Green synthesis of biodiesel from jatropha oil and comparative study of biodiesel synthesized from traditional and green synthesis method

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Abstract
Green chemistry concerned with developing process and product to reduce or eliminate hazardous substance. One of the goals of green chemistry is to prevent the pollution at its source and to get maximum yield of product. We developed green ways of obtaining biodiesel from jatropha oil using enzymatic catalyst for the trans-esterification reaction. We have synthesized biodiesel from jatropha oil, by using methyl alcohol with base catalyst and ethyl acetate with enzyme catalyst via trans-esterification reaction and characterized above prepared biodiesel by both processes. We have also compared the characteristic of prepared biodiesel from green method and traditional method i.e. which is prepared by methyl alcohol in presence of base and ethyl acetate with enzyme catalyst via trans-esterification reaction. It is found that the biodiesel which is prepared by enzyme catalyst give maximum yield, good quality and eco-friendly as compared to the methyl alcohol with base catalyst method. Biodiesel is of great interest because it enables motor vehicle transport using a renewable resource, while reducing the amount of CO₂ from fossil fuels being released into the environment. Enzyme catalyzed trans-esterification reactions have the advantage that strong acids/bases are not required, resulting in safer and non-corrosive processes.

Keywords: Jatropha oil, Biodiesel, Green method, Traditional method

1. Introduction
Biodiesel is an alternative fuel for diesel engine that is produced by chemically reacting a vegetable oils or animals fat with an alcohol such as methanol. Biodiesel is quite a fashionable word now days, due to the fact that it is purportedly environmentally friendly and is made from renewable resources [1, 2]. Biodiesel is a term “applied to a fuel derived from the trans-esterification of used vegetable oils or animal fats. In the production of biodiesel, the tri-glycerides in the fats and oils are reacted with methanol to make methyl esters and glycerine. The glycerine produced can be sold as a by-product, however, due to large supplies of glycerine produced during soap manufacture, the income from the sale is likely to be small [3]. The history of biodiesel has been well summarized elsewhere [4]. The recent interest in biodiesel is explained by the rise in oil prices and the vanishing resources of fossil fuels (a presentation to a House of Commons All-Party Committee on 7 July 1999 forecasts a major crisis for fossil fuel availability and price in 2010–2020 [5-7], which is why biodiesel made from both animal and vegetable fats has received considerable attention. Intensive usage of petroleum is an important factor in air pollution: the problem of pollution is critical, as mankind is now facing a global warming crisis [8, 9]. The reaction requires a catalyst usually a strong base such as sodium or potassium hydroxide and produces new chemical compounds called methyl esters; these are collectively known as biodiesel. It is a domestic, renewable fuel for diesel engine derived from natural oil like Jatropha oil. Biodiesel has an energy content of about 12% less then petroleum-based diesel fuel on a mass basis. It has a higher molecular weight, viscosity, density, and flash point than diesel fuel. Biodiesel is considered to be renewable since the carbon in the oil or fat originated methyl from CO₂ in the air. diesel engine operated on biodiesel have lower emission of carbon monoxide, unburned hydrocarbons, particulate matter, and air toxics than when operated on petroleum based diesel fuel [10-11]. Jatropha is a special plant that produces seeds from which oil can be extracted. Many plants produce oil-bearing seeds, and oil such as...
sunflower oil, peanut oil, and even canola oil have been used for cooking and flavoring food, lubricating mechanical parts and even treating a variety of human ailments. However, jatropha oil is completely different. The oil power a diesel engine [12].

In this study, biodiesel were prepared by traditional as well as green synthesis methods. After preparation Determine different properties such as calorific value, Flash Point, Cloud Point, Pour Point, Cetane number and Fire point etc. We have also compared different parameters of above prepared biodiesel by both processes.

2. Materials and Methods
We have collected Jatropha oil from Chhattisgarh renewable energy development authority (CREDA) Raipur and purchase the glassware and chemicals from kasliwal brother Raipur such as Methanol, Sodium Hydroxide, Ethyl Acetate, Novozyme-435 Lipase Enzyme. Further this filtered oil have been taken in round bottom flask and added methyl alcohol and sodium hydroxide base, then oil react with the methanol and NaOH and trans-esterification process is carried out inside the flask at 60 °C temperature. After this process the treated oil keep to settling for 1:30hr. After 1:30 hr, sample takes to check whether the chemical reaction was complete properly. The separate layer of raw bio-diesel and glycerol is form. Now this raw bio-diesel have been washed continuous till the pH of water become 7. This washed raw bio-diesel was drying into dryer above 100 °C temperature for about 1 to 2 hr so that the moisture present in the bio-diesel was evaporated. Now again above process repeats i.e filtered oil have taken in round bottom flask and added ethyl acetate and novozyme-435 enzyme catalyst, then oil react with the ethyl acetate and novozyme-435 and trans-esterification process is carried out inside the flask at 60 °C temperature. Then again washed and dried it.

2.1 Traditional Method
- Conventional batch method with NaOH catalyst, Jatropha Oil and Methanol at 55 °C.
- Wash with water to remove soap.
- Separate Glycerol from Biodiesel.
- Test for presence and quality of biodiesel by GC/Mass Spectrometer and Bomb Calorimetry.

![Flow Chart of traditional Process for Trans-esterification](image-url)

Esterified oil/oil FFA≤4
\[\downarrow\]
Temp.to 55°C-60°C
\[\downarrow\]
NaOH+Methanol (called sodium methoxide)
\[\downarrow\]
Maintaining temp. and stirring for ½ hrs
\[\downarrow\]
Sample taken in test tube
\[\downarrow\]
Precipitation occurs in form of Glycerol
\[\downarrow\]
Reaction completes; stir for another one hrs
\[\downarrow\]
Taking in a separating flask
\[\downarrow\]
Two layer form
\[\downarrow\]
Glycerol (Bottom)
\[\downarrow\]
Biodiesel (upper)
\[\downarrow\]
Biodiesel separated
\[\downarrow\]
Biodiesel (ready to use)
2.2 Green Synthesis Method
- Green synthesis with jatropha oil, ethyl acetate as the reactant and lipase enzyme as the catalyst.
- Allow to run ~6 hours for optimal.
- Test for reaction presence and quality of biodiesel with bomb calorimetry and GC/Mass Spectrometer.

Chemical Reaction

Flow Chart of green synthesis Trans-esterification Process

Esterified oil
↓
Temp. to 55°C-60°C
↓
Lipase enzyme + Ethyl acetate
↓
Maintaining temp. and stirring for ½ hrs
↓
Sample taken in test tube
↓
Precipitation occurs in form of Trace tin
↓
Reaction completes; stir for another one hrs
↓
Taking in a separating flask
↓
Two layer form
↓
Trace tin (Bottom)
↓
Biodiesel (upper)
↓
Biodiesel separated
↓
Biodiesel (ready to use)

3. Results and Discussion
The optimal reaction time for oil to be completely converted to biodiesel is 6 to 8 hours this was determined by an indirect method of measuring the calorific values of samples taken at different points during the reaction process. Further testing showed that after this time period, the equilibrium point is reached for the reaction and it begins to shift back to the reactant side. It was also noted as the concentration of ethyl acetate in biodiesel in the reaction decreases, the calorific value increases. We find that from 2.5 kg jatropha seeds prepare approximate 500 ml biodiesel shown in table 1.
The biodiesel which is prepared by traditional method i.e using alkali catalyst is required higher temperature as compared to green method i.e using lipase enzyme as a catalyst. It is also observed that in case of enzymatic catalyst percentage yield is higher as compared to alkali catalyst shown in table 2.

### Table 2: Comparison between yield of Traditional and Green synthesis method:

<table>
<thead>
<tr>
<th>Variable</th>
<th>Alkali catalysis</th>
<th>Lipase catalysis</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reaction Temperature (°C)</td>
<td>60-70</td>
<td>30-40</td>
</tr>
<tr>
<td>Yield of methyl ester</td>
<td>Normal</td>
<td>Higher</td>
</tr>
<tr>
<td>Water in raw materials</td>
<td>Interference with reaction</td>
<td>No influence</td>
</tr>
<tr>
<td>% Yield</td>
<td>70</td>
<td>82</td>
</tr>
</tbody>
</table>

If we compare the different properties of diesel and biodiesels then find that bio-diesel is more boiling point and carbon content (shown in table 3) and it is ecofriendly as compare to diesel.

### Table 3: Comparison between Bio-Diesel & Diesel:

<table>
<thead>
<tr>
<th>Property</th>
<th>Bio-Diesel</th>
<th>Diesel</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kinematic viscosity at 40 °C</td>
<td>4.0-6.0</td>
<td>1.3-4.1</td>
</tr>
<tr>
<td>Specific gravity (Kg/l) at 60°F</td>
<td>0.88</td>
<td>0.85</td>
</tr>
<tr>
<td>Density at 15 °C (lb/gallon)</td>
<td>7.328</td>
<td>7.079</td>
</tr>
<tr>
<td>Water &amp; Sediments (vol %)</td>
<td>0.05 max</td>
<td>0.05 max</td>
</tr>
<tr>
<td>Carbon wt (%)</td>
<td>77</td>
<td>87</td>
</tr>
<tr>
<td>Hydrogen wt (%)</td>
<td>12</td>
<td>13</td>
</tr>
<tr>
<td>Oxygen wt % (By difference)</td>
<td>11</td>
<td>0</td>
</tr>
<tr>
<td>Sulphur wt (%)</td>
<td>0.02-0.0024</td>
<td>0.05 max</td>
</tr>
<tr>
<td>Boiling Point (°C)</td>
<td>315-350</td>
<td>180-340</td>
</tr>
<tr>
<td>Flash Point (°C)</td>
<td>100-170</td>
<td>60-80</td>
</tr>
<tr>
<td>Cloud Point (°C)</td>
<td>-3 to 12</td>
<td>-15 to 5</td>
</tr>
<tr>
<td>Pour Point (°C)</td>
<td>-15 to 10</td>
<td>-35 to -15</td>
</tr>
</tbody>
</table>

After preparation of biodiesels from both methods we characterize it and found that bio-diesel which is prepared by green method have high value of Density, Cloud Point, Pour Point, Calorific value and Refractive index as compare to alkali catalyzed methods (shown in table 3).

### Table 4: Comparison between biodiesel produced from Traditional Method and biodiesel produced from Green Synthesis Method

<table>
<thead>
<tr>
<th>Property</th>
<th>Traditional Method</th>
<th>Green Synthesis Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kinematic viscosity at 40 °C</td>
<td>4.5</td>
<td>4.1</td>
</tr>
<tr>
<td>Density at 15 °C (lb/gallon)</td>
<td>7.28</td>
<td>8.09</td>
</tr>
<tr>
<td>Boiling Point (°C)</td>
<td>320</td>
<td>280</td>
</tr>
<tr>
<td>Flash Point (°C)</td>
<td>128</td>
<td>109.5</td>
</tr>
<tr>
<td>Cloud Point (°C)</td>
<td>4</td>
<td>5</td>
</tr>
<tr>
<td>Pour Point (°C)</td>
<td>5.7</td>
<td>6.3</td>
</tr>
<tr>
<td>Cetane number</td>
<td>49.8</td>
<td>48</td>
</tr>
<tr>
<td>Calorific value(cal/ml)</td>
<td>8559.30</td>
<td>9137.69</td>
</tr>
<tr>
<td>Fire point</td>
<td>136</td>
<td>135</td>
</tr>
<tr>
<td>Refractive index</td>
<td>1.7</td>
<td>2.9</td>
</tr>
</tbody>
</table>

4. Summary and conclusions
We have prepared biodiesel from jatropha oil by Traditional Method i.e. using methyl alcohol with base catalyst and Green Synthesis Method i.e. using ethyl acetate with lipase enzyme catalyst. After preparation of biodiesel from both methods, we characterize the biodiesels and found that:
- The biodiesels which is prepared by green synthesis method give maximum yield.
- The biodiesels prepared by green synthesis method is High calorific value.
- The biodiesels which is prepared by green synthesis method have High density.
- The biodiesels prepared by green synthesis method have High refractive index.
- The biodiesels prepared by green synthesis method have Low Specific gravity.
- The biodiesels prepared by green synthesis method have Low boiling point.
- The biodiesels which is prepared by green synthesis method have Low flash point.
- Biodiesels prepared by green synthesis method have Low cloud point.
- Biodiesels which is prepared by green synthesis method have Low pour point.
- It has been also found that Green Synthesis Method is environment friendly process as compared to Traditional Method.

5. References