Coconut husk ash is effectively used in the production of fuel grade biodiesel even by room temperature transesterification reaction of non-edible/used triglyceride oils.
3.1 Introduction

As an important source of oil and income, coconut tree is an inevitable part of Kerala life [1]. The name Kerala has the meaning “the land of coconut” (kera in malayalam), which is called so due to the abundance of coconut tree [2]. Among the wide variety of useful components from the coconut tree, coconut husk has been considered as an agricultural waste material. Coconut oil and coconut water processing firms generate a lot of coconut husk and in most of the cases it is usually discarded or burned [3]. The improper treatments of these materials will result in land and air pollution. The coconut husk has been used as a biomass fuel since it contains a high amount of lignin and cellulose, and hence possesses high calorific value [4]. The coconut husk can be used as a value-added clean combustion fuel, which can replace wood and other traditional fuel sources. The combustion of coconut husk produces a lot of ash as waste. Coconut is a permanent crop and there is no scarcity of the husks. Both in terms of its availability and cost, coconut husk has good potential for use in power plants. The coconut husk bears 40% of coconut fruit and it contains 30% fiber with a chemical composition of cellulose, lignin, tar, tannin, potassium etc [5]. At present, coconut husks are used as a fuel for coconut processing, as a domestic fuel and as a source of fiber for making rope and mats. The charcoal made from coconut husk by direct combustion method has a number of applications [6]. The activated carbon derived from coconut husk is highly efficient for wastewater treatment processes [7]. Manju et al have used copper impregnated coconut husk carbon as an adsorbent for the removal of
arsenic from contaminated water [8]. Chromium (VI) is removed from aqueous solutions using activated carbon produced from coconut husk fiber [9]. Phenol, acid red 27 dye, and Cu$^{2+}$ ions are also removed by employing activated carbon from coconut fiber using CO$_2$ and phosphoric acid as the activators [10]. Cationic dyes like methylene blue has been removed by adsorption on coir pith carbon [7]. Coconut husk carbon is used as an additive in the preparation of activated carbon from digested sewage sludge using ZnCl$_2$ as an activating agent [11]. There are some other reports related to the use of coconut husk ash as a stabilizing agent for improving the quality of infertile lateritic soil, as an enhancement of concrete for improving the toughness torsion and the tensile stress of concrete whereas the coconut fibers also ensures long-term durability of the concrete [12]. Furthermore, fermentable sugar extracted from relatively abundant lignocellulosic material obtained by suitable pretreatment of coconut husk makes it a cheap and potential substrate for the bioethanol production through enzymatic hydrolysis [13].

In the present work, coconut husk is utilized for the preparation of a base catalyst in the production of biodiesel. Since it is inexpensive and locally available in plenty, it is a suitable raw material for the bulk production of catalyst. The use of ash based materials for biodiesel production offers the best route for waste management and its natural availability, environmental friendliness, renewable nature and low cost stimulate its importance in making a solid catalyst for biodiesel production [14]. The use of palm empty fruit bunch ash [15], rice husk ash [16], cocoa pod husk ash [17], wood ash [18] etc as precursors of
the catalyst or as catalyst supports for biodiesel production is already established and is already mentioned in chapter 1, in section 1.12. However, in all those cases higher amount of catalyst of around 20 wt% of the oil is required for the production of biodiesel or high calcination temperature is required for the catalyst development [15, 18]. The catalytic performance was further improved by chemical treatment with K or Ca containing compounds [15-18]. Here, the catalyst preparation from coconut husk has been done by a simple procedure, by means of controlled heat treatment (combustion) alone without any chemical processing. The ash obtained is used as such as catalyst for the preparation of biodiesel. The advantage of coconut husk derived catalyst is the presence of high potassium content, which is sufficient for giving excellent catalytic activity for the production of biodiesel that meets international standards even by room temperature reaction. A simple method of heat treatment employed for the bulk scale preparation of ash from coconut husk makes the pilot scale production of biodiesel easy and economically viable.

3.2 Experimental

3.2.1 Preparation of coconut husk ash

Coconut husks were washed with deionized water and dried under sunlight. Then the catalysts were prepared by the combustion of coconut husk at different temperatures starting from 300 °C to 500 °C with an interval of 50 °C. The calcination (combustion of coconut husk) was performed by placing the dried coconut husk as such into a cleaned muffle furnace under the selected temperature for 1 h. The
different catalytic systems thus prepared were designated as CHAT, where CHA is the short form of coconut husk ash and T indicates the catalyst treatment temperature in °C. For example, the catalyst treated at 350 °C is designated as CHA350. The ash content of coconut husk is found to be ~5%. The preparation of catalyst from coconut husk is depicted in figure 3.1.

![Figure 3.1 Preparation of coconut husk ash catalyst](image)

The ashes prepared by the controlled combustion of coconut husk at different temperatures were analyzed thoroughly using FTIR spectroscopy, XRD and SEM-EDS characterization techniques. The catalytic activity of the coconut husk ash derived catalysts in the biodiesel production was investigated in the transesterification of *jatropha carcus* oil. The activity of CHA350 in UCO transesterification is also analyzed. The detailed procedures for the investigation of reaction parameters in the transesterification reaction, pilot scale production of biodiesel from *jatropha carcus* oil as well as used cooking oil, biodiesel analysis, and the determination of fuel properties are explained in chapter 2 in the sections 2.5, 2.12.2, 2.7 and 2.13 respectively.
3.3 Results and discussion

The coconut husks treated at different calcination temperatures were characterized using various techniques in order to find out the active components and surface morphology of the systems. Initially, the catalytic activity of the coconut husk derived ash based catalysts was investigated in the laboratory scale by the transesterification of jatropha oil with methanol at different reaction conditions. The influence of calcination temperature on the activity was monitored first. Effect of the reaction parameters such as methanol to oil molar ratio, dosage of catalyst, duration of the reaction and reaction temperature of the catalytic reaction was investigated. The biodiesel production was upgraded in the pilot plant at the best suited reaction condition to ensure its applicability in the large scale production process.

3.3.1 Catalyst characterization

3.3.1.1 SEM-EDS analysis

The mass percentage of the components of coconut husk and the heat treated varieties as obtained from EDS analyses are given in Table 4.1. It is seen that carbon and oxygen content of the coconut husk decreased upon combustion. It can be concluded from the nature of the components that K is the main active ingredient responsible for the high activity of these catalysts in biodiesel production. From the elemental analysis data, it is observed that majority of potassium exists as its chloride.
The SEM images of the coconut husk and its thermally treated systems are provided in the figure 3.2. Images of the heat treated samples reveal the presence of mineral aggregates of complex morphology with macropores. It is evident from the SEM images that, CH has no porous structure and it displayed a flake like structure. Temperature treatment caused the elimination of organic matter and created pores in the remaining ash. There are many reports on macroporous heterogeneous catalysts active for biodiesel production [19-21].

Table 4.1. SEM-EDS analysis data of coconut husk/coconut husk treated at various temperatures

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>C (mass %)</th>
<th>O (mass %)</th>
<th>Na (mass %)</th>
<th>Mg (mass %)</th>
<th>Si (mass %)</th>
<th>Cl (mass %)</th>
<th>K (mass %)</th>
<th>Others (mass %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH</td>
<td>61.77</td>
<td>16.43</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>8.06</td>
<td>10.91</td>
<td>2.82</td>
</tr>
<tr>
<td>CHA300</td>
<td>8.47</td>
<td>6.35</td>
<td>1.95</td>
<td>2.05</td>
<td>1.68</td>
<td>33.54</td>
<td>41.73</td>
<td>4.23</td>
</tr>
<tr>
<td>CHA350</td>
<td>1.29</td>
<td>4.44</td>
<td>2.92</td>
<td>1.21</td>
<td>3.25</td>
<td>43.57</td>
<td>42.90</td>
<td>0.43</td>
</tr>
<tr>
<td>CHA400</td>
<td>2.22</td>
<td>6.63</td>
<td>3.63</td>
<td>1.36</td>
<td>4.25</td>
<td>34.34</td>
<td>46.71</td>
<td>0.87</td>
</tr>
<tr>
<td>CHA450</td>
<td>1.72</td>
<td>6.34</td>
<td>0.98</td>
<td>0.69</td>
<td>4.92</td>
<td>29.54</td>
<td>55.81</td>
<td>-</td>
</tr>
<tr>
<td>CHA500</td>
<td>-</td>
<td>5.71</td>
<td>0.92</td>
<td>-</td>
<td>3.20</td>
<td>35.7</td>
<td>54.47</td>
<td>-</td>
</tr>
</tbody>
</table>

Elemental analysis via CHNS is also performed. The result indicated the presence of S (0.23%) in CHA350 in addition to C (4.29%), H (0.99%) and N (0.03%).
3.3.1.2 FTIR spectral analysis

The FTIR spectra of different ash samples derived from coconut husk are shown in figure 3.3. All the systems showed similar spectral patterns with little variation in the spectral band intensities. The peaks observed around 3400 cm\(^{-1}\) and 1640 cm\(^{-1}\) correspond to stretching and bending vibrations of adsorbed water or surface hydroxyl groups [22]. The absorption of atmospheric CO\(_2\) on the basic sites may be the reason for the presence of band for basic carbonates in
the range of 1300-1500 cm\(^{-1}\) [23]. Peak around 1000 cm\(^{-1}\) may be due to the silica component; i.e., stretching of Si-O-Si bond [24].

![FTIR spectra](image)

**Fig 3.3 FTIR spectra of coconut husk treated at various temperatures**

### 3.3.1.3 XRD analysis

The components responsible for the activity of the coconut husk ash in biodiesel production are revealed from the X-ray diffraction analysis. Figure 3.4 shows the XRD patterns of the catalysts prepared at different calcination temperatures. The 2\(\theta\) values corresponding to the diffraction from various components of ash such as KCl, K\(_2\)Si\(_2\)O\(_5\), K\(_2\)SO\(_4\), K\(_2\)S\(_3\), KAIO\(_2\), K\(_4\)CaSi\(_3\)O\(_9\), Ca\(_2\)FeAl\(_2\)BSi\(_4\)O\(_{15}\)(OH) etc., as matched with the JCPDS (73-0380, 04-
Chapter 3

010-3964, 005-0613, 31-1095, 00-053-0809, 00-039-1427 and 070-1856) data [15, 18]. The diffraction bands at 2θ values of 28.3°, 40.5°, 50.2°, 66.4° and 73.7° corresponds to the (002), (022), (222), (024) and (224) respective planes of KCl in the cubic lattice. The diffraction bands at 2θ values 32.7°, 34.3° and 38.6° from the (221), (202) and (222) planes of K₂S₃ in the crystal lattice is also visible.

Fig 3.4 XRD of coconut husk treated at various temperatures

3.3.2 Catalytic activity studies

The catalytic activity of the prepared systems is initially analyzed in the transesterification of JCO with methanol. At first, the suitable calcination temperature for the preparation of coconut husk ash catalyst was determined.
Coconut husk ash derived catalyst for biodiesel production
3.3.2.1 Effect of calcination temperature

Fig 3.5 Effect of calcination temperature on FAME content under the reaction conditions of catalyst weight 5 wt%, methanol to oil molar ratio 15:1 and at 45 °C and 65 °C for 1h.

Among the different catalysts prepared from the coconut husk, CHA350, the coconut husk treated at 350 °C was found to show the highest activity at different reaction temperatures and is evident from the results shown in figure 3.5. Room temperature reaction was conducted for 3 h. The catalyst is superior to other basic ash based catalysts used for biodiesel production [15-18]. So this particular catalyst production process and hence the biodiesel preparation is much more energy efficient compared to the other ash based catalysts. The effects of other reaction parameters, methanol/oil molar ratio,
catalyst weight, reaction time and reaction temperature are analysed over CHA350 catalyst.

**3.3.2.2 Effect of methanol/oil molar ratio**

![Graph showing the effect of methanol/oil molar ratio on FAME content over CHA350 catalyst at various temperatures.](image)

Fig 3.6 Effect of methanol/oil molar ratio on FAME content under the reaction conditions of catalyst weight 5 wt%, at reaction temperatures of RT, 45 °C, 55 °C and 65 °C over CHA350.

Figure 3.6 shows the effect of methanol/oil molar ratio on the transesterification of jatropha oil over CHA350 catalyst at various reaction temperatures. All the reactions are carried out for 1 h, except for room temperature reaction, which was conducted for 3 h. A FAME content of about 80% is achieved even at a lower methanol/oil ratio of 6:1 at high temperatures. Further increase in the amount of methanol...
consequently raised the FAME content and acquired a fuel grade value of above 96.5% from a methanol/oil molar ratio of 12:1 onwards. Within 1 h of reaction, excellent results were obtained for a methanol/oil molar ratio of 12:1 at reaction temperatures of 45 °C and 65 °C. It can be concluded from the plots shown in figure 4.5 that 45 °C is the best-suited lowest reaction temperature for the transesterification of jatropha oil over coconut husk ash catalyst at 12:1 methanol/oil molar ratio and the best suited methanol/oil ratio for room temperature reaction was 15:1 when 5 wt% of the catalyst is used for 3 h reaction.

3.3.2.3 Influence of catalyst dosage

From the figure 3.7, it is observed that increase in the catalyst weight will result in high conversion at all the selected temperatures. For a dosage of 5 wt% of the CHA350 catalyst, a FAME content of 99.77% is achieved and a further increase in catalyst weight resulted in more or less similar FAME content and thus we selected a catalyst weight percentage of 5 wt% for further studies.
3.3.2.4 Effect of time

Production of biodiesel at a faster rate is economically viable and preferred in industrial scale applications. Here the duration for transesterification reaction is varied at room temperature, 45 °C and 65 °C (figure 3.8 and figure 3.9).
It is seen that fuel grade biodiesel with FAME content of more than 96.5% is obtained within 30 minutes of the reaction from 45 °C onwards. At room temperature, it requires 3 h to obtain fuel grade biodiesel at a methanol/oil molar ratio of 15:1. Further raise in the reaction time maintained the FAME content above 99% at 15:1 and 12:1 methanol/oil molar ratios.
Fig 3.9 Effect of reaction time on FAME content under the reaction conditions of 15:1 and 12:1 methanol/oil at room temperature over CHA350

### 3.3.3 Reusability of CHA350

Reusability of the CHA350 catalyst was investigated at the reaction conditions of 5 wt% of catalyst at a methanol/oil molar ratio of 12:1 at reaction temperature of 65 °C for 1 h. Catalyst recovered from the reaction medium was washed with methanol to remove the traces of biodiesel and was dried. The catalyst was then activated at 350 °C for 1 h and repeated the reaction. It found that the catalyst lost its activity. It may be caused by leaching of the active components responsible for the reaction.
3.3.4 Leaching studies of CHA350

Leaching study of CHA350 is performed to investigate the nature of the catalytic process, since the catalyst was found to be inactive in the second cycle itself. The catalyst corresponding to 5 wt% of oil was first stirred with methanol for 1 h at 65 °C. It was then filtered and the filtrate was used for the transesterification reaction with oil in such a way that the methanol to oil molar ratio was 12:1. The FAME content obtained with the leached out homogenous catalyst was 96.1%. The result is compared with the reaction done at 65 °C for 1 h over 5 wt% of the solid catalyst; more efficient performance (above 99% FAME) is obtained by the use of the solid catalyst as such under the selected reaction conditions and the total time required for the entire reaction was also found to be less. The activity of the residue after the reaction is checked and it is found that the solid residue is not active in the reaction. It is possible that the active component in the catalyst is leached to methanol and removed during the filtration process losing the activity of the solid material.

So as to get an idea about the components of the catalyst that are reached out to the reaction mixture, elemental analysis of the fresh CHA350 and used up catalyst was investigator via ICP-AES analysis. The amount of metal components (in mg/g catalyst) are Al: 1.3342 (1.2764), Ca: 21.5366 (19.8516), Fe: 2.2352 (2.2857), K: 336.49 (92.4741), Mg: 17.349 (17.5163) and Na: 41.98 (23.0274). Data in the parenthesis stands for the used catalyst. The results reveal the leaching of Potassium and Sodium species to the reaction mixture, while retaining other components. This further confirms the role of potassium in the reaction.
3.3.5 Pilot scale production of biodiesel

The feasibility for the scale-up of the low cost solid CHA350 catalyst in biodiesel production is analyzed by performing the reaction in the pilot scale setup. At the reaction condition of 12:1 methanol/oil ratio at a temperature of 45 °C, the transesterification of JCO as well as UCO is upgraded in the pilot plant over 5 wt% of CHA350 catalyst for 1 h reaction. The biodiesel produced from JCO and UCO contains the FAME contents of 99.77% and 99.97% respectively indicating the high efficacy of the process.

3.3.6 Fuel properties of biodiesel

The fuel properties of the JCO and UCO biodiesel produced in the pilot plant are analyzed using various test methods [25, 26]. From the data shown in table 3.3, it is evident that the prepared biodiesel samples meet the international standard specifications.

Table 3.3 Fuel properties of biodiesel produced from JCO and UCO over CHA350 catalyst

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Unit</th>
<th>Limits</th>
<th>Standards</th>
<th>JCO</th>
<th>UCO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ester content</td>
<td>% m/m</td>
<td>96.5 min</td>
<td>EN 14214</td>
<td>99.77</td>
<td>99.97</td>
</tr>
<tr>
<td>Monoglyceride</td>
<td>% m/m</td>
<td>1.00 max</td>
<td>D 6751</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>Triglyceride</td>
<td>% m/m</td>
<td>0.25 max</td>
<td>D 6751</td>
<td>0.04</td>
<td>0.02</td>
</tr>
<tr>
<td>Free glycerol</td>
<td>% m/m</td>
<td>0.02 max</td>
<td>D 6751</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>Total glycerol</td>
<td>% m/m</td>
<td>0.38 max</td>
<td>D 6751</td>
<td>0.03</td>
<td>0.01</td>
</tr>
<tr>
<td>Acid value</td>
<td>mg KOH/g</td>
<td>0.80 max</td>
<td>D 6751</td>
<td>0.00</td>
<td>0.24</td>
</tr>
<tr>
<td>Water content</td>
<td>Vol.%</td>
<td>0.50 max</td>
<td>D 6751</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>Iodine value</td>
<td>mg I/100 g</td>
<td>120 max</td>
<td>EN 14214</td>
<td>109</td>
<td>92</td>
</tr>
<tr>
<td>Viscosity</td>
<td>mm2/s</td>
<td>1.96-6.0</td>
<td>D 6751</td>
<td>4.07</td>
<td>3.78</td>
</tr>
<tr>
<td>Density</td>
<td>kg/ m3</td>
<td>860-890</td>
<td>D 6751</td>
<td>873</td>
<td>868</td>
</tr>
</tbody>
</table>
3.3.7 Composition of biodiesel

The percentage composition of the fatty acid methyl esters present in the biodiesel sample obtained from jatropha oil are given in Table 3.4; and it matches the reported data of fatty acid profile of jatropha oil [27].

Table 3.4 Percentage composition of fatty acid methyl ester found in the biodiesel produced from JCO over CHA350 catalyst

<table>
<thead>
<tr>
<th>Fatty acid</th>
<th>No. of carbon in the fatty acid chain: Double bond</th>
<th>Weight (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Myristic</td>
<td>14:0</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>Palmitic</td>
<td>16:0</td>
<td>15.48</td>
</tr>
<tr>
<td>Stearic</td>
<td>18:0</td>
<td>6.61</td>
</tr>
<tr>
<td>Arachidic</td>
<td>20:0</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>Behenic</td>
<td>22:0</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>Palmitoleic</td>
<td>16:1</td>
<td>0.86</td>
</tr>
<tr>
<td>Oleic</td>
<td>18:1</td>
<td>37.05</td>
</tr>
<tr>
<td>Linoleic</td>
<td>18:2</td>
<td>37.42</td>
</tr>
<tr>
<td>Linolenic</td>
<td>18:3</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>Others</td>
<td></td>
<td>2.55</td>
</tr>
</tbody>
</table>

3.4 Conclusions

A highly efficient ash based catalyst has been developed from coconut husk for the large-scale production of fuel grade biodiesel in a cost-effective way that made the entire process economically viable. The catalyst activity is excellent in the transesterification reaction even at room temperature. At a reaction temperature of 45 °C, with the catalyst CHA350, prepared from coconut husk at a low calcination temperature of 350 °C, the FAME content of biodiesel was found to be
more than 97% within 30 minutes of reaction time. The biodiesel produced from JCO and UCO at the selected reaction conditions in the pilot plant over CHA350 met the international standard specifications for the biodiesel fuel. The most attractive factor of the present cost-effective, solid catalyst developed from waste material for biodiesel production is its low temperature activity.
Chapter 3

References


