Characterization of Bio-chars Obtained at Static and Nitrogen Atmosphere

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Abstract—Biomass is increasingly considered as an important resource for alternative fuels with significant environmental advantages. The role of pyrolysis is important in the thermal processing of biomass. This study presents the characterization of bio-chars obtained from safflower seed press cake (SPC) produced by pyrolysis. The bio-chars were obtained in a fixed-bed reactor, at 500 °C pyrolysis temperature, 50 °C min⁻¹ heating rate, under static and nitrogen pyrolysis atmosphere. The bio-chars were analyzed to determine their elemental composition, high heating rate and surface area. The chemical compositions of bio-chars were investigate using FTIR spectroscopy. It was found that the bio-chars can be characterized as carbon rich, high heating value and relatively pollution-free potential solid biofuels.

Keywords—Biomass, Pyrolysis, Bio-char, Characterization.

I. INTRODUCTION

Renewable energy is of growing importance is satisfying environmental concerns over fossil fuel usage. Wood and other forms of biomass including energy crops and agricultural and forestry wastes are some of the main renewable energy resources available [1].

The biomass resources generally consisting of carbon, hydrogen, oxygen and nitrogen are the organic matters in which solar energy is stored in chemical bonds [2]. Among all the renewable sources of energy biomass is unique as it effectively stores solar energy and is the only renewable source of carbon which can be converted into convenient solid, liquid, gaseous fuels and chemical feedstock trough different conversion methods such as thermochemical and biochemical technologies. Among the thermochemical conversion processes (e.g. pyrolysis, gasification and combustion), pyrolysis is recognized as a promising technology for bio-oil and bio-char [2-5].

Pyrolysis can be described as the direct thermal decomposition of the organic matrix in the absence or very limited quantity of oxygen to obtain array of solid, liquid and gas products. Unlike fossil fuels, biomass is renewable source of carbon and using it to produce bio-char from farm wood-waste appears to be one promising method of achieving greater levels of certainty and flexibility for integrating carbon sequestration accounting and renewable energy generation into conventional agricultural production. The process has been practiced for centuries for production of charcoal (bio-char) from biomass and requires relatively slow reaction at very low temperatures to maximize bio-char yield. Bio-char carbon species range in complexity from graphite-like carbon to high molecular weight aromatic rings, which are known to persist in soil for thousands to millions of years [6-7].

The bio-char can be used be as a fuel the form of briquettes or as a char-oil water slurry, or it can be upgraded to chemicals such as activated carbon for use in chemical, pharmaceutical and food industries [8-9].

A number of studies regarding bio-char production from various source of biomass have been showed that solid fuels can be produced from biomass [10-14].

Safflower (Charthamus tinctorius L.) has been grown for centuries, primarily for its colorful petals to use as a food coloring and flavoring agent, for vegetable oil and also for preparing textile dye. The principle countries where safflower is grown are India, USA and Mexico. However, Turkey is one of the small scale safflower producers. Usually safflower seed and cake were used for animal feeding. Safflower oil has many uses, including as an edible oil, a medicinal, and as an industrial oil. The safflower oil has also been extensively studied as a raw material for fatty acid methyl esters biodiesel production by transesterification [15]. Previous studies at our laboratory on the pyrolysis of safflower seed press cake and rapeseed cake have shown the competitive potential of fuel production from oil seed cakes [16-17].

In this study, the safflower seed press cake (SPC) was chosen as the renewable energy source and the various characteristics of the bio-char acquired under static and nitrogen pyrolysis atmosphere conditions in a fixed-bed reactor were identified.

II. EXPERIMENTAL

In this study, the safflower seed was supplied from Eskişehir Anatolia Agricultural Research Institute (ATAEM). Safflower seed press cake (SPC) was obtained from mixture of Dincer and Yenice species by hot-press extraction method. Prior to use, the SPC was air dried and then screened to give the fraction of 1.8 mm average particle size. The sample was kept in glass jars and used up during the experiments.

Elemental analysis of the SPC sample gave C 49.5%, H 6.9%, N 3.0% and O 40.6%. SPC sample contains 3.0% ash.
and 83.0% volatile matter. Fixed carbon content was obtained as 14.0% by finding the difference and the moisture content is 6%. All the values were expressed on a dry basis by weight percentage. Oil, cellulose and protein contents of the SPC sample were found as 17.0%, 40.0% and 18.8%, respectively [15].

The pyrolysis experiments were performed with a 20 g of biomass feedstock in a fixed-bed reactor with a length of 104 mm and internal diameter 70 mm; heated externally by an electric furnace with the temperature being controlled by a thermocouple inside in the bed. The connection pipe between the reactor and the cooling system was heated to 400 °C to avoid condensation of tar vapour.

The pyrolysis experiments of SPC were performed at 50 °C.min\(^{-1}\) heating rates while the final temperature was 500 °C under static and nitrogen (100 cm\(^3\) min\(^{-1}\)) pyrolysis atmosphere.

To characterize the bio-char samples, the following tests and calculations were performed. The chemical and physical properties of bio-chars were identified with standard test methods.

**Proximate analysis:** Moisture content, volatile matter content, and ash content were determined according to the ASTM D 3173, ASTM D 3175 and ASTM D 3174 standard methods, respectively. Fixed carbon content was calculated by difference.

**Elemental analysis:** Elemental analysis was performed according to ASTM D 5373 by Leco CHNS 932 instrument.

**Heating value:** Heating value was determined by Bomb Calorimetry according to the ASTM D 240 standard method.

**FTIR analysis:** Fourier transform infra-red (FTIR) analysis was carried out by a Perkin Elmer FTIR Spectrometer Spectrum 2000 instrument.

**Scanning electron microscopy (SEM):** This was performed by using a JEOL-JSM-5600LV Scanning Electron Microscopy instrument.

**Brunauer-Emmett-Teller (BET) surface area:** This was performed by using Micromeritics Gemini V instrument.

### III. RESULTS AND DISCUSSION

Table 1 shows the yields of pyrolysis products. The bio-oil yield increased in nitrogen pyrolysis atmosphere. But the bio-char yield has not been a serious change.

<table>
<thead>
<tr>
<th>Product yields (wt%)</th>
<th>Static (^a)</th>
<th>Nitrogen (^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bio-oil</td>
<td>33.82</td>
<td>36.06</td>
</tr>
<tr>
<td>Bio-char</td>
<td>26.29</td>
<td>25.21</td>
</tr>
<tr>
<td>Gas</td>
<td>20.38</td>
<td>19.22</td>
</tr>
</tbody>
</table>

\(^a\) Obtained at 500 °C, 50 °C min\(^{-1}\).

\(^b\) Obtained at 500 °C, 50 °C min\(^{-1}\), sweeping gas flow rate of 100 cm\(^3\)min\(^{-1}\).

The chemical and physical properties of bio-chars obtained from SPC under static and nitrogen atmosphere were determinate and presented in Table 2. As can be seen from the table, the bio-char samples are characterized by higher carbon content than that of the raw material (SPC). The increase in the carbon content of the bio-char provides an advantage since it can use as the fuel. In comparison with raw material, a decrease in volatile matter was observed for bio-chars, as expected. The presence of volatile matter in bio-chars shows incomplete thermal degradation during pyrolysis. There was also a noticeable decrease in the hydrogen content, probably due to the great proportion of hydrogen compounds in the volatile matter [12]. The ash content of bio-chars are also found higher than the SPC due to the mineral matter which form ash remains in bio-char after pyrolysis [14].

The chemical composition of the bio-chars that are a carbon-rich product are \(\text{CH}_0_{40}\text{N}_{0.04}\text{O}_{0.32}\) and \(\text{CH}_0_{36}\text{N}_{0.06}\text{O}_{0.38}\). The high heating values of the bio-chars are higher than that of the SPC (24.8 MJ kg\(^{-1}\)) [15].

#### Table 2: Main characteristics of the bio-chars.

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>Static</th>
<th>Bio-Char</th>
<th>Nitrogen</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Proximate analysis(^a) (%)</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Volatile Matter</td>
<td>10.54</td>
<td>16.30</td>
<td></td>
</tr>
<tr>
<td>Ash</td>
<td>9.60</td>
<td>10.50</td>
<td></td>
</tr>
<tr>
<td>Fixed carbon(^c)</td>
<td>78.41</td>
<td>71.84</td>
<td></td>
</tr>
<tr>
<td><strong>Ultimate analysis(^b)(%)</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Carbon</td>
<td>66.23</td>
<td>62.45</td>
<td></td>
</tr>
<tr>
<td>Hydrogen</td>
<td>2.21</td>
<td>1.85</td>
<td></td>
</tr>
<tr>
<td>Oxygen(^d)</td>
<td>28.33</td>
<td>31.63</td>
<td></td>
</tr>
<tr>
<td>Nitrogen</td>
<td>3.23</td>
<td>4.07</td>
<td></td>
</tr>
<tr>
<td>H/C molar ratio</td>
<td>0.40</td>
<td>0.36</td>
<td></td>
</tr>
<tr>
<td>O/C molar ratio</td>
<td>0.43</td>
<td>0.51</td>
<td></td>
</tr>
<tr>
<td>Empirical formula</td>
<td>(\text{CH}<em>0</em>{40}\text{N}<em>{0.04}\text{O}</em>{0.32})</td>
<td>(\text{CH}<em>0</em>{36}\text{N}<em>{0.06}\text{O}</em>{0.38})</td>
<td></td>
</tr>
<tr>
<td>Higher heating value</td>
<td>30.14</td>
<td>31.81</td>
<td></td>
</tr>
<tr>
<td>(MJ kg(^{-1}))</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BET surface area (m(^2)g(^{-1}))</td>
<td>3.64</td>
<td>14.14</td>
<td></td>
</tr>
</tbody>
</table>

\(^a\) Weight percentage on dry basis.

\(^b\) Weight percentage on dry ash free (daf) basis.

\(^c\) Weight percentage on dry basis.

![Figure 1: FTIR spectra](image_url)

Figure 1: FTIR spectra of (a) SPC and bio-char samples (b) Static atmosphere and (c) Nitrogen atmosphere.
The high heating value of the bio-chars were similar in comparison with that of other bio-chars [2,12], higher even that of the biomass before pyrolysis, the low ash content and low oxygen content are the reasons that explain the high heating value of the bio-char.

Nitrogen level in the bio-chars were 3.23% and 4.07% important information for predicting NOx emission from combustion of bio-char.

BET surface area of bio-chars at static and nitrogen atmosphere are 3.64 and 14.14 m²/g, respectively. Larger surface area was obtained at nitrogen atmosphere compared with static atmosphere.

The FTIR spectrum of bio-char samples and SPC are given in Figure 1. The FTIR spectrum of bio-char samples and SPC contains several identified absorption peaks. The FTIR spectrum also indicated the presence of the hydroxyl group (O-H) stretching vibrations between 3400 and 3500 cm⁻¹. The absorbance of peaks between 2200 and 2250 cm⁻¹ represent C≡N stretching vibrations indicative of nitril group. The band of the carbonyl groups appeared in the range between 1660 and 1725 cm⁻¹. Olefinic vibration take place between 650 and 750 cm⁻¹.

IV. Conclusion

In this study, the SPC bio-chars obtained at static and nitrogen pyrolysis atmosphere were characterized by using different analysis methods. Analysis results showed that chemical compositions of bio-chars obtained at different pyrolysis atmosphere are similar to each other. The main conclusions from this study are follows:

- The bio-chars can be transformed to activated carbon.
- The bio-chars may also be useful as a potential solid fuel.
- The produced bio-chars can be utilized in various industrial applications.

REFERENCES


Figure 2. SEM Photograpy of bio-chars (a) static atmosphere (b) Nitrogen atmosphere (x1000).