Full Length Research Paper

Development of a mathematical model for the esterification of *Jatropha curcas* seed oil

K. Mu’azu¹*, I. A. Mohammed-Dabo², S. M. Waziri², A. S. Ahmed², I. M. Bugaje¹ and A. S. Ahmad³

¹National Research Institute for Chemical Technology, Zaria, Nigeria.
²Department of Chemical Engineering, Ahmadu Bello University, Zaria, Nigeria.
³Center for Renewable Energy Research, Umaru Musa Yar’Ａdua University, Katsina, Nigeria.

Accepted 18, January, 2013

In this study, a mathematical model for the esterification reaction of *Jatropha curcas* seed oil was developed in terms of catalyst concentration, methanol to oil ratio and reaction time. Analysis of the crude *Jatropha* oil indicates that the free fatty acid (FFA) of the oil was 16.1% having composition of 37.24, 37.13, 15.85 and 9.76% of linoleic, erucic, palmitic and stearic acids, respectively. FFA (%) measurement was used in determining the extent of esterification of the oil. The experimental results demonstrated that methanol to oil ratio was the only significant model term affecting FFA reduction at 95% confidence level. Comparison of experimentally obtained FFA with predicted values by the developed model showed high correlation coefficient ($R^2 = 0.9657$). The developed mathematical model can be employed in optimization and simulation of FFA reduction during vegetable oil esterification within the range of parameters studied.

Key words: Esterification, *Jatropha* oil, free fatty acid, response surface methodology (RSM).

INTRODUCTION

In the last century, industrialization and fast growth in the world population has resulted in surge in energy demand nearly 10 times the rest of the centuries (Emin, 2008). Consequently, there is the need for secured energy sources that are renewable, environmentally friendly, affordable and above all sustainable (Emin, 2008). Various feedstocks have been proposed for the production of biodiesel, one of the contending candidates is the *Jatropha curcas*. This plant has numerous advantages in that its seed oil is non-edible as it contains compounds that are highly toxic. In addition to that, the plant is resistant to drought and pests, and as such it can be grown in any tropical condition. The seed yield under cultivation can range from 1,500 to 2,000 kg ha⁻¹, corresponding to extractable oil yields of 540 to 680 L ha⁻¹ (58 to 73 US gallons per acre) and they have the potential to get as much as 1,600 gallons of diesel fuel per acre in a year. *J. curcas* tree can also be intercropped with other cash crops such as coffee, sugar, fruits and vegetables (Mohammed-Dabo et al., 2012).

At present, biodiesel otherwise known as fatty acid methyl ester (FAME) is obtained by reacting triglycerides with lower alcohols such as methanol or ethanol in the presence of a strong base as a catalyst; the reaction yields glycerol as a by-product. The triglycerides used come from a variety of oils including rapeseed, sunflower, soybean, palm and peanut oil, as well as from animal fat (Antolin et al., 2002; Al-widyan and Al-Shyoukh, 2002; Ma et al., 1999). The use of these materials, however, is restricted by their high cost, which has led some authors (Zhang et al., 2003) to recommend employing non-edible oils such as *Jatropha* seed oil and some animal fats as alternative raw materials. According to several researchers, the oil or fat used in alkaline transesterification reactions should contain no more than 1% free fatty acids (FFAs), which is equivalent to 2 mg KOH/g triglyceride, (Freedman et al., 1984; Liu, 1994; Mittelbach et al., 1994). If the FFA level exceeds this threshold, saponification hinders separation of the ester from
glycerine and reduces the yield and formation rate of FAME. However, it has been recommended that acidity below 1 mg KOH/g triglyceride (that is, a 0.5% FFA content) is suitable for biodiesel production (Canakci and Van Gerpen, 2001). Van Gerpen (2004) found that the FAME yield from unrefined oil to decrease from 93 - 98% to 86 - 87% in the presence of 6.66% of FFA and ascribed it to phospholipids destroying the catalyst.

In this study, a mathematical model equation to predict the best reaction conditions for the reduction of FFA in J. curcas seed oil at minimal concentration of methanol (expensive reagent) was developed using response surface methodology (RSM). The factors considered for the study were catalyst concentration, methanol to oil ratio and reaction time.

MATERIALS AND METHODS

J. curcas seed was obtained from National Research Institute for Chemical Technology (NARICT), Zaria, Nigeria. Methanol, sulphuric acid, potassium hydroxide, phenolphthalein, carbon tetrachloride, potassium iodide, potassium dichromate, Wij's solution and other chemicals/reagents were obtained from ROMPTECH Chemicals and Scientific Suppliers Co. Ltd. Zaria, Nigeria. All chemicals/reagents were of analytical grade with purity > 99%.

Seed preparation

The J. curcas seeds were separated from foreign matters, weighed and de-hulled using grinding machine (pulvariser). The de-hulled seed were separated into kernel and hull by winnowing method. 69 kg of the kernel was ground to fine particles (100 mesh) to expose large surface area of the cells containing oil for the extraction of the oil.

Oil extraction

The ground kernel in an Aluminum tray was transferred to an electric oven (Manufacturer: Qingdao Brilliant Tolstoy, Model: 1003A) and set the temperature to 100°C for 30 min. 4 L of boiled water was thoroughly mixed with the heated ground kernel and transferred to manually operated mechanical oil expeller and expelled the oil. The water in the Jatropha oil was removed by heating the oil in a glass beaker placed on a heating mantle and set the temperature to 100°C and agitated for an hour at a speed of 450 rpm. The temperature was later increased to 130°C for 30 min to boil up the water and allowed to cool. The oil yield was obtained using Equation 1. The material balance of the extraction process is shown in Table 3.

\[
\text{Oil yield} = \frac{\text{Mass of oil obtained}}{\text{mass of seed used}} \times 100 \%
\]  

\[ \text{Oil yield} = \frac{\text{Mass of oil obtained (kg)}}{\text{mass of seed used (kg)}} \]  

Determination of acid value

The acid value is defined as the mg of potassium hydroxide necessary to neutralize fatty acids in 1 g of sample and is measured as per AOCS method 1a - 64. It reflects the amount of FFA content in Jatropha oil. An indicator solution (1.0% phenolphthalein indicator in isopropyl alcohol) was added to the required amount of solvent (equal parts by volume of isopropyl alcohol and toluene) in ratio of 2 to 125 ml and neutralize with alkali to a faint but permanent pink colour. 5 g of the sample was weighed into an Erlenmeyer flask and 125 ml of the neutralized solvent mixture was added. It was well shaken and ensured that the sample was well completely dissolved before titration. The sample was then titrated against standard solution of alkali (0.1N KOH) until the first permanent pink colour was reached. The colour persisted for 30 s. The acid value was calculated as follows:

\[
\text{Acid value} = \text{Titre value} \times \text{normality of KOH} \times 28.2 / \text{mass of Jatropha oil}
\]

Determination of free fatty acid (FFA)

This is the percentage by weight of specified fatty acid present in the oil. The method applied for this analysis, is the AOCS method 5a - 40. 5 g of the Jatropha was measured in a 250 ml conical flask and dissolved with 25 ml diethyl ether. The mixture was boiled on hot plate until all the oil dissolved completely. Three drops of indicator (phenolphthalein) was added to the mixture and titrated with 0.1N sodium hydroxide with constant shaken until a pink colour persists for 30s. The percentage of FFA was calculated using Equation 3 (Mohammed-Dabo et al., 2012).

\[
\text{FFA} = \frac{\text{[Titre value} \times \text{normality of KOH} \times 56.1]}{\text{weight of Jatropha oil}}
\]

Determination of specific gravity

A cleaned dried density bottle of 25 ml capacity was weighed (Wo). The bottle was filled with the Jatropha oil, inserted stopper and reweighed (Wo). The oil was substituted with water after washing and drying the bottle and weighed (W). The specific gravity was then calculated using Equation 3 (Mohammed-Dabo et al., 2012):

\[
\text{Specific Gravity} = \frac{W_1 - W_0}{W_0 - W_1}
\]

Determination of viscosity

The viscosity of Jatropha oil was measured at 40°C using Digital Rotary Viscometer (Manufacturer: Brookfield, Model NDJ-85). The sample cup was removed and the spindle CP-40 was carefully attached to the lower shaft (rotor number 2) and inserted into the cup containing 25 g of the oil sample. The motor switch was turned “on” and rotates at a speed of 60 rpm until the display reading stabilized (Mohammed-Dabo et al., 2012).

Moisture content determination

The moisture content of the raw oil was also determined using oven drying method. The oil was heated at 130°C for 1 h and filtered using muslin cloth to drive off the water and remove the solid particles, respectively (Mohammed-Dabo et al., 2012).

Determination of fatty acid composition

The FFA composition of the J. curcas seed oil was determined using gas chromatography/mass spectrometer (GC-MS) and using Helium as carrier gas at the following experimental conditions (Table 1) and the results obtained are presented in Table 5.
Pretreatment of Jatropha oil

The Jatropha oil obtained is a mixture consisting of tri, di, mono glycerides, water, solid particles, FFAs and many other impurities. The presence of such impurities creates problem during both esterification and transesterification reactions resulting in lower yield of the biodiesel. The procedure for the removal of these impurities is as follows (Ahmad, 2012): 500 g of the Jatropha oil in a glass beaker was placed in a heating mantle and set the temperature to 100°C and agitated for an hour at a speed of 450 rpm. The temperature was increased to 130°C for 10 min to boil up any traces of water that might be present and allowed to cool for 15 min. The cooled-heated oil was filtered (100 mesh) to remove the solid particles and impurities.

Experimental design

In order to develop mathematical model for the esterification of Jatropha oil, central composite rotary design (CCRD) of RSM was used using a two level-three-factors (2^3) (Aigbodion, 2010). The factors selected for the study are shown in Table 1 and coded (-1) for low and (+1) for high values. The reaction experimental design generated by the Design Expert 6.0 software using actual values is shown in Table 2. However, the choice of reaction conditions were based on the information provided in the literature (Masato et al., 2009).

<table>
<thead>
<tr>
<th>Condition</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Column oven temperature</td>
<td>70°C</td>
</tr>
<tr>
<td>Injection temperature</td>
<td>250°C</td>
</tr>
<tr>
<td>Injection mode</td>
<td>Split</td>
</tr>
<tr>
<td>Flow control mode</td>
<td>Linear velocity</td>
</tr>
<tr>
<td>Pressure</td>
<td>116.9 kPa</td>
</tr>
<tr>
<td>Total flow</td>
<td>40.8 ML/min</td>
</tr>
<tr>
<td>Column flow</td>
<td>1.80 ML/min</td>
</tr>
<tr>
<td>Linear velocity</td>
<td>49.2 cm/s</td>
</tr>
<tr>
<td>Purge flow</td>
<td>3.0 ML/min</td>
</tr>
<tr>
<td>Split Ratio</td>
<td>20.0</td>
</tr>
<tr>
<td>Oven program final temperature</td>
<td>280°C</td>
</tr>
<tr>
<td>Hold time</td>
<td>10.00 min</td>
</tr>
<tr>
<td>Ramp</td>
<td>5°C/min</td>
</tr>
<tr>
<td>Equilibrium temperature</td>
<td>3.0 min</td>
</tr>
<tr>
<td>Ion Surface temperature</td>
<td>200°C</td>
</tr>
<tr>
<td>Interface temperature</td>
<td>250°C</td>
</tr>
<tr>
<td>Solvent cut time</td>
<td>2.50 min</td>
</tr>
<tr>
<td>Detector gain</td>
<td>0.00 KV</td>
</tr>
<tr>
<td>Threshold</td>
<td>2000</td>
</tr>
<tr>
<td>Starting time</td>
<td>3.00 min</td>
</tr>
<tr>
<td>End time</td>
<td>24.00 min</td>
</tr>
<tr>
<td>Event time</td>
<td>0.50 s</td>
</tr>
<tr>
<td>Scan speed</td>
<td>666</td>
</tr>
</tbody>
</table>


RESULTS AND DISCUSSION

Extraction of Jatropha curcas seed oil

Table 3 presents the results of the extraction of Jatropha oil using locally fabricated oil expeller. It is evident from Table 1 that the maximum extracted oil that could be obtained from this machine was 14.49% (w/w) based on the seed weight. However, it has been reported that an oil yield as high as 47.30 (w/w)% was obtained using solvent extraction technique such as hexane (Sepidar et al., 2009). This indicates that the efficiency of solvent extraction method in terms of oil recovery is about thrice of this locally fabricated machine. The relatively low value (14.49%) of the oil yield could also be attributed to the
method of the extraction process, efficiency of the oil expeller, plant species and plant maturity. The oil content of *Jatropha* plant of about 2 years old is about half of 4 to 5 years old plant (Anja, 2009). However, in this study the seeds of 2 years old *Jatropha* plant were used.

**Analysis of crude *Jatropha* oil**

The results of crude *Jatropha* oil analysis presented in Table 4 represents mean of triplicate analysis of each parameter. It is evident from Table 4 that the properties of *Jatropha* seed oil used in this study compared favourably with literature values (El-Diwani et al., 2010). The high value of FFA (16.1%) in the oil sample indicates that the oil contained more unsaturated fatty acids (linoleic and oleic acids) than the saturated fatty acids (palmitic and stearic acids) which require esterification process before transesterification. High value of FFA > 1% adversely affect the transesterification reaction in which the FFA in the oil reacts with the alkali catalyst to produce soap (saponification) hence, decreasing the catalyst amount needed for the transesterification reaction (El-Diwani et al., 2010). The formation of emulsion (saponification) usually results in low biodiesel yield and difficulties in the downstream recovery and purification process of the biodiesel (Emir, 2008). It must also be noted that the oxidative stability of biodiesel is a function of the fatty acid composition of the parent oil. The higher the amount of saturated fatty acid in the parent oil the greater the oxidative stability of the oil and vice versa (Mohammed-Dabo et al., 2012).

The high value of water content (7.3%) in the oil suggests pretreatment of the oil by reducing the water content to < 0.5% before the reaction. Water in the oil reacts with the triglyceride to form free fatty esters and

<table>
<thead>
<tr>
<th>Material</th>
<th>In Kg</th>
<th>%</th>
<th>Out Kg</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Seed</td>
<td>69.00</td>
<td>100.00</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Shell</td>
<td>25.88</td>
<td>37.50</td>
<td>37.50</td>
<td></td>
</tr>
<tr>
<td>Oil</td>
<td>10.00</td>
<td>14.49</td>
<td>14.49</td>
<td></td>
</tr>
<tr>
<td>Spent kernel</td>
<td>30.00</td>
<td>43.49</td>
<td>43.49</td>
<td></td>
</tr>
<tr>
<td>Losses</td>
<td>3.12</td>
<td>4.52</td>
<td>4.52</td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>69.00</td>
<td>100.00</td>
<td>69.00</td>
<td>100.00</td>
</tr>
</tbody>
</table>

Table 2. Factors and their levels for central composite design.

<table>
<thead>
<tr>
<th>Factor</th>
<th>Unit</th>
<th>Low level (-1)</th>
<th>High level (+1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Catalyst concentration</td>
<td>Wt.%</td>
<td>1.0</td>
<td>3.00</td>
</tr>
<tr>
<td>Methanol /oil</td>
<td>w/w,%</td>
<td>0.20</td>
<td>0.70</td>
</tr>
<tr>
<td>Reaction time</td>
<td>min.</td>
<td>60.00</td>
<td>120.00</td>
</tr>
</tbody>
</table>

Table 3. Material balance of the extraction process based on seed weight.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit</th>
<th>Value</th>
<th>Test method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density</td>
<td>kg/m³</td>
<td>870.1</td>
<td>ASTMD 287</td>
</tr>
<tr>
<td>Viscosity at 40°C</td>
<td>mm²/s</td>
<td>151.4</td>
<td>ASTMD 445</td>
</tr>
<tr>
<td>Neutralization No</td>
<td>mgKOH/g</td>
<td>0.93</td>
<td>AOCS 1a-64</td>
</tr>
<tr>
<td>Free fatty acid</td>
<td>mgKOH/g</td>
<td>16.1</td>
<td>AOCS (Ca5a-40)</td>
</tr>
<tr>
<td>Moisture content</td>
<td>%</td>
<td>7.3</td>
<td>Oven Method</td>
</tr>
<tr>
<td>Monoglyceride</td>
<td>wt (%)</td>
<td>-</td>
<td>ASTM 6584</td>
</tr>
<tr>
<td>Diglyceride</td>
<td>wt (%)</td>
<td>2.50</td>
<td>ASTM D6584</td>
</tr>
<tr>
<td>Triglyceride</td>
<td>wt (%)</td>
<td>95.16</td>
<td>ASTM D6584</td>
</tr>
<tr>
<td>Iodine value</td>
<td>mgIodine/g</td>
<td>94.1</td>
<td>AOCS (16-87)</td>
</tr>
</tbody>
</table>

Nd, Not detected.
Table 5. Free fatty acid composition of the *Jatropha* oil.

<table>
<thead>
<tr>
<th>Acid</th>
<th>Value</th>
<th>Molecular weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>Linoleic acid (18:2)</td>
<td>37.24 wt.%</td>
<td>280</td>
</tr>
<tr>
<td>Euric acid (18:1)</td>
<td>37.13 wt.%</td>
<td>338</td>
</tr>
<tr>
<td>Palmitic acid (16:0)</td>
<td>15.85 wt.%</td>
<td>256</td>
</tr>
<tr>
<td>Stearic acid (18:0)</td>
<td>9.76 wt.%</td>
<td>284</td>
</tr>
<tr>
<td>Average molecular weight</td>
<td>894 g/mol</td>
<td></td>
</tr>
</tbody>
</table>

Table 6. The experimental results for esterification reaction using actual values.

<table>
<thead>
<tr>
<th>Standard</th>
<th>Run</th>
<th>Catalyst (A) (w/w) %</th>
<th>MeOH/Oil (B) (w/w) %</th>
<th>Time (C) Min.</th>
<th>FFA %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5</td>
<td>1.00</td>
<td>0.20</td>
<td>60.00</td>
<td>2.13</td>
</tr>
<tr>
<td>2</td>
<td>7</td>
<td>3.00</td>
<td>0.20</td>
<td>60.00</td>
<td>1.96</td>
</tr>
<tr>
<td>3</td>
<td>11</td>
<td>1.00</td>
<td>0.70</td>
<td>60.00</td>
<td>0.78</td>
</tr>
<tr>
<td>4</td>
<td>17</td>
<td>3.00</td>
<td>0.70</td>
<td>60.00</td>
<td>0.74</td>
</tr>
<tr>
<td>5</td>
<td>10</td>
<td>1.00</td>
<td>0.20</td>
<td>120.00</td>
<td>1.72</td>
</tr>
<tr>
<td>6</td>
<td>12</td>
<td>3.00</td>
<td>0.20</td>
<td>120.00</td>
<td>1.42</td>
</tr>
<tr>
<td>7</td>
<td>1</td>
<td>1.00</td>
<td>0.70</td>
<td>120.00</td>
<td>0.9</td>
</tr>
<tr>
<td>8</td>
<td>9</td>
<td>3.00</td>
<td>0.70</td>
<td>120.00</td>
<td>0.73</td>
</tr>
<tr>
<td>9</td>
<td>2</td>
<td>0.32</td>
<td>0.45</td>
<td>90.00</td>
<td>0.73</td>
</tr>
<tr>
<td>10</td>
<td>16</td>
<td>3.68</td>
<td>0.45</td>
<td>90.00</td>
<td>1.08</td>
</tr>
<tr>
<td>11</td>
<td>15</td>
<td>2.00</td>
<td>0.03</td>
<td>90.00</td>
<td>1.75</td>
</tr>
<tr>
<td>12</td>
<td>3</td>
<td>2.00</td>
<td>0.87</td>
<td>90.00</td>
<td>0.56</td>
</tr>
<tr>
<td>13</td>
<td>14</td>
<td>2.00</td>
<td>0.45</td>
<td>39.55</td>
<td>2.08</td>
</tr>
<tr>
<td>14</td>
<td>8</td>
<td>2.00</td>
<td>0.45</td>
<td>140.45</td>
<td>2.21</td>
</tr>
<tr>
<td>15</td>
<td>4</td>
<td>2.00</td>
<td>0.45</td>
<td>90.00</td>
<td>0.68</td>
</tr>
<tr>
<td>16</td>
<td>13</td>
<td>2.00</td>
<td>0.45</td>
<td>90.00</td>
<td>0.62</td>
</tr>
<tr>
<td>17</td>
<td>20</td>
<td>2.00</td>
<td>0.45</td>
<td>90.00</td>
<td>0.63</td>
</tr>
<tr>
<td>18</td>
<td>18</td>
<td>2.00</td>
<td>0.45</td>
<td>90.00</td>
<td>0.68</td>
</tr>
<tr>
<td>19</td>
<td>6</td>
<td>2.00</td>
<td>0.45</td>
<td>90.00</td>
<td>0.73</td>
</tr>
<tr>
<td>20</td>
<td>19</td>
<td>2.00</td>
<td>0.45</td>
<td>90.00</td>
<td>0.76</td>
</tr>
</tbody>
</table>

could also lead to the hydrolysis of alkyl ester produced during transesterification reaction (Emin, 2008). On the contrary, high value of triglyceride (95.16%) in the oil indicates potential of high biodiesel yield. Similarly, high level of viscosity (151.4 MPa.S) also indicates that the oil is too high for direct combustion (Pramanik, 2003).

Analysis of FFA composition (Table 5) of the crude *Jatropha* oil indicates that the predominant FFA is linoleic acid (37.24%) followed by Euric acid (37.13%), Palmitic acid (15.86%) and stearic acid (9.76%).

Development of mathematical model for the esterification reaction

The results of the experiments performed as per the experimental design shown in Table 2 is presented in Table 6. These results were input into the Design Expert 6.0 software for further analysis.

Response surface plots

The response surface plot corresponding to the second-order model (Figure 1) indicates that at any given catalyst concentration, the reduction in FFA revealed some linear dependency pattern at both low and high methanol to oil ratio (0.2 and 0.7% w/w). It is evident from Figure 1 that increasing methanol to oil ratio from 0.2 to 0.7% resulted in significant decrease in FFA from 1.3357 to 0.3748%. At higher methanol to oil ratio (0.7% w/w), lowest FFA of about 0.560% was obtained at catalyst concentration of 1.0% w/w.

This confirmed the fact that methanol to oil ratio had a significant effect on acid value or FFA reduction and the effect of change in catalyst concentration beyond 1% was
Mu'azu et al.

Figure 1. Effect of methanol to oil ratio and catalyst concentration on FFA.

Figure 2. Effect of catalyst concentration and reaction time on FFA.

Insignificant on the FFA at any given methanol oil ratio. However, the effect of water produced during the esterification reaction significantly affects the process which could be improved by water removal in the mixture continuously (Hanny and Shizuko, 2008).

It is evident in Figure 2 that at low catalyst concentration (1wt. %), there was moderate decrease in FFA as the reaction time increases from 60 min until it reached somewhere at intermediate reaction time of about 90 min. Beyond 90 min, the FFA sharply increased from about 0.587% to 1.200% when the reaction time reached 120 min. Similar behaviour was also observed as the catalyst concentration increased beyond 1%. However, the lowest FFA of about 0.545% was obtained
Table 7. ANOVA table for response surface quadratic model.

<table>
<thead>
<tr>
<th>Source</th>
<th>Sum of squares</th>
<th>DF</th>
<th>Mean square</th>
<th>F-value</th>
<th>Prob &gt; F</th>
<th>Remark</th>
</tr>
</thead>
<tbody>
<tr>
<td>Model</td>
<td>6.40</td>
<td>9</td>
<td>0.71</td>
<td>20.20</td>
<td>0.0001</td>
<td>Significant</td>
</tr>
<tr>
<td>A</td>
<td>$6.1 \times 10^{-4}$</td>
<td>1</td>
<td>$6 \times 10^{-4}$</td>
<td>0.017</td>
<td>0.8978</td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>2.71</td>
<td>1</td>
<td>2.21</td>
<td>76.87</td>
<td>0.0001</td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>0.028</td>
<td>1</td>
<td>0.028</td>
<td>0.80</td>
<td>0.3914</td>
<td></td>
</tr>
<tr>
<td>A2</td>
<td>0.0.32</td>
<td>1</td>
<td>0.032</td>
<td>0.91</td>
<td>0.3623</td>
<td></td>
</tr>
<tr>
<td>B2</td>
<td>0.26</td>
<td>1</td>
<td>0.26</td>
<td>7.52</td>
<td>0.0208</td>
<td></td>
</tr>
<tr>
<td>C2</td>
<td>3.40</td>
<td>1</td>
<td>8 $\times 10^{-3}$</td>
<td>96.45</td>
<td>0.0001</td>
<td></td>
</tr>
<tr>
<td>AB</td>
<td>$8.5 \times 10^{-3}$</td>
<td>1</td>
<td>$8 \times 10^{-3}$</td>
<td>0.24</td>
<td>0.6349</td>
<td></td>
</tr>
<tr>
<td>AC</td>
<td>$8.5 \times 10^{-3}$</td>
<td>1</td>
<td>0.14</td>
<td>0.24</td>
<td>0.6349</td>
<td></td>
</tr>
<tr>
<td>BC</td>
<td>0.14</td>
<td>1</td>
<td>0.035</td>
<td>3.99</td>
<td>0.0738</td>
<td></td>
</tr>
<tr>
<td>Residual</td>
<td>0.35</td>
<td>10</td>
<td>0.067</td>
<td>22.59</td>
<td>0.0019</td>
<td>Not significant</td>
</tr>
<tr>
<td>Lack-of-fit</td>
<td>0.34</td>
<td>5</td>
<td>3 $\times 10^{-3}$</td>
<td>1.02</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pure error</td>
<td>0.015</td>
<td>5</td>
<td>1.02</td>
<td>22.59</td>
<td>0.0019</td>
<td>Not significant</td>
</tr>
<tr>
<td>Cor total</td>
<td>6.76</td>
<td>19</td>
<td>1.02</td>
<td>22.59</td>
<td>0.0019</td>
<td></td>
</tr>
<tr>
<td>SD</td>
<td>0.19</td>
<td>R²</td>
<td>0.9654</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mean</td>
<td>1.14</td>
<td>Adj R²</td>
<td>0.9009</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PRESS</td>
<td>2.50</td>
<td></td>
<td>13.678</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

at catalyst concentration of 1.00% w/w and reaction time of 90 min and at these conditions the maximum biodiesel yield was 96%. This indicates that the effect of catalyst concentration was somehow insignificant on the reduction of FFA within the experimental conditions of methanol to oil ratio and reaction time studied.

Analysis of variance

ANOVA is commonly used to summarize the test perform for significance of the regression model, significance on the individual model coefficient and lack-of-fit. Table 7 presents ANOVA table for response surface quadratic model for the FFA reduction.

The values of $F_{calculated}$ ($F = $ Fishers distribution) are compared with $F_{critical}$ at (1, 5) degrees of freedom and 95% confidence level (Aigbodion et al., 2010). Thus, the value of “Prob. > F” (Table 7) for the model is less than 0.05 which indicates that the model is significant, which is desirable as it indicates that the terms in the model have a significant effect on the response (FFA) (Vicente et al., 1998; Abulsalam, 2004). From the statistical analysis, methanol to oil ratio and secondary effect of time ($C^2$) were the most significant model terms associated with the reduction of FFA. Other terms were insignificant but provided only secondary contribution to the reduction of FFA.

The coefficient of regression ($R^2 = 0.9654$) is relatively high, close to 1, which is desirable and is in reasonable agreement with the adjusted $R^2$ value (0.9009). Adequate precision compares the range of the predicted values at the design points to the average prediction error. Ratios greater than 4 indicate adequate model discrimination. In this particular case, the value (13.678) is well above 4 (Zivorad, 2004). The model equation was obtained after calculating each of the coefficients of Equation 4 (Table 8) and the final model equation in terms coded values for the reduction of FFA in Jatropha oil can be expressed in Equation 5.

$$
\text{FFA (\%)} = 0.69 - 6.691 \times 10^{-3}A - 0.46B - 0.045C + 0.047A^2 + 0.14B^2 + 0.49C^2 + 0.033AB - 0.032AC + 0.13BC
$$

Diagnostic plots

The normal probability plots of the residuals and the plots of the residuals versus the predicted response for FFA reduction are presented in Figures 3 and 4.

A check on the plots in Figure 3 revealed that the residuals generally fall on a straight line implying that the errors are distributed normally. Also, Figure 4 revealed that they have no obvious pattern and unusual structure. This implies that the model proposed is adequate and there is no reason to suspect any violation of the independence or constant variance assumption (Noordin et al., 2004).

Validation of the developed model

In order to determine the accuracy of the model developed, experimental data were substituted in the model equation at various conditions of catalyst concentration, methanol to oil ratio and reaction time, the corresponding predicted FFA obtained was plotted.
Table 8. Regression coefficient and significance of response quadratic model.

<table>
<thead>
<tr>
<th>Factor</th>
<th>Coefficient estimate</th>
<th>DF</th>
<th>Standard error</th>
<th>95%CI low</th>
<th>95%CI high</th>
<th>VIF</th>
</tr>
</thead>
<tbody>
<tr>
<td>Intercept</td>
<td>0.69</td>
<td>1</td>
<td>0.077</td>
<td>0.52</td>
<td>0.86</td>
<td>-</td>
</tr>
<tr>
<td>A-catalyst conc.</td>
<td>$-6.69 \times 10^{-3}$</td>
<td>1</td>
<td>0.051</td>
<td>-0.12</td>
<td>0.11</td>
<td>1.00</td>
</tr>
<tr>
<td>B-MeOH/Oil</td>
<td>-0.45</td>
<td>1</td>
<td>0.051</td>
<td>-0.56</td>
<td>-0.33</td>
<td>1.00</td>
</tr>
<tr>
<td>C-Time</td>
<td>-0.45</td>
<td>1</td>
<td>0.051</td>
<td>-0.16</td>
<td>0.068</td>
<td>1.00</td>
</tr>
<tr>
<td>$A^2$</td>
<td>0.047</td>
<td>1</td>
<td>0.049</td>
<td>-0.063</td>
<td>0.16</td>
<td>1.00</td>
</tr>
<tr>
<td>$B^2$</td>
<td>0.14</td>
<td>1</td>
<td>0.049</td>
<td>0.025</td>
<td>0.25</td>
<td>1.00</td>
</tr>
<tr>
<td>$C^2$</td>
<td>0.49</td>
<td>1</td>
<td>0.049</td>
<td>0.38</td>
<td>0.60</td>
<td>1.00</td>
</tr>
<tr>
<td>AB</td>
<td>0.033</td>
<td>1</td>
<td>0.066</td>
<td>-0.12</td>
<td>0.18</td>
<td>1.00</td>
</tr>
<tr>
<td>AC</td>
<td>-0.032</td>
<td>1</td>
<td>0.066</td>
<td>-0.18</td>
<td>0.12</td>
<td>1.00</td>
</tr>
<tr>
<td>BC</td>
<td>0.13</td>
<td>1</td>
<td>0.066</td>
<td>-0.015</td>
<td>0.28</td>
<td>1.00</td>
</tr>
</tbody>
</table>

Figure 3. Normal probability plot of residuals.

Figure 4. Plot of residuals versus predicted.

However, the developed model predicted that the best set of reaction conditions to obtain FFA of less than 1% at minimum methanol quantity (expensive reagent) were catalyst concentration of 1.05%, w/w, MeOH/Oil of 0.46 (w/w) and reaction time of 90 min. These set of experimental condition reduced the FFA to as low as 0.72% which is desirable for transestrification reaction.

Conclusions

In this study, mathematical model for the esterification of J. curcas seed oil was developed by studied effect of methanol to oil ratio, catalyst concentration and reaction time on FFA. The conclusions derived from this study are as follows:

1) Methanol to oil ratio has the maximum influence on the reduction of FFA in J. curcas seed oil,
2) The main and interaction effects of FFA reduction parameters can be studied emphatically by RSM experimentation technique,
3) The model predicted that to obtain FFA of 0.76%, the following reaction conditions holds; methanol to oil ratio of 0.46, reaction time of 90 min and catalyst concentration of 1.00%,
4) The predicted values of FFA by the model equation is in good agreement with the experimental values having high correlation coefficient ($R^2 = 0.9657$),
5) The developed mathematical model can be used to predict the FFA reduction in terms of the process parameters investigated from any given conditions within the range studied,
6) The developed model can also be employed for simulation of FFA reduction within the range of process parameters studied.

ACKNOWLEDGEMENT

The authors gratefully acknowledged the financial
assistance of the Director-General/CEO of National Research Institute for Chemical Technology, Zaria, Nigeria towards this work.

REFERENCES