DEVELOPMENT OF AGRICULTURAL WASTE BASED HETEROGENEOUS CATALYST FOR PRODUCTION OF BIODIESEL FROM MIXED WASTE COOKING OIL AND ITS PERFORMANCE ON DIESEL ENGINE

PROJECT REFERENCE NO.: 39S_R_MTECH_1508

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INTRODUCTION:
Increasing uncertainty about global energy production and supply, environmental concerns due to the use of fossil fuels and the high price of petroleum based products are the prime reasons to search for alternatives to petro diesel. In this perspective, considerable attention has been given towards the production of biodiesel as a diesel substitute. Moreover, biodiesel fuel has become more attractive because of its environmental benefits, due to the fact that plants and vegetable oils and animal fats are renewable biomass sources.

Biodiesel which is accepted as an attractive alternative fuel is prepared by transesterification of vegetable oils and animal fats with an alcohol in presence of a catalyst. The use of waste cooking oil (WCO) as biodiesel feedstock reduces the cost of biodiesel production. Hence, the use of waste cooking oils and non-edible oils should be given higher priority over the edible oils as biodiesel feedstock. Due to the presence of FFAs in such oils, the oils cannot be subjected to transesterification because this would lead to soap forming side reactions. Therefore, it is necessary to reduce the FFAs levels to ≤1 wt% prior to transesterification by a pretreatment step.

In general the catalysts that can be used for producing biodiesel are divided into three groups: alkaline, acidic and enzymatic. The alkali catalyst is composed of sodium hydroxide or potassium hydroxide. They have high conversion rate of triglycerides into their methyl esters, but has some disadvantages. When feedstock has FFAs more than 1% produces soap water that hindered the separation of the methyl ester phase during the washing step. The last catalyst that this present work proposes is a heterogeneous catalyst. When activated, heterogeneous catalysts have proved to have a high catalytic transesterification activity, and moreover eliminate the additional cost associated with the homogeneous sodium hydroxide to remove the catalyst after transesterification. The production of biodiesel by transesterification process employing alkali catalyst has been industrially accepted for its high conversion and reaction rates but agricultural waste based heterogeneous catalysts seem to be a promising option for research and develop. Especially this agricultural waste based solid catalysts used to reduce FFA’s of waste cooking oil. These catalysts are more effective to other catalysts because of their more surface area, pore volume and acid density. Compare to other catalysts are more environmentally friendly and recyclable.

OBJECTIVE:
The main objective of the project is characterization of waste cooking oil and
mixed waste cooking oil, development of agricultural waste based heterogeneous catalyst using saw dust, rice husk and post harvested banana stem for the esterification of waste cooking oil and characterization of prepared agricultural waste based catalysts. Next conventional homogeneous alkaline biodiesel production using pre-esterified WCO. Optimization of esterification reaction and comparison of activity of produced catalyst in terms of % FFA conversion of WCO. Optimization of transesterification reactions. Analysis of produced biodiesel properties at different blends (B100, B30, B20, B5) as prescribed by ASTM D6751-12 methods and its performance test on diesel engine.

**METHODODOLOGY:**

Waste cooking oil samples were collected from MIT food court mess and Goli Vada Pav Chat Centre, Manipal. The oil used for frying in MIT food court mess was edible sunflower oil and palm oil in and Goli Vada Pav Chat Centre. The received waste cooking oil was filtered through normal sieve to remove food debris and unwanted solids. The filtration process should be performed in advance of a transesterification reaction. After treatment of MIT food court oil and chat centre oil, named it as sample no 01 and 02 respectively. Received waste cooking oils were mixed in 50:50, 75:25 and 25:75 ratios.

The quality of oil is expressed in terms of the physico-chemical properties such as moisture, acid value, saponification value, iodine value, unsaponified matter, density, specific gravity, viscosity, peroxide value.

**Preparation of catalyst**

Catalysts are prepared by using agricultural waste biomasses such as husk, saw dust, post harvested banana. The process of pyrolysis was carried out at different temperatures i.e.350°C, 450°C and 550°C. The production of biochar was performed in laboratory by using muffle furnace, since there is no oxygen or limited supply of air. Next step is activation of produced carbon rich mass using KOH as chemical activating agent. For activation of biochar, selected impregnation ratio was 4 (Impregnation ratio is ratio of dry chemical agent to dry biochar weight). 30 g of grounded biochar was mixed with 305.57 mL of 7 mol/L KOH solution and stirred for overnight at room temperature. After filtration, the resultant carbon material was dried in oven at 110°C. Dried biochar samples were then carbonized at temperature 650°C for 2.5 hour under no air supply. The obtained samples were washed with distilled water followed by neutralisation with 0.1 mol/L HCl solution. Another 3-4 washing steps with distilled water was conducted in order to remove the HCl and to attain neutral pH and the resultant activated biochar samples were dried in oven at 110°C overnight.

After activated biochar with KOH, the biochar samples were functionalised using concentrated H₂SO₄ (99%). The activated 25 g of biochar samples were mixed with 100 mL concentrated sulphuric acid and stirred for 6 hrs at room temperature and. After completion of mixing, excess acid was decanted. The mass ratio of Acid/Biochar was 4/1. The resultant samples were washed with hot distilled water until the pH of the wash water became neutral. The sulfonated biochar sample was then dried in oven at 110°C overnight and produced functionalised catalyst stored in air tight bottle.

**Esterification reaction using sulfonated agricultural waste catalysts**

The esterification reactor consists of a 2500 ml flat bottom flask provided with three necks; it has been kept in magnetic stirrer heating mantle which has rpm controller and a temperature controller. Out of three necks, in one neck spiral condenser has been fixed, in second thermometer was fixed, and other neck had been used to put the raw oil
inside the reactor as well. The temperature and rpm was controlled.

25 gm of oil (Sample 05) was taken in the setup. Heat is supplied to the setup using a magnetic stirrer heating mantle. A known amount of sulfonated catalyst was taken in beaker and known quantity of methanol was added to it and stirred properly. This catalyst-methanol mixture was added to oil. The reaction stared, maintained specified rpm and specified time at specified temperature to carry out the reaction. After completion of the specified time the heating was stopped and the products were allowed cool. The un-reacted residual methanol was heated to evaporate. Next esterified oil was taken to determine the acid value and FFAs content. The remaining product is further used for transesterification to obtain methyl esters using conventional homogeneous catalyst.

![Figure 1: Set up of esterification reaction](image)

**Transesterification reaction**

The transesterification reactor consists of a 500 ml round bottom flask provided with three necks; it has been kept in magnetic stirrer heating mantle which has rpm controller and a temperature controller. Out of three necks, in one neck spiral condenser has been fixed, in second thermometer was fixed, and other neck had been used to put the raw oil inside the reactor as well. The temperature and rpm was controlled.

50 gm of oil was taken in the above mentioned setup. Heat is supplied to the setup using a magnetic stirrer heating mantle. A known amount of alkaline catalyst was taken in conical flask and known quantity of methanol was added to it and stirred properly to dissolve KOH pellets. This catalyst-methanol mixture was added to oil. The reaction stared, maintained specified rpm and specified time at specified temperature to carry out the reaction. After completion of the specified time the heating was stopped and the products were allowed cool. Product transferred to separating funnel and allowed to separate. The separated crude biodiesel heated to remove residual methanol content present in it, this heated crude biodiesel washed with hot distilled water to remove non reacted catalyst, residual glycerol and soap particles. This washed biodiesel heated to remove water molecules present in it and stored in air tight bottle for further use.

The optimization of transesterification reaction was done by changing one reaction
condition and maintaining other three constant. Optimization was done by varying the catalyst concentration, oil to methanol ration, reaction time and temperature.

**RESULTS AND DISCUSSION:**

Estimation of physio-chemical properties of the waste cooking oil

Physio-chemical properties of mixed waste cooking oil discussed.

Sample 01: MIT food court oil (Sunflower oil), Sample 02: Goli vada pav chat centre (Palm oil), Sample 03: Food court oil and chat centre oil in 25:75 ratios, Sample 04: Food court oil and chat centre oil in 50:50 ratio, Sample 05: Food court oil and chat centre oil in 75:25 ratio

<table>
<thead>
<tr>
<th>Oil properties</th>
<th>Oil samples name</th>
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<tbody>
<tr>
<td></td>
<td>Sample 01</td>
</tr>
<tr>
<td>Moisture content (%)</td>
<td>0.11</td>
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<tr>
<td>Specific gravity</td>
<td>0.886</td>
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<tr>
<td>Viscosity (cSt)</td>
<td>31.46</td>
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<tr>
<td>Acid value (mg/g)</td>
<td>1.28</td>
</tr>
<tr>
<td>FFA (%)</td>
<td>0.64</td>
</tr>
<tr>
<td>Saponification value (mg of KOH/g of oil)</td>
<td>121.59</td>
</tr>
<tr>
<td>Molecular weight (g)</td>
<td>1397.95</td>
</tr>
<tr>
<td>Iodine number</td>
<td>78.50</td>
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<tr>
<td>Unsaponifiable</td>
<td>0.18</td>
</tr>
<tr>
<td>Peroxide value (meq/kg)</td>
<td>16</td>
</tr>
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</table>

**Figure 2:** Set up of transesterification reaction
Surface area of sulfonated catalyst
Post harvested banana stem

<table>
<thead>
<tr>
<th>MIT</th>
<th>Model: Scout Tyco 9259</th>
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<tr>
<td>Date: May 10, 2018</td>
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</table>

- Sample Type: SBD
- Sample 95% (gpm): 9170
- Sample 99% (gpm): 9230
- Temperature (°C): 54

- Graph for Sample: SBD

Surf ace Area in (Sq. micron): 1611.36

Saw dust

<table>
<thead>
<tr>
<th>MIT</th>
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<tr>
<td>Date: May 10, 2018</td>
<td></td>
</tr>
</tbody>
</table>

- Sample Type: SBD
- Sample 95% (gpm): 9170
- Sample 99% (gpm): 9170
- Temperature (°C): 54

- Graph for Sample: SBD

Surface Area in (Sq. micron): 970.22

Rice husk

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<td>Date: May 10, 2018</td>
<td></td>
</tr>
</tbody>
</table>

- Sample Type: SBD
- Sample 95% (gpm): 9170
- Sample 99% (gpm): 9170
- Temperature (°C): 54

- Graph for Sample: SBD

Surface Area in (Sq. micron): 993.14

Optimization of esterification reaction
Effect of oil to methanol molar ratio

<table>
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<th>MIT</th>
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</thead>
<tbody>
<tr>
<td>Date: May 10, 2018</td>
<td></td>
</tr>
</tbody>
</table>

- Sample Type: SBD
- Sample 95% (gpm): 9170
- Sample 99% (gpm): 9170
- Temperature (°C): 54

- Graph for Sample: SBD

OFA conversion (%): 90

Figure 3: Effect of oil to methanol ratio on esterification process

Figure 4: Effect of catalyst concentration on esterification process
Effect of catalyst concentration

Effect of stirring speed

Figure 5: Effect of time on esterification process

Figure 6: Effect of stirring speed on esterification process

Optimization of transesterification reaction

Effect of catalyst concentration

Figure 7: Effect of catalyst concentration on transesterification process
Effect of oil to methanol molar ratio

Figure 8: Effect of oil to methanol ratio on transesterification process

- Effect of temperature

Figure 9: Effect of temperature on transesterification process

- Effect of time

Figure 10: Effect of time on transesterification process
• Analysis of pure biodiesel and biodiesel blends properties

Table 2: Properties of biodiesel and its blends

<table>
<thead>
<tr>
<th>Properties</th>
<th>Diesel</th>
<th>B5</th>
<th>B20</th>
<th>B30</th>
<th>B100</th>
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<tbody>
<tr>
<td>Density (kg/m³)</td>
<td>830</td>
<td>838</td>
<td>854</td>
<td>860</td>
<td>868</td>
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<tr>
<td>Specific gravity</td>
<td>0.833</td>
<td>0.839</td>
<td>0.854</td>
<td>0.860</td>
<td>0.869</td>
</tr>
<tr>
<td>Kinematic viscosity (cSt)</td>
<td>2.2</td>
<td>2.4</td>
<td>3.5</td>
<td>3.65</td>
<td>3.95</td>
</tr>
<tr>
<td>Acid value (mg KOH/gm)</td>
<td>0.35</td>
<td>0.37</td>
<td>0.40</td>
<td>0.42</td>
<td>0.48</td>
</tr>
<tr>
<td>Flash point (°C)</td>
<td>60</td>
<td>64</td>
<td>72</td>
<td>80</td>
<td>160</td>
</tr>
<tr>
<td>Fire point (°C)</td>
<td>68</td>
<td>70</td>
<td>82</td>
<td>92</td>
<td>170</td>
</tr>
<tr>
<td>Calorific value (kJ/kg)</td>
<td>44800</td>
<td>43926.8</td>
<td>42639.14</td>
<td>41091.06</td>
<td>38987.6</td>
</tr>
</tbody>
</table>

• IC engine test of biodiesel and its blends

Figure 11: Break thermal efficiency Vs Break power

Figure 12: Specific fuel consumption Vs Break power
• Emission test of Biodiesel and its blends

Figure 13: Break specific energy consumption Vs Break power

Figure 14: CO (Carbon monoxide) emission Vs Break power

Figure 15: HC (Unburned hydro carbons) emission Vs Break power
Figure 16: CO₂ (Carbon dioxide) emission Vs Break power

Figure 17: O₂ (Oxygen) emission Vs Break power

Figure 18: NOₓ (Nitrogen oxides) emission Vs Break power
CONCLUSION:

In the present project work, waste cooking oil was selected as feedstock for production of biodiesel. It’s found that mixing of waste cooking oil in different ratio is effective and cheaper method to reduce free fatty acid of waste cooking oil. Collected oils mixed in different ratio such as 25:75, 50:50 and 75:25. It is found that ratio of 75:25 reduced free fatty acid of waste cooking oil below 1 wt% FFA, which is favourable for homogeneous alkaline catalysed transesterification reaction. Physio-chemical properties of waste cooking oil found out according to AOCS methods.

Agricultural waste based heterogeneous catalysts are prepared from locally available post harvested banana stem, rice husk and saw dust. Characterization of catalysts was done. Activity of catalysts depends on the surface area and attachment of HSO₃ groups on surface of catalysts.

Free esterified oil used in biodiesel production using KOH as homogeneous catalyst. Optimization of biodiesel production was done. Highest biodiesel yield was obtained at catalyst loading 0.65 wt%, oil to methanol ratio 1:8, temperature 60 °C and time 60 minutes. Analysis of biodiesel and its blends properties were done as per ASTM D6751-12. Properties of biodiesel and its blends found in accordance with ASTM standards.

Performance of prepared biodiesel B100 and its blends B5, B20, B30 was done on single cylinder, 4 strokes IC engine. Here diesel fuel performance on engine was taken as bench mark to study the performance of biodiesel blends. Emission test was done using NDIR analyzer. Emission of CO, HC and CO₂ from biodiesel blends lower than that of diesel fuel. Emission of NOₓ was higher for B100 compare to other blends and diesel.

Hence, biodiesel from waste cooking oil considerably reduces production cost of biodiesel. A biodiesel blend in diesel engine is safer, ecofriendly and considerably increases engine performance without any engine modification. Further it substantially reduces emissions from diesel engine; hence it is more environmental friendly.

FUTURE WORK:

The present work only focused on the development of agricultural based waste catalysts from banana stem, saw dust and rice husk. Further work that can still be done using variety of agricultural wastes as a breakthrough in heterogeneous catalysts and preparation methods with less complex or refined steps, sustainable and environmentally benign precursors and/or materials as well as reaction conditions, which are less severe to be competitive with conventional homogeneous reaction system. Work can be done on recovery
of catalysts and activation of catalysts for further use.

Further studies on improving the catalyst morphology and investigating the catalytic activity of agricultural waste based catalysts should be the focus of future research directions. Further studies on utilization and conversion of the crude glycerol phase to valuable products can be done.