An Experimental Study of Biodiesel Synthesis Using Groundnut Oil. Part II: Kinetics Study of the Reaction

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Abstract: Biodiesel was produced from groundnut oil using the process of transesterification at different temperature, reaction time and catalyst concentration. Based on the results obtained, the optimum operating conditions for the reaction were identified. The optimum operating temperature, catalyst concentration and time were found to be 70°C, 1% (wt of oil) and 1 hour respectively. The details of the effect of these conditions have been reported in by Yusuf and Sirajo. This paper reports the kinetics of the reaction. From the experimental result obtained, a rate curve was plotted and the equation of this curve was determined using POLYMATH 5.1. From the rate equation obtained, graph of biodiesel production against its concentration and time were plotted. The reaction was found to be very fast within the first 20 minutes and the rate reaction reduces was observed to reduce with reaction time. From the shape of the rate/concentration curve, it is obvious that the reaction is of shifting order.

Key words: Biodiesel; Transesterification; Reaction conditions; Kinetics, Ground nut oil.

INTRODUCTION

The increasing growth in world population as drastically increased the quest for a renewable source of energy which should be environmentally friendly. This may also be attributed to the limited resources of petroleum crude and the environmental problems associated with fossil fuel. In that case it becomes an utmost necessity to search for alternative fuels which are renewable. It is in line with this that the developed and now the developing world want future transport fuels and technologies that deliver lower toxic emissions, lower green house gases, greater efficiency of energy use, less dependence on foreign oil imports and affordable transport. Biofuel is an alternative considered to replace petroleum gas (gasoline or petrol). Most transportation vehicles require high power density provided by internal combustion engines. These engines require clean burning fuels, which are generally in liquid form, and to a lesser extent, compressed gaseous phase. Liquids are more portable because they have high energy density, and they can be pumped, which makes handling easier. This is why most transportation fuels are liquids (Sheehan, 1998).

Biofuel is now a major contributor to the economic growth of any nation that intends to be self reliant. Diesel and jet fuel are the fastest growing segments of the refined fossil fuels market. According to petroleum economists, global diesel demand is likely to continue to grow at around 3% per year while demand for certain other refined production is likely to flatten and even decline (Tony, 2003). This brings about biodiesel to complement the extra need.

Biodiesel is a cleaner burning fuel than diesel and a suitable replacement. It is made from non-toxic, biodegradable, renewable sources (vegetable oils and fats). Biodiesel can be produced in many ways (Chandrashekhar, 2007). The method used in laboratory is transesterification which is actually a replacement of alcohol group from an ester by another alcohol.

Vegetable oils (both edible and non edible) are abundantly produced in this country. Though we have a very large area of arable land for the production of groundnut, less than 60% of it is being utilised. This presents an excellent oil source for the production of biodiesel if well utilised.

This research work is aimed at optimising the production of biodiesel from groundnut oil through transesterification reaction and studying some of the factors affecting its production in order to establish the kinetics of the reaction. The proper understanding of the kinetics of reaction of biodiesel production through transesterification reaction will go a long way in the design of biodiesel reactors.

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Transesterification:

Transesterification or alcoholysis is the displacement of alcohol from an ester by another in a process similar to hydrolysis, except that alcohol is used instead of water (Srivastava, 2000). This process has been widely used to reduce the high viscosity of triglycerides. The transesterification reaction is represented by the general equation below;

$$\text{CH}_2\text{OCOR}_1 + 3\text{CH}_3\text{OH} \xrightarrow{\text{Catalyst}} \text{CH}_2\text{OH} + \text{R}_1\text{COOCH}_3$$

In the Transesterification process, the long chain fatty acid alkyl group is replaced by a methyl or ethyl group. In so doing the viscosity of the oil is drastically reduced as a result of decrease in molecular weight, thereby enhancing the properties of the biodiesel.

Method of Production:

A simple method for producing alcohol esters is to use a batch (stirred tank reactor). A more sophisticated method is the use of a continuous stirred tank reactor where intense mixing, either from pumps or motionless mixers is supplied to initiate the esterification reaction. Instead of allowing time for the reaction in an agitated tank, the reactor is made tubular. The reaction mixture moves through the tube, with little mixing in the axial direction. Alcohol to triglyceride ratios from 4:1 to 20:1 (mole:mole) have been reported, with a 6:1 ratio most common. (Freedman, 1984) The reactor may be sealed or equipped with a reflux condenser. The operating temperature is usually about 65°C, although temperatures from 25°C to 85°C have been reported. The most commonly used catalyst is sodium hydroxide, with potassium hydroxide also used. Typical catalyst loadings range from 0.3% to about 1.5% (Van Gerpen, 2002).

Kinetics of Transesterification reaction:

Diglycerides and monoglycerides are the intermediates in the transesterification reaction. The step wise reactions are reversible and a little excess of alcohol is used to shift the equilibrium towards the formation of esters. In the presence of excess alcohol, the forward reaction has been reported to be pseudo-first order and the reverse reaction is found to be of second order (Gupta, 2006). The general transesterification reaction is shown below

$$\text{Triglycerides} + \text{R}_1\text{OH} \rightarrow \text{Diglyceride} + \text{RCOO}_1 \quad (1)$$

$$\text{Diglycerides} + \text{R}_1\text{OH} \rightarrow \text{Monoglyceride} + \text{RCOO}_1 \quad (2)$$

$$\text{Monoglyceride} + \text{R}_1\text{OH} \rightarrow \text{Glycerol} + \text{RCOO}_1 \quad (3)$$

Even though the mechanism and kinetics of the reaction is similar, catalyst type affects the transesterification process. The reaction can be catalyzed by acid or base or by direct use of an organic methoxide. In this study NaOH was used as the catalyst. Base catalyzes reaction have been reported to be faster. (Ma, 1999)

Reactions can be classified based on their order. In the power law rate equation (Perry, 1997).

$$\tau = kC_1^{p}C_2^{q}$$

the exponent to which any particular reactant concentration is called the order p or q with respect to that substance, and the sum of the exponent p+q is the overall order of the reaction. At times the order is identical with the molecularity, but there are many reactions with experimental orders of zero or fractions or negative numbers. Complex reactions may not conform to any power law (Levenspiel, 1999).

Rate of Reaction:

The term rate of reaction means the rate of decomposition or formation of a material per unit volume.
with units of mol/(unit time)(unit volume).

A rate of formation will have the opposite sign. The negative sign is required for the rate of decomposition to be positive number. When the volume is constant

\[ r = -\frac{dC_A}{dt} \]

(3)

Where \( n_a \) = number of moles of component A

\( V \) = volume of material A

\( t \) = time of reaction

\( C_A \) = concentration of component A.

Reactions of Shifting Order:

In searching for a kinetic equation, it may be found that the data are well fitted by one reaction order at high concentration and by another order at low concentrations (Levenspiel, 1999). The general rate form for reactions of shifting order is

\[ -r_A = -\frac{dC_A}{dt} = \frac{k_1C_A^m}{1 + k_2C_A^n} \]

(4)

which shifts from order \( m-n \) at high concentration of reactant A to order \( m \) at low concentration of that reactant, the transition taking place where \( k_2C_A^n = 1 \). This type of equation can then be used to fit data of any two orders.

The rate form of equation 4 and some of its generalizations are used to represent a number of widely different kinds of reactions. For example, in homogeneous system this form is used for enzymes-catalyzed reactions where it is suggested by mechanistic studies (Michealis Menten kinetics).

MATERIAL AND METHOD

Using the molecular mass of the biodiesel (Methyl trioleate i.e. assuming oleic acid is dominant component) and mass of each sample obtained from the laboratory, the number of moles of biodiesel was determined.

The molecular mass of methyl oleate was calculated from its molecular formula given below

\[ \text{CH}_3\text{COO(CH}_2\text{)}_7\text{CH}=\text{CH(CH}_2\text{)}_7\text{CH}_3 \]

this gives the molecular mass as 297g/gmol.

\[ \text{Number of moles} = \frac{\text{Mass in grams}}{\text{Molecular mass}} \]

(5)

The Table below gives the ratio of moles and concentration ratio using the volume of the respective samples.

\[ \text{Concentration} = \frac{\text{Number of moles}}{\text{Molar mass}} \]

(6)

<table>
<thead>
<tr>
<th>Cat Conc. (%)</th>
<th>Vol. (cm³)</th>
<th>Mass (g)</th>
<th>No of moles (moles)</th>
<th>ratio of moles</th>
<th>Conc. ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2</td>
<td>20.4</td>
<td>18</td>
<td>0.0606</td>
<td>1.490191</td>
<td>2.921943</td>
</tr>
<tr>
<td>0.5</td>
<td>26</td>
<td>23</td>
<td>0.0774</td>
<td>1.904133</td>
<td>2.929435</td>
</tr>
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<td>1</td>
<td>28.8</td>
<td>27</td>
<td>0.0909</td>
<td>2.235286</td>
<td>3.104564</td>
</tr>
<tr>
<td>1.5</td>
<td>24.8</td>
<td>22</td>
<td>0.0741</td>
<td>1.821344</td>
<td>2.937652</td>
</tr>
<tr>
<td>2</td>
<td>13.2</td>
<td>11</td>
<td>0.037</td>
<td>0.910672</td>
<td>2.759613</td>
</tr>
</tbody>
</table>

Table 1: Moles and Concentration Yield for Catalyst variation.
Figure 1 shows the effect of varying catalyst concentration when moles of biodiesel formed is compared with moles of oil fed to the reactor. The molecular mass of the oil is considered to be that of triolein being the major constituent. Molecular mass of triolein = 886g/gmol. The plot for the above variation based on concentration comparison is shown in Figure 2.

Similar from Tables 2 graphs of reaction time against ratio of moles and concentration are plotted as shown in Figure 3 and 4 respectively.

From Table 3, following the same argument as in the case of catalyst concentration variation, a plot of ratio of moles and concentration ratio against temperature were drawn as shown in Figure 5 and 6. These plots give a better picture of how the Transesterification reaction is affected by temperature change.

Table 2: Moles and Concentration Yield for reaction time variation.

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>Vol. (cm³)</th>
<th>Mass (g)</th>
<th>No of moles</th>
<th>ratio of moles</th>
<th>Conc. ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>24.2</td>
<td>21</td>
<td>0.0707</td>
<td>1.7386</td>
<td>2.873646</td>
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<tr>
<td>20</td>
<td>25.4</td>
<td>23</td>
<td>0.0774</td>
<td>1.9041</td>
<td>2.998634</td>
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<tr>
<td>40</td>
<td>28.8</td>
<td>27</td>
<td>0.0909</td>
<td>2.2352</td>
<td>3.104564</td>
</tr>
<tr>
<td>60</td>
<td>30.6</td>
<td>29</td>
<td>0.0976</td>
<td>2.4009</td>
<td>3.138383</td>
</tr>
<tr>
<td>80</td>
<td>30.8</td>
<td>29</td>
<td>0.0976</td>
<td>2.4009</td>
<td>3.118004</td>
</tr>
</tbody>
</table>

Table 3: Moles and Concentration Yield for temperature variation.

<table>
<thead>
<tr>
<th>Temp. (°C)</th>
<th>Vol. (cm³)</th>
<th>Mass (g)</th>
<th>No of moles (moles)</th>
<th>Ratio of moles</th>
<th>Conc. ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>32</td>
<td>20</td>
<td>17</td>
<td>0.057239</td>
<td>1.4074</td>
<td>2.8148</td>
</tr>
<tr>
<td>40</td>
<td>20.8</td>
<td>18</td>
<td>0.060606</td>
<td>1.4902</td>
<td>2.8658</td>
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<td>55</td>
<td>25.4</td>
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<td>0.077441</td>
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<td>2.9986</td>
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<td>70</td>
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<td>27</td>
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<td>3.1046</td>
</tr>
<tr>
<td>80</td>
<td>29</td>
<td>27</td>
<td>0.090909</td>
<td>2.2353</td>
<td>3.0832</td>
</tr>
</tbody>
</table>
Fig. 3: Time variation based on ratio of moles.

Fig. 4: Time variation based on concentration ratio.

Fig. 5: Temperature variation based on ratio of moles.
RESULTS AND DISCUSSION

Transesterification and the Rate Curve:

From the experimental results obtained in the laboratory, it was found that for the reaction time from the concentration yield versus time graph, it is obvious that

\[ \frac{C_B}{C_O} = f(t) \]  

(7)

Where

- \( C_B \) = concentration of Biodiesel in mol/cm\(^3\)
- \( C_O \) = concentration of groundnut oil in mol/cm\(^3\)
- \( f(t) \) = Function of time

And knowing that \( C_O \), the initial oil concentration is constant, it is perfectly feasible to say that, having a plot of \( C_B \) versus time, \( C_B \) is a function of time. Thus,

\[ C_B = f(t) \]  

(8)

From the experimental results, the plot of \( C_B \) versus time is shown below.

Fig. 7: Biodiesel’s concentration versus Time curve.

The equation of this curve was determined using mathematical software (POLYMATH 5.1) in order to calculate the rate values at different times. The program has been used and the equation obtained is given below while the POLYMATH.
\[ C_B = \frac{A \cdot t}{1 + B \cdot t} \]  \hspace{1cm} (9)

Where \( C_B \) is the Biodiesel concentration,
\( t \) is the reaction time and
\( A \) and \( B \) are constants determined using the software.
\( A = 0.0020166 \)
\( B = 0.6174748 \)

This shows that
\[ C_B = \frac{0.0029166t}{1+0.6174748t} \]  \hspace{1cm} (10)

The rate of reaction, as defined in chapter two, is the change in concentration of products or reactants per unit time, or in differential form, as the derivative of concentration with respect to time.

\[ \text{Rate} \quad R_B = \frac{dC_B}{dt} \]  \hspace{1cm} (11)

Differentiating equation 9, we have;
\[ \frac{dC_B}{dt} = \frac{0.0029166}{(1+0.6174748t)^2} \]  \hspace{1cm} (11)

This rate can be evaluated at different experimental times and plotted against concentration. Table 4 gives the values of \( R_B \) with the corresponding values of \( C_B \) at the times of reaction recorded for this experimental work.

<table>
<thead>
<tr>
<th>( t ), min.</th>
<th>( C_B ), mol/cm(^3)</th>
<th>( R_B ), mol/min.cm(^3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>0.002947636</td>
<td>1.9149E-05</td>
</tr>
<tr>
<td>20</td>
<td>0.003021238</td>
<td>1.13159E-05</td>
</tr>
<tr>
<td>40</td>
<td>0.0031388</td>
<td>3.05343E-06</td>
</tr>
<tr>
<td>60</td>
<td>0.003180048</td>
<td>1.39298E-06</td>
</tr>
<tr>
<td>80</td>
<td>0.00320108</td>
<td>7.93951E-07</td>
</tr>
</tbody>
</table>

From this data, a plot of biodiesel rate against its concentration is shown in Figure 8.

\[ \text{Fig. 8: Rate of Biodiesel production against its concentration.} \]

A similar plot showing biodiesel rate against time is given in Figure 9. Combining these two graphs a very good inference concerning the reaction behaviour with respect to both time and concentration can be deducted.
Deductions from the Rate Curve:
From the rate versus time plot and rate versus concentration curve, the following can be inferred:
1. The reaction is very fast at the beginning i.e. first 20 minutes.
2. The rate of reaction reduces with reaction time.
3. The rate of reaction is virtually constant after 1 hour, meaning that the optimum reaction time is 1 hour.
4. At \( C_0 \) (initial oil concentration) the reaction rate is maximum.
5. From the shape of the rate/concentration curve, it is obvious that the reaction is of shifting order i.e. shifting from a higher order to a lower order.

Conclusions:
Transesterification reaction of the triglycerides in groundnut oil is a reaction of shifting order, shifting from a higher order to a lower one. Moreover, the rate decreases more rapidly for the first 40 minutes of reaction, then slowly after 40 min.

REFERENCES