments were performed using the crude jatropha oil without preheating. A three-necked round-bottomed flask was filled with a mixture of 200 g of crude jatropha oil and methanol in a concentration of (6:1 w/w oil).

A water-cooled condenser and a thermometer with cork were connected to the side openings on either side of the round-bottomed flask. The mixture was warmed up to 50°C by placing the round-bottomed flask in a heater and stirred using a magnetic stirrer fixed into the flask as shown in Figure 2(a). At that point, H$_2$SO$_4$ at ratio of 0.225% (v/v oil) was added to the mixture and the reaction was conducted for three hours at maintained temperature of 65°C.

After the reaction was completed, the reacted mixture was poured into the separating funnel and allowed to separate and settle the methanol phase for 30 minutes to separate the methanol phase as shown in Figure 2(b). Before starting the second step, the FFA was analyzed and found to be within the desired range for the next step. This esterified oil was subjected to base-catalyzed reaction.

5.1.2 Base Catalyzed Step

The esterified oil from the first step was poured into the round-bottomed flask. The required amount of catalyst KOH (1.2% w/w oil) was weighed and dissolved completely in methanol (4.5:1 w/w oil) to form potassium methoxide. Meanwhile, the esterified oil was warmed up, and the prepared methoxide was added into the oil at 60°C.

The reaction conducted in vigorous mixing for two hours then, it has been allowed to separate and settle in a funnel for 30 min to remove the glycerol layer which was formed in the bottom of the funnel as shown in Figure 2(c). The final product in the funnel after 30 min settling was a clear, golden liquid biodiesel without glycerol layer as shown in Figure 2(d).

5.1.3 Sample Treatment

In this step, the produced methyl ester was washed several times with warm distilled water at 50 °C till the pH of the water was less than 8 as shown in Figure 2(e). To remove the moisture, the final product was heated up to 70°C for 30 min under vacuum condition.

This resulted in a clear light liquid with a viscosity close to petro-diesel as shown in Figure 2(f). The final yield was found to be 82%. The sequences of this production steps are shown in Figure 2.

Figure 2 Transesterification process steps of jatropha methyl ester in lab scale

5.2 Production of Biodiesel from Jatropha Oil in Pilot Scale

The biodiesel pilot plant is located in FKKSA, Universiti Malaysia Pahang. In this pilot plant, 35 liter of patropha oil was pretreated by heating to 100°C in the reactor of capacity of 75 liter for 30 minutes to remove the additives. The transesterification process of crude jatropha oil took place in two steps. The first esterification step was performed using 0.225% v/v H$_2$SO$_4$, 4.5:1 (molar ratio) methanol to oil, reaction temperature of 60°C and 180 min reaction time.

The specified amount of methanol is added to the oil and the mixture heated up to 50°C, at this point the required amount of H$_2$SO$_4$ was added to the mixture of oil and methanol in vigorously stirring mode. The reaction was conducted for three hours and maintained at temperature of 65°C. After that, the reaction was stopped and the mixture was allowed to settle overnight. The mixture was then separated into two layers.

The upper layer was removed and sample from the bottom layer which is the esterified oil was analyzed for FFA, which was found to be less than 1%. Then the esterified oil was subjected to the second step of transesterification process with base catalyst. In this step, the optimum parameter values were selected to be 1.2 (w/w oil) KOH, methanol to oil mole ratio.
4.5:1, reaction temperature of 60 °C, and 2 hours of reaction time. The required amount of catalyst KOH was weighed and dissolved completely in methanol to form potassium methoxide.

Meanwhile, the esterified oil was warmed up to 50 °C, and then the prepared methoxide was added into the oil. The reaction conducted in vigorous mixing for 120 minute at maintained temperature of 60±2°C. After the reaction was completed, it was left to settle for 1 hour, then it was separated into two layers. The lower glycerol layer was drawn off from the bottom of the settling tank and the remaining was crude biodiesel without glycerol.

The reaction tank was used as a washing tank and warm distilled water of 50°C was used for the washing process in gentle agitation to avoid the formation of emulsion. The washing process was repeated four times until the pH of the drained water from washing process has reached 7. The step followed was the purification process where the crude biodiesel was cleared of the residual water remained from the washing process by heating to 70°C under vacuum condition for 30 minute, and then the transparent final product was ready for storing. The photograph of the biodiesel pilot plant is in Figure 3.

![Figure 3](image_url)  
**Figure 3** Biodiesel pilot plant

### 6.0 RESULTS AND DISCUSSION

While the esterification of FFA with methanol in the presence of acidic catalysts is the most commonly applied method, the percentage of acid catalyst used and the molar ratio of alcohol should be in their optimum value to enhance the process and decrease the total production cost. Based on the experimental procedure used in this work, a two-step transesterification process has been conducted to produce biodiesel from two samples of crude jatropha oil with different levels of FFA contents (4.5% and 8%). This high level will decrease the final yield due to soap formation during base-catalyst trans-

**Table 6** Transesterification process parameters

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Acid pretreatment step</th>
<th>Base catalyzed step</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CJO (Sudan)</td>
<td>CJO (Bionas)</td>
</tr>
<tr>
<td>Catalyst (% v/v oil)</td>
<td>H₂SO₄ 0.225</td>
<td>H₂SO₄ 0.225</td>
</tr>
<tr>
<td>Alcohol molar ratio (w/w)</td>
<td>MeOH 6:1</td>
<td>MeOH 4.5:1</td>
</tr>
<tr>
<td>Reaction Time (min)</td>
<td>180</td>
<td>180</td>
</tr>
<tr>
<td>Reaction Temp. (°C)</td>
<td>65</td>
<td>65</td>
</tr>
</tbody>
</table>
Cost-effective large-scale production of biodiesel from non-edible oil feedstock requires that free fatty acids be below 1%, failing this, a highly effective system should be developed to deal with higher FFA levels. In practice, while properly extracted Jatropha oil should have FFA below 1%, it is not unusual for levels to rise due to a number of factors during storage and transport. This paper identified how well a preliminary acid-catalyst esterification step reduces higher FFA level in jatropha oil feedstock from different two sources. In addition, the paper also identified some potential optimization (a reduced molar ratio) of necessary chemical inputs that will improve the economics of large-scale production. The maximum final biodiesel yield of 82% and 90% was achieved from jatropha oil samples sourced from Sudan and Malaysia, respectively. The basic physiochemical properties of the produced biodiesel from the two jatropha oil samples were both found to be within the ASTM D6751 specified limits.

Acknowledgement

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