Effects of Molar Ratio, Alkali Catalyst Concentration and Temperature on Transesterification of Jatropha Oil with Methanol under Ultrasonic Irradiation

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Received December 28, 2010; revised March 10, 2011; accepted March 21, 2011

Abstract

For transesterification of Jatropha oil into biodiesel, ultrasound assisted transesterification seems to be promising in terms of reduction in process time and stages of operation. Effects of process variables such as the catalyst loading, the molar ratio of methanol to oil, reaction temperature and the reaction time were investigated on the conversion of Jatropha oil to biodiesel. The conversion was above 93% under the conditions of 50°C, methanol to oil molar ratio of 9:1, reaction time 30 min and catalyst amount (catalyst/oil) of 1% wt%. A kinetic study of transesterification of Jatropha oil based on ultrasound assisted synthesis is presented in this paper. Rate equation obtained is also presented.

Keywords: Transesterification; Ultrasound; Triglyceride; Jatropha Oil, Alkali Catalyst

1. Introduction

Vehicular pollutant emissions caused by the combustion of fossil fuels and crude oil price fluctuations brought into focus the need for developing alternate fuels which could create less pollution, produced from renewable feedstocks and operate without much modification in the existing design of the engine. Biodiesel (fatty acid alkyl ester) derived from transesterification of vegetable oils or an animal fat with methanol (Figure 1) is a potential substitute for petroleum based diesel fuels. Even 5% replacement of petroleum fuel by biofuel can save a country like India Rs. 4000 crores per year in foreign exchange [1].

Government of India has already given due importance to biofuel and announced a National Biofuel policy in year 2006. The focus is on collection and distribution of renewable feedstocks for biofuel products and R & D at pilot plant scale and later scaling upto commercial level technologies for production of biodiesel using Jatropha oil and Karanja oil. At present, the biodiesel is usually produced by reacting methanol and a vegetable oil in a batch stirred tank reactor using a liquid alkaline catalyst. Ultrasound assisted transesterification process offers a number of advantages over current technology, namely the simplification of the process and downstream separation. The present study involved transesterification of Jatropha oil with methanol catalyzed by alkali catalyst. Effects of various parameters were studied.

2. Ultrasound Technology

Influence of ultrasound on transesterification reaction is of purely physical nature. Formation of fine emulsion between oil and alcohol due to microturbulence generated by cavitation bubbles generates enormous interfacial area, which accelerates the reaction [2]. Ultrasound is the process of propagation of the compression waves with frequencies above the range of human hearing. Ultrasound frequency ranges from 20 kHz to 10 MHz, with associated acoustic wavelengths in liquids of about 100-0.15 mm. These wavelengths are not on the scale of molecular dimensions. Instead, the chemical effects of ultrasound derive from several nonlinear acoustic phenomena, of which cavitation is the most important. Acoustic cavitation is the formation, growth, and implo-
sive collapse of bubbles in a liquid irradiated with sound or ultrasound. When sound passes through a liquid, it consists of expansion (negative pressure) waves and compression (positive pressure) waves. These cause bubbles (which are filled with both solvent and solute vapour and with previously dissolved gases) to grow and recompress. Under proper conditions, acoustic cavitation can lead to implosive compression in such cavities. Such implosive bubble collapse produces intense local heating, high pressures, and very short life-times. Cavitation is an extraordinary method of concentrating the diffused energy of sound into a chemically useable form. Ultrasoundication provides the mechanical energy for mixing and the required activation energy for initiating the transesterification reaction. Low-frequency ultrasonic irradiation is useful tool for emulsification of immiscible liquids. The collapse of the cavitation bubbles disrupts the phase boundary and causes emulsification, by ultrasonic jets that impinge one liquid on another [3,4].

Effect of low-frequency ultrasound was studied on the production of biodiesel via transesterification of Jatropha oil with methanol using sodium hydroxide as homogeneous catalyst.

3. Experimental Work

3.1. Reagents and Materials

Methanol (99.5%) and sodium hydroxide (98%) purchased from Yash Enterprise, Ahmedabad, Gujarat, India. Jatropha oil was purchased from Nidhita marketing, Ahmedabad, Gujarat, India. Properties of purchased Jatropha oil as carried out at Nirma University are shown in Table 1.

3.2. Transesterification Procedure

Methanol and Jatropha oil were used as a raw material to study the effect of low frequency ultrasound on biodiesel production at 303 K, 313 K, 323 K using molar ratio of oil to methanol ranging from 1:3, 1:6, 1:9 and 1:12, and the quantity of alkali catalyst from 0.5%, 1.0%, 1.5%, and 2% (wt/wt) of the weight of Jatropha oil. The reaction mixture consists of Jatropha oil, methanol, and sodium hydroxide. Sodium hydroxide was dissolved into methanol followed by addition of Jatropha oil to the solution. Since, the Jatropha oil and methanol were not completely miscible, two layers were observed: the upper layer was of methanol and the lower layer was of oil. Reaction mixture was taken in conical flask and it is placed into water bath of Toshniwal Ultrasonic Cleaner (30 kHz frequency), which was used for ultrasonication, after achieving desired reaction temperature of water in ultrasonic cleaner. During reaction under ultrasound irradiation, no external stirring is provided. The mixing took place due to the effect of ultrasound wave mechanism in water-bath. The reaction mixture was kept for the predecided reaction time under ultrasonic effect and then taken for centrifugation at 1800 to 2000 rpm using laboratory centrifuge. Later the mixture was allowed to settle in separating funnel to get two separate layers of biodiesel and glycerine. Separation of biodiesel and glycerine was done using a separating funnel. Water wash was given to the separated biodiesel to remove water soluble impurities and then dried to remove moisture by putting under calcination.

4. Results and Discussion

4.1. Properties of Biodiesel

Biodiesel produced was analyzed and compared with the fuel properties of petro-diesel as per ASTM Standards (Table 2). The Jatropha oil, however, was found to have much higher values of fuel properties, especially kinematic viscosity (Table 1), restricting the direct use as a fuel in diesel engine. After transesterification, the kinematic viscosity value reduced to permissible limit. The flash points were in a limit of safe storage and handling conditions. The pour point and cloud points were little higher than petro-diesel. This might be due to presence of wax, which begins to crystallize with the decrease in temperature. This problem could be solved by using blend of biodiesel with petro-diesel.

4.2. Influence of Reaction Parameters

Experiments were carried out by changing different process parameters.

Table 2. Comparison fuel properties of petro-diesel, biodiesel and ASTM D6751.

<table>
<thead>
<tr>
<th>Property</th>
<th>Fuel properties</th>
<th>Petro-diesel</th>
<th>Biodiesel (B100)</th>
<th>ASTM D6751</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific gravity at 15°C</td>
<td></td>
<td>0.846</td>
<td>0.875</td>
<td>0.86 - 0.90</td>
</tr>
<tr>
<td>Kinematic viscosity (mm²/s) at 40 °C</td>
<td></td>
<td>1.9 - 6.0</td>
<td>4.756</td>
<td>4 - 6</td>
</tr>
<tr>
<td>Flash Point (°C)</td>
<td>Minimum 130</td>
<td>165</td>
<td>100 - 170</td>
<td></td>
</tr>
<tr>
<td>Cloud Point (°C)</td>
<td>−5</td>
<td>−3</td>
<td>−3 to 12</td>
<td></td>
</tr>
<tr>
<td>Pour Point (°C)</td>
<td>−10</td>
<td>−8</td>
<td>−15 to 10</td>
<td></td>
</tr>
<tr>
<td>Cetane number</td>
<td>Minimum 47</td>
<td>54.25</td>
<td>48 - 65</td>
<td></td>
</tr>
</tbody>
</table>
4.2.1. Methanol to Oil Molar Ratio
Stoichiometrically, the methanolysis of Jatropha oil requires three moles of methanol for each mole of oil. Since, transesterification of triglycerides is a reversible reaction; excess methanol is required to shift the equilibrium towards the direction of ester formation. As can be seen from Figure 2 (at 303 K) and Figure 3 (at 323 K), the maximum conversion was achieved at methanol to oil molar ratio 9:1. It is comparable to the work carried out by H. D. Hanh et al. [5] obtained 90% conversion using methanol as an alcohol with triolein oil to alcohol molar ratio of 1:6 and KOH as a catalyst. D. Kumar et al. [6] have obtained above 98% yield using 1:9 Jatropha oil to methanol molar ratio and heterogeneous solid catalyst used was Na/SiO2. Present study shows that with molar ratio of oil to methanol of 1:12, maximum conversion was achieved in 30 minutes only and after that it almost a constant over an extended reaction time. Molar ration of 1:3 and 1:6 are not showing good results. One of the reasons for the same may be the predominance of esterification reaction at the initial phase, to transesterify the FFA present in the Jatropha oil, of transesterification which can consume methanol present in the reaction mixture and hence, the amount of methanol available for transesterification may not be sufficient to drive the reaction forward for longer time.

4.2.2. Amount of Catalyst
Effect of variation of amount of catalyst on conversion was also studied. Catalyst amount was varied in the range of 0.5% to 2.5% (wt/wt of the oil taken). As shown in Figure 4, the conversion increased firstly with the increase of catalyst amount from 0.5% to 1.5%. But, with further increase in the catalyst amount from 1.5% to 2.5%, the conversion decreased due to soap formation. D. Kumar et al. [6] obtained their best result at 3% wt% catalyst amount which is higher than the present study. Separation of heterogeneous catalyst is adding one more stage in the process presented by D. Kumar. H. D. Hanh et al. [5] obtained about 90% conversion with 1% wt% of NaOH catalyst. The conversion obtained by them is less than what obtained in present study using same amount of catalyst.

4.2.3. Reaction Time and Temperature
Figure 5 shows the conversion versus reaction time at different temperatures. It could be seen from the plot that the conversion increased in the reaction time range of 10 to 45 minutes with the increase in temperature, and there after remained nearly constant as a representative of a nearby equilibrium conversion. The nearly equilibrium conversion was found to be about 93.5% at 45 minutes of reaction time. Effect of reaction temperature is not studied by D. Kumar et al. [6] using heterogeneous solid catalyst but results published (Table 5) for feedstocks other than Jatropha oil shows that reaction time obtained in present study is at par with other published results.

5. Reaction Kinetics
Experiments were carried out at three different tempera-
Figure 5. Effect of reaction temperature on triglyceride conversion. Reaction conditions: Jatropha oil 50 g, catalyst amount 1%, Oil to Methanol Molar Ratio 1:9.

It could be seen from Figure 5 that with increase in reaction temperature conversion also increased. The overall rate equation \( k \) can be found using (1) for first order reaction and (2) for second order reaction.

\[
k = -\ln(1 - X_d)/t \quad (1)
\]

\[
k C_A = -\ln(X_d/(1 - X_d))/t \quad (2)
\]

where \( X_d \) is the conversion of triglyceride.

The experimental data collected at 303 K, 313 K and 323 K were tested for 1st order kinetics (Figures 6 to 8 and Table 3) and 2nd order kinetics (Figures 9 to 11, and Table 3). The experimental data fitted well for 1st order kinetics. The rate data collected were subjected to Arrhenius equation as follows:

\[
k = k_0 \times \exp(-E/RT) \quad (3)
\]

\[
\ln k = (-E/RT) + \ln k_0 \quad (4)
\]

where, \( E \) is activation energy, \( R \) is the gas constant (J/mol-K), \( T \) is an absolute temperature, and \( k_0 \) is a frequency factor.

From the plot of \( \ln k \) versus \( 1/T \) (Figure 12, Table 4), \(-E/R = \text{Slope of the graph} = -2039\). Therefore, Activation energy \( E = 2039 \times 1.987 = 4051.49 \) cal/mol, and \( \ln k_0 = 3.918 \)

\[
k_0 = 50.30
\]

Table 3. Reaction rate constant \( k \) (min\(^{-1}\)) at different temperatures for first order and second order reactions assumption, respectively.

<table>
<thead>
<tr>
<th>Order of Reaction (Assumed)</th>
<th>Reaction Temperature, K</th>
<th>Rate Constant, ( k )</th>
<th>( R^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>First</td>
<td>303</td>
<td>0.06 min(^{-1})</td>
<td>0.944</td>
</tr>
<tr>
<td></td>
<td>313</td>
<td>0.075 min(^{-1})</td>
<td>0.967</td>
</tr>
<tr>
<td></td>
<td>323</td>
<td>0.091 min(^{-1})</td>
<td>0.974</td>
</tr>
<tr>
<td>Second</td>
<td>303</td>
<td>353.10 ml/mol*min(^{-1})</td>
<td>0.807</td>
</tr>
<tr>
<td></td>
<td>313</td>
<td>447.96 ml/mol*min(^{-1})</td>
<td>0.807</td>
</tr>
<tr>
<td></td>
<td>323</td>
<td>534.92 ml/mol*min(^{-1})</td>
<td>0.807</td>
</tr>
</tbody>
</table>
Table 4. Database for determination of activation energy.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$1/T$</th>
<th>Rate Constant, $k$ (min$^{-1}$)</th>
<th>$\ln k$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature, $T$ (K)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>303</td>
<td>0.0033</td>
<td>0.06 min$^{-1}$</td>
<td>−2.81341</td>
</tr>
<tr>
<td>313</td>
<td>0.003195</td>
<td>0.075</td>
<td>−2.59027</td>
</tr>
<tr>
<td>323</td>
<td>0.003096</td>
<td>0.091</td>
<td>−2.3969</td>
</tr>
</tbody>
</table>

Rate equation derived from the above data of activation energy for the ultrasound assisted transesterification reaction is:

$$-r_d = \frac{dX_4}{dt} = kC_{do} (1 - X_4)$$  \hspace{1cm} (5)

where, $k = k_0 \exp(-E/RT)$

Substituting the values of $k_0$, $E$ and $R$ in (3) and also substituting (3) in (5) the rate equation for the reaction is:

$$-r_d = 50.30 \times C_{do} \exp(-4051.49/(1.987 \times T)) \times (1 - X_4)$$  \hspace{1cm} (6)

6. Conclusions

Ultrasound assisted transesterification reaction for the production of biodiesel was found to be very promising from the results obtained. The optimum conditions for the production of biodiesel from Jatropha oil under the full ultrasound condition were molar ratio of oil to methanol of 1:9 with NaOH concentration of 1 wt% and reaction time of 30 min. Increasing reaction time and temperature as well as the molar ratio contributes to high conversion of triglyceride. The transesterification of Jatropha oil under ultrasound condition provides a possibility for producing cheap alternative fuels, which will reduce pollution and protect the environment. The conversion is comparable to the results reported by C. Stavarache et al. [7] where they used n-propanol as a solvent which is higher molecular weight alcohol compared to methanol used in this study. Other reported result was for the feedstock...
Table 5. Comparative study of ultrasound assisted transesterification [8].

<table>
<thead>
<tr>
<th>Oil/Triolein</th>
<th>Catalyst</th>
<th>Alcohol</th>
<th>Oil to Alcohol Molar Ratio</th>
<th>Ultrasonic Frequency</th>
<th>Source of Ultrasound</th>
<th>Reaction Conditions</th>
<th>Ester Yield, %</th>
<th>Ester Conversion, %</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Triolein</td>
<td>KOH</td>
<td>Methanol</td>
<td>1:6</td>
<td>40 kHz</td>
<td>Ultrasonic Cleaner (1200 W)</td>
<td>25°C, 10 min</td>
<td>-</td>
<td>&gt; 90</td>
<td>[5]</td>
</tr>
<tr>
<td>NA</td>
<td>NaOH</td>
<td>Ethanol</td>
<td>1:6</td>
<td>40 kHz</td>
<td>Ultrasonic Cleaner (1200 W)</td>
<td>25°C, &lt; 20 min</td>
<td>-</td>
<td>98</td>
<td>[9]</td>
</tr>
<tr>
<td>Soybean frying Oil</td>
<td>NaOH</td>
<td>Methanol</td>
<td>NA</td>
<td>24 kHz</td>
<td>Ultrasonicator (200 W)</td>
<td>60°C, 20 min</td>
<td>97</td>
<td>-</td>
<td>[10]</td>
</tr>
<tr>
<td>Fish Oil</td>
<td>C₂H₅ONa</td>
<td>Ethanol</td>
<td>1:6</td>
<td>20 kHz</td>
<td>Ultrasonic Probe</td>
<td>60°C, 60 min</td>
<td>98.2</td>
<td>-</td>
<td>[8]</td>
</tr>
</tbody>
</table>

of soybean frying oil [10]. The present study compares favourably with the results reported in literature. Other comparable published results of different researchers are presented in Table 5. Since, the process seems economic; the economic study is to be carried out.

7. Acknowledgements

The authors thank the authorities of the Nirma University, Ahmedabad for supporting the investigation.

8. References


