Study on Yield percentage of Biodiesel from Waste cooking oil using Transesterification

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Abstract
The study focuses on the production of biodiesel from waste cooking oil using the transesterification method. A maximum yield of 94% of biodiesel is achieved using transesterification method in the presence of base alkali catalyst, KOH, 0.5 wt\%, at a temperature of 60\degree C and 1:06 oil: methanol ratio in 30 min at 600 rpm. Other properties such as Kinematic viscosity, flash point, acid value, \%FFA, density of waste cooking oil and biodiesel are also estimated. Waste Cooking Oil being easily available and cheaper as compared to vegetable oil it is highly recommended for production of biodiesel, to be used in different applications including transportation. This will help in addressing the issues of natural resource depletion, environmental pollution and climate change.

Keywords: Biodiesel, Waste cooking oil (WCO), Transesterification, KOH, methanol, kinematic viscosity, acid value, \% FFA.

1. INTRODUCTION
Currently, global energy is being obtained mainly from fossil fuels including petrochemical sources, coal, and natural gas which are limited and non-renewable resources, and with an increased industrial activities and population growth there has been an increase in the demand for use of fossil fuels which has added to major environmental issues like climate change and global warming. In view of this scientists around the globe have been encouraged to develop substituting fuels which are renewable and sustainable [1,2].

Biodiesel has been invented from vegetable oils and animal fats as it is found to be promising renewable & clean fuel that can replace conventional diesel in different applications such as boilers, I.C engine without having to modify the engines and it is known to provide similar performance to that of a fossil fuel [3].

Biodiesel was first used in the diesel engine by Dr. Rudolf Diesel, who developed the first diesel engine that ran on peanut oil in Paris in 1990 [4].

With right proportion of catalyst, triglycerides (such as vegetable oil/ animal fats) and alcohol reacts to form biodiesel. Since pure biodiesel can’t be used in conventional engine, it is thus, blended with diesel to form (B2, B5, B10, B15, B20) types of biodiesel in order to enhance the performance level of engine [5].

In India, National Policy on biofuel was approved in December 2009, encouraging the use of renewable and clean energy resources as an alternative to conventional sources of energy such as petrol & diesel [6].

Biodiesel is known to have a number of advantages as it is renewable, biodegradable and oxygenated, having less CO2, CO, THC, PM emission, less toxic and safer to handle as compared to petroleum, and it is a good lubricant [7,8,9,10,11,12].

1.1 Sources of Biodiesel:
Biodiesel consists of several renewable resources such as edible and non edible vegetable oils, animal fats, waste cooking oils, that include Jatropha [13], Neem [14,15], Karanja [16], Mahua [17], Rice bran [18], Soyabean [19], Sunflower [20], Papaya [21], Mustard oil [22], Used cooking oil [23], Canola oil [24], Palm Oil [25], Vegetable fats [26], Dairy waste scum [27], Algae [28].

1.2 Mechanisms:
Some of the mechanisms involved in processing of biodiesel are:
Direct use or blending in diesel fuel, Micro emulsions in diesel fuel, Thermal cracking of vegetable oils, Transesterification [29].

1.) Thermal cracking (Pyrolysis) - This method involves the use of catalyst in absence of oxygen to convert one substance into another by heat i.e. at a temperature range of 400-600\degree C. It is a pollution free and effective method [30,31].
2.) Direct use or blending- Simply proportionate mixture of vegetable oils and diesel for use in diesel engine is not
recommended as it has many inherent failings, thus chemical modifications before use in the engine is required [32].

3.) Micro emulsions- A micro-emulsion is defined as a colloidal equilibrium dispersion of optically isotropic fluid microstructure with dimensions generally 1-150 range formed from two normally immiscible liquids and one or more ionic amphiphiles [33]. It improves spray characteristics by explosive vaporization of low boiling constituents in the micelles. It is prepared from vegetable oils, esters and co-solvents (dispersing agents), or from vegetable oils, alcohol and surfactants, blended or not with diesel [34].

4.) Trans-esterification- Transesterification is a process in which alcohol is displaced from an ester by the use of catalyst. This helps in reduction of high viscosity of triglycerides [35]. Figure 1 shows the mechanism of triglycerides to monoglycerides.

Comparatively, vegetable oil is much costlier than waste cooking oil, which is easily and abundantly available in restaurants, fast food outlets, and food processing industries at all the times and places. Thus WCO can be used as a potential raw material for biodiesel production [36,37]. However, when the same oil is being repeatedly for several times, it will be subjected to more heat and water which in turn increases the acid value of WCO affecting the transesterification reaction. Thus, in this case the WCO needs to be first esterified to reduce the acid value for production of biodiesel [38].

This paper focuses on transesterification process which is most commonly employed in biodiesel synthesis/production. During transesterification the fatty acid present in oil reacts with alcohol (methanol) in presence of the catalyst potassium hydroxide (best catalyst for transesterification of waste cooking oil) [39,40].

A) Esterification

\[
\text{FFA} + \text{MET} \xleftarrow{\text{Catalyst, Heat}} \text{FAME} + \text{H}_2\text{O} \quad Eq.A.1
\]

B) Transesterification

\[
\text{TG} + \text{MET} \xleftarrow{\text{Catalyst, Heat}} 3 \text{FAME} + \text{H}_2\text{O} \quad Eq.B.1
\]

C) Transesterification mechanism

\[
\text{TG} + \text{MET} \xleftarrow{\text{Catalyst, Heat}} \text{DG} + \text{FAME} \quad Eq.C.1
\]

\[
\text{DG} + \text{MET} \xleftarrow{\text{Catalyst, Heat}} \text{MG} + \text{FAME} \quad Eq.C.2
\]

\[
\text{MG} + \text{MET} \xleftarrow{\text{Catalyst, Heat}} \text{GLY} + \text{FAME} \quad Eq.C.3
\]

Fig.1. Simple mechanism of triglyceride with alcohol

- FFA- free fatty acid, MET- methanol
- MG- mono-glyceride, DG- di-glyceride
- TG- tri-glyceride
- FAME- fatty acid methyl esters,
- GLY- glycerol

**Objective:**

1.) Optimal Production of biodiesel from Waste Cooking oil.
2.) Reuse of Waste Cooking Oil.
3.) Conservation and Preservation of Natural Resources.

2. MATERIALS AND METHODS

2.1. Material

Waste cooking oil (WCO) was collected from the nearby restaurants in Nagpur.

2.1.1. Pre-treatment:

Initially the WCO was pre-treated by filtration where the solid dirt content in the waste cooking oil was removed through filters or 24hrs and excess amount of water was removed by heating. The purified oil was dark brown in colour. The acid
value of oil was evaluated to be 1.122 mg KOH/g Oil (% FFA= 0.561%).

2.1.2. Post Treatment:

Transesterification was carried out using a 500 ml conical three neck flask where WCO, methanol and catalyst were added. The process was carried out in 30 min., at three different temperatures: 55°C, 60°C, 65°C with constant mass of oil of 100 ml, with varying catalyst loading of 0.1%, 0.5%, 1%, 2% and four different oil: methanol ratio; 1:4, 1:5, 1:6, 1:7. The agitation speed was maintained constant at 600rpm.

Fig.3. Biodiesel Batch Reactor

2.2. Method

Alkali transesterification was carried out at a temperature of 60°C, with 1:06 oil to methanol ratio and 0.5% KOH (catalyst) in 30 min. in batch reactor. After the reaction completion biodiesel was transferred to separating funnel for 24 hrs for glycerol and biodiesel separation. Biodiesel was then washed with distilled water for leftover glycerol, methanol and catalyst present.

Sample calculation for different molar ratios and catalyst concentration:

\[ A = \text{ml of oil} \]
\[ B = \text{ml of alcohol (methanol)} \]
\[ C = \text{wt\% of catalyst} \]

Data required-

- Weight of oil- 90.72gm
- Density of oil- 0.9072 gm/ml
- Molecular weight of oil- 880.78 gm
- Density of alcohol (methanol)- 0.7899 gm/ml
- Molecular weight of alcohol- 32 gm
- Oil/methanol ratio- 1:5
- Catalyst % - 0.5wt\% of oil

\[ A + B + C = 107 \text{ gm} \]

\[ \frac{1}{5} = \frac{\text{vol.of oil}\times \text{density of oil}}{\text{molecular wt.of oil}} = \frac{\text{vol.of alcohol}\times \text{density of alcohol}}{\text{molecular wt.of alcohol}} \]

\[ \frac{1}{5} = \frac{A}{(5\times 32)} \]

\[ \frac{A}{B} = \text{molar ratio of oil to methanol} \]

Therefore, \[ \frac{A}{B} = \frac{880.78}{(5\times 32)} \]

\[ \frac{A}{B} = 5.50 \]

\[ B = 0.1818 \]

\[ A = \frac{B}{0.1818} \]

\[ A = 550 \text{ gm} \]

\[ B + 0.1818A + 0.005A = 107 \text{ gm} \]

\[ 1.1868A = 107 \text{ gm} \]

\[ A = \frac{107}{1.1868} \text{ gm} \]

Therefore, \[ A = 90.8 \text{ gm} \]

\[ A = (\text{weight of oil/Density of oil}) \text{ ml} \]
\[ A \text{ (oil)} = 100\text{ml} \]
\[ B \text{ (methanol)} = 0.1818\times 100 \]

\[ = 18.18 \text{ ml} \]
\[ C \text{ (catalyst)} = 0.005\times 108 \]

\[ = 0.54 \text{ gm} \]

Calculation for biodiesel yield%

\[ \text{yield} \% = \frac{\text{weight of methyl ester (gms)}}{\text{weight of oil (gms)}} \times 100 \]

3. RESULT AND DISCUSSION

3.1. Observation table

As per above calculation amount of oil, amount of methanol and catalyst wt% is calculated and the result obtained by varying catalyst amount, oil/methanol ratio and temperature is shown below in observation table.
Table 1: % Yield of biodiesel at different operating conditions

<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>Oil/methanol ratio</th>
<th>Catalyst concentration (wt %)</th>
<th>Volume of oil (ml)</th>
<th>Weight of methyl ester (biodiesel) after washing (gm)</th>
<th>% Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1:4</td>
<td>0.1</td>
<td>100</td>
<td>45.4</td>
<td>50</td>
</tr>
<tr>
<td>2</td>
<td>1:4</td>
<td>0.5</td>
<td>100</td>
<td>57.204</td>
<td>63</td>
</tr>
<tr>
<td>3</td>
<td>1:4</td>
<td>1</td>
<td>100</td>
<td>46.308</td>
<td>51</td>
</tr>
<tr>
<td>4</td>
<td>1:4</td>
<td>2</td>
<td>100</td>
<td>43.584</td>
<td>48</td>
</tr>
<tr>
<td>7</td>
<td>1:5</td>
<td>0.1</td>
<td>100</td>
<td>53.57</td>
<td>59</td>
</tr>
<tr>
<td>8</td>
<td>1:5</td>
<td>0.5</td>
<td>100</td>
<td>67.192</td>
<td>74</td>
</tr>
<tr>
<td>9</td>
<td>1:5</td>
<td>1</td>
<td>100</td>
<td>55.388</td>
<td>61</td>
</tr>
<tr>
<td>10</td>
<td>1:5</td>
<td>2</td>
<td>100</td>
<td>52.664</td>
<td>68</td>
</tr>
<tr>
<td>13</td>
<td>1:6</td>
<td>0.1</td>
<td>100</td>
<td>55.66</td>
<td>60.2</td>
</tr>
<tr>
<td>14</td>
<td>1:6</td>
<td>0.5</td>
<td>100</td>
<td>85.352</td>
<td>94</td>
</tr>
<tr>
<td>15</td>
<td>1:6</td>
<td>1</td>
<td>100</td>
<td>71.732</td>
<td>79</td>
</tr>
<tr>
<td>16</td>
<td>1:6</td>
<td>2</td>
<td>100</td>
<td>65.376</td>
<td>72</td>
</tr>
<tr>
<td>17</td>
<td>1:7</td>
<td>0.1</td>
<td>100</td>
<td>54.026</td>
<td>59.5</td>
</tr>
<tr>
<td>18</td>
<td>1:7</td>
<td>0.5</td>
<td>100</td>
<td>71.732</td>
<td>79</td>
</tr>
<tr>
<td>19</td>
<td>1:7</td>
<td>1</td>
<td>100</td>
<td>60.83</td>
<td>67</td>
</tr>
<tr>
<td>20</td>
<td>1:7</td>
<td>2</td>
<td>100</td>
<td>52.664</td>
<td>58</td>
</tr>
</tbody>
</table>

Table 2: Biodiesel yield% obtained with varying catalyst loading rate at 1:6 oil to methanol ratio and 60°C temperature

<table>
<thead>
<tr>
<th>Catalyst %</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>60.2</td>
</tr>
<tr>
<td>0.5</td>
<td>94</td>
</tr>
<tr>
<td>1</td>
<td>79</td>
</tr>
<tr>
<td>2</td>
<td>72</td>
</tr>
</tbody>
</table>

Table 3: Biodiesel yield% obtained with different oil/methanol ratio at 0.5% catalyst loading and 60°C temperature

<table>
<thead>
<tr>
<th>Oil/methanol</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:4</td>
<td>63</td>
</tr>
<tr>
<td>1:5</td>
<td>74</td>
</tr>
<tr>
<td>1:6</td>
<td>94</td>
</tr>
<tr>
<td>1:7</td>
<td>79</td>
</tr>
</tbody>
</table>

Table 4: Biodiesel yield% obtained at different temperatures at 1:6 oil to methanol ratio and 0.5% catalyst

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>55</td>
<td>65</td>
</tr>
<tr>
<td>60</td>
<td>94.5</td>
</tr>
<tr>
<td>65</td>
<td>74</td>
</tr>
</tbody>
</table>

3.2. Effect of catalyst on biodiesel yield

Yield of biodiesel is greatly governed by the presence of catalyst and its quantity. The transesterification reaction rate is greatly affected by the presence of catalyst. Highest yield of 94% was noted at 0.5wt% catalyst loading in 30 min, oil/methanol ratio of 1:6 and temperature 60°C. It has been observed from figure 4 that beyond and below 0.5% weight catalyst, a decrease in biodiesel yield was observed. In this study, the catalyst concentration of KOH to waste cooking oil was varied within a range of 0.1-2%.

![effect of catalyst on yield %](image)

Fig. 4. Effect of catalyst loading on biodiesel yield

Therefore, for the economic point of view, 0.5% amount of catalyst was decided as the optimum condition, and it was selected for further studies.
3.3. Effect of oil/methanol ratio on biodiesel yield

The present studies were conducted at four different molar ratios i.e. 1:4, 1:5, 1:6, 1:7 (oil: methanol ratio). In the present study the maximum ester conversion was at 1:6 oil: methanol ratio, where 94% yield of biodiesel was observed in 30 min. with 0.5 wt% catalyst and temperature 60°C. From the table no. 3 and figure 5 it has been observed that an increase in oil to methanol ratio beyond the optimum point (1:6) had a negative impact on the biodiesel yield. Due to the dilution effect the yield decreased drastically to 79%, at oil to methanol ratio of 1:7. Thus, carrying out distillation process will help in removal of excess methanol from biodiesel.

![Fig.5. Effect of oil/methanol ratio on biodiesel yield](image)

3.4. Effect of temperature on biodiesel yield

Temperature has an impact on the biodiesel yield: In different studies it was observed that maximum yield of biodiesel happened at temperature of 60°C which is the boiling point of methanol under optimal conditions (catalyst loading 0.5wt%, oil: methanol ratio- 1:6, time- 30 min.). As shown in table no 4 and figure 6 increase in the temperature beyond 60°C resulted in a decrease in the yield of biodiesel as the methanol beyond 60°C starts vaporising. In this current research, when the temperature has raised to 65°C there will be higher energy input and reduced mass transfer resistance which leads to increase in reaction rate resulting in lesser yield of biodiesel.

![Fig.6. Effect of temperature on biodiesel yield](image)

4. CONCLUSION

The aim of this project was to access biodiesel production from waste cooking oil in the presence of a homogenous catalyst KOH. Three factors were investigated – oil-to-methanol ratio, catalyst loading and temperature – in order to optimize the process. Optimal reaction conditions were obtained at oil to methanol molar ratio (1:6), catalyst loading (0.5 %) and temperature (60°C) which gives 94% yield of biodiesel. Hence, in order to shift the reaction towards formation of FAME, with respect to oil it was assumed that the catalyst was used in sufficient amount. It was observed that the catalyst KOH showed an excellent activity in mediating the transesterification of waste cooking oil containing 0.561% FFA to biodiesel production.

<table>
<thead>
<tr>
<th>Properties</th>
<th>Units</th>
<th>WCO</th>
<th>Waste cooking oil Methyl Ester (Biodiesel)</th>
<th>BIS standard</th>
<th>ASTM D-6751</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density @ 25°C</td>
<td>g/cm³</td>
<td>0.90724</td>
<td>0.880</td>
<td>860-890 kg/m³</td>
<td></td>
</tr>
<tr>
<td>Specific gravity</td>
<td></td>
<td>0.90724</td>
<td>0.883</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Kinematic viscosity at 40°C</td>
<td>cSt</td>
<td>32.85</td>
<td>4.2</td>
<td>2.5-6.0 (mm²/s)</td>
<td>1.9-6.0 (mm²/s)</td>
</tr>
<tr>
<td>Saponification value</td>
<td>mg KOH/g oil</td>
<td>189.04</td>
<td>-</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total acid number</td>
<td>mg KOH/g oil</td>
<td>1.122</td>
<td>0.16</td>
<td>0.8</td>
<td>0.5</td>
</tr>
<tr>
<td>Cloud point</td>
<td>ºC</td>
<td>11</td>
<td>-2.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pour Point</td>
<td>ºC</td>
<td>10</td>
<td>-6.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Flash Point</td>
<td>ºC</td>
<td>308.03</td>
<td>125</td>
<td>120</td>
<td>130</td>
</tr>
<tr>
<td>%FFA</td>
<td>%</td>
<td>0.561</td>
<td>0.191</td>
<td></td>
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</table>
CONFLICT OF INTEREST:
The authors declare no conflict of interest.

REFERENCE:


