CHAPTER 6

Characterisation of selected biochars

Objective
To study the various characteristic features of certain selected biochars and their potential as a tool to combat climate change

6.1 Study rationale
Biochar, being derived from a variety of biological feedstocks that have been thermally degraded under a range of conditions exhibit various composition and chemistry. Due, in part to the complex set of chemical reactions that occur during thermal processing; a large degree of chemical and physical heterogeneity extends to the microscopic level, even with a single biochar. Thus, in the strict sense, each biochar made with a particular feedstock and process combination presents a unique mixture of phases and micro environments that give rise to a unique set of chemical, physical and biological properties. Characterization methods exist or can be developed to provide biochar property information such that biochar production parameter effects can be understood and controlled, and biochars and their effects can be differentiated from each other.

6.2 Introduction
Biochar is commonly defined as charred organic matter, produced with the intent to deliberately apply to soils to sequester carbon and improve soil properties (Lehmann and Joseph, 2009). Biochar is a stable carbon (C) compound created when biomass (feedstock) is heated to temperatures between 300 and 1000ºC, under low (preferably zero) oxygen concentrations. The objective of the biochar concept is to abate the enhanced greenhouse effect by sequestering C in soils, while concurrently improving soil quality. Biochar is subsequently created through pyrolysis of the plant material thereby potentially increasing its recalcitrance with respect to the original plant
material. Pyrolysis is the chemical decomposition of an organic substance by heating in the absence of oxygen and pyrolysis occurs spontaneously at high temperatures (generally above approximately 300°C for wood, with the specific temperature varying with material). The high temperatures used in pyrolysis can induce polymerisation of the molecules within the feedstocks, whereby larger molecules are also produced (including both aromatic and aliphatic compounds), as well as the thermal decomposition of some components of the feedstocks into smaller molecules. Feedstock is the term conventionally used for the type of biomass that is pyrolysed and turned into biochar. Feedstock along with pyrolysis conditions, is the most important factor controlling the properties of the resulting biochar (Lehmann and Joseph, 2009).

Terra Preta soils have been shown to contain about 50 t C ha\(^{-1}\) in the form of biochar, down to a depth of approximately 1 meter (approximately double the amount relative to pre-existing soil), and these soils are highly fertile when compared to the surrounding soils. This has led to the idea of biochar being applied to soil to sequester carbon and maintain or improve the soil production function (e.g. crop yields), as well as the regulation function and habitat function of soils. The estimated residence time of biochar-carbon is in the range of hundreds to thousands of years while the residence time of carbon in plant material is in the range of decades. Consequently, this would reduce the CO\(_2\) release back to the atmosphere if the carbon is indeed persistently stored in the soil. Considering the multi-dimensional and cross-cutting nature of biochar, an imminent need is anticipated for a balanced scientific review to effectively inform policy development on the current state of knowledge with reference to biochar application to soils.

### 6.3 Methodology

Six different feedstocks were selected for the preparation of biochars. They are:

1. Cow dung
2. Coconut husk
3. Coconut shell
4. Rice husk
5. Rubber seed shell
6. *Eichhornia* plant
Fig. 6.1 Different Feedstocks used for biochar preparation
6.3.1 Collection and preparation of feedstock

Raw feedstocks were collected from local environment and dried properly under natural conditions to remove the water content to the maximum and drying was continued till obtaining a constant weight. After drying, the materials were cut into desirable size and sorted separately and stored properly under air tight condition.

6.3.2 Pyrolysis and biochar preparation

Simple mound kiln method referred by FAO (1983) was adopted for pyrolysis process. Moreover the traditional knowledge of laymen who have expertise in making pit kilns was also used in this study. A small pit kiln of 2 sq. feet was prepared on the ground where the feedstock was stuffed under which a stack of smoldering wood in the ground was placed. A small fire was then started in the pit and additional wood was added to make the fire strong. At this point a canopy of branches and leaves were added to support a layer of earth or clay of about 0.2m in depth. A small vent was left on one side for the gas to escape. Carbonization proceeded up to 5 to 6 hours or more. The pit was later uncovered and the after the char was left to cool. It was collected carefully without any ash content and other debris, and later crushed and sieved through 2mm sieve.
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**Fig. 6.2** Different biochars prepared
6.3.3 Characterization

The biochar thus prepared was subjected to further physical and chemical characterisation. Biochar characterization was done according to the method described by Ahmedna et al. (1998). The bulk density was determined according to Masulili (2010), by filling a 10ml tube with dry ground biochar. The tubes were capped, tamped to a constant volume, and weighed. Bulk density was calculated by dividing the weight of the dry sample with the volume of the packed materials. Biochar pH was measured according to Ahmedna et al. (1998). The method consisted of preparing a 1% (wt/wt) suspension of biochar in deionized water. The suspension was heated to about 90°C and stirred for 20 minutes to allow dissolution of the soluble biochar components. After cooling to room temperature, the pH of the biochar suspension was measured using a pH meter. The biochar percent ash content (wt/wt) was determined by dry combustion at 760°C in air for 6 hrs using a laboratory muffle furnace (Novak et al., 2007). The nutrient content N, P and K were determined as per Masulili, (2010). Energy-dispersive spectroscopy (EDS) was used to quantify the major elemental distribution of the chars. Scanning electron microscopic (SEM) images of the chars were obtained for morphological features analysis. Solid-state Nuclear Magnetic Resonance (NMR) spectral pattern (IISC, Bangalore) of the biochar was obtained to understand the distribution and presence of C functional groups in various chars.

6.4 Results and discussion

Table 6.1: Characteristics of different biochars

<table>
<thead>
<tr>
<th>Material</th>
<th>pH</th>
<th>CEC (c mol kg⁻¹)</th>
<th>Moisture %</th>
<th>BD (g/cm³)</th>
<th>N %</th>
<th>P %</th>
<th>K (%)</th>
<th>Ash content (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td><em>Eichhornia</em></td>
<td>9.6</td>
<td>14.9</td>
<td>10.5</td>
<td>0.80</td>
<td>0.95</td>
<td>0.85</td>
<td>0.97</td>
<td>25.5</td>
</tr>
<tr>
<td>Cow dung</td>
<td>8.9</td>
<td>13.6</td>
<td>13.9</td>
<td>0.78</td>
<td>0.73</td>
<td>0.57</td>
<td>0.69</td>
<td>65.2</td>
</tr>
<tr>
<td>Coconut husk</td>
<td>7.5</td>
<td>11.3</td>
<td>8.2</td>
<td>0.81</td>
<td>0.35</td>
<td>0.26</td>
<td>0.89</td>
<td>35.3</td>
</tr>
<tr>
<td>Coconut shell</td>
<td>9.7</td>
<td>14.2</td>
<td>7.6</td>
<td>0.88</td>
<td>0.34</td>
<td>0.10</td>
<td>0.84</td>
<td>7.4</td>
</tr>
<tr>
<td>Rubber seed shell</td>
<td>7.9</td>
<td>11.2</td>
<td>6.5</td>
<td>0.81</td>
<td>0.26</td>
<td>0.21</td>
<td>0.6</td>
<td>8.6</td>
</tr>
<tr>
<td>Rice husk</td>
<td>7.3</td>
<td>12.6</td>
<td>6.9</td>
<td>0.86</td>
<td>0.32</td>
<td>0.12</td>
<td>0.2</td>
<td>7.3</td>
</tr>
</tbody>
</table>

*pH p < 0.01; CEC p < 0.01; BD p < 0.05; P p < 0.01; K p < 0.01; Ash content p < 0.01*
Variation of pH in different biochars

Variation of CEC in different biochars

Variation of moisture in different biochars

Variation of BD in different biochars

Variation of N, P, K in different biochars

Variation of ash in different biochars

Fig. 6.3 Characteristics of different biochars
6.4.1 Chemical characteristics

The properties of biochars produced from various feedstocks are shown in Table 6.1 and Fig. 6.3. It is seen that all chars are alkaline in nature as the pH ranges from 7.5 to 9.7. Considering the very large heterogeneity of its properties, biochar pH values are relatively homogeneous, i.e., they are largely neutral to basic. Chan and Xu (2009) reviewed biochar pH values from a wide variety of feedstocks and found a mean of pH 8.1 in a total range of pH 6.2 – 9.6. Biochar from coconut shell is highly alkaline (9.7) followed by *Eichhornia* biochar (9.6). The CEC values varied between 14.9 and 11.2. *Eichhornia* biochar had a highest CEC whereas biochar from the shells of rubber seed produced lowest value (11.2). Maximum moisture content was seen in the cow dung char whereas it was minimum in rubber seed shell. The bulk density (BD) values varied significantly between the biochars and the maximum value was noted in coconut shell biochar (0.88g/cm$^3$) whereas the least value is noted in *Eichhornia* (0.80). The nutrient values fluctuated widely between the samples. Maximum N, P and K values were noted in *Eichhornia* biochar followed by cow dung and coconut husk biochar. In the rubber seed shell and rice husk chars, the nutrient status was comparatively low. Maximum ash content was produced by cow dung char followed by *Eichhornia*. It was reported earlier that feedstock like grain husk, grass or fodders and manures like cow dung have very high ash content (Ravindran *et al.*, 1995) whereas woody material have less ash content.

The different feedstocks used to make biochar contain various amounts of ash, and it represents a greater proportion of the overall material present. Wood contains less ash (< 1%) than straw and other crop residues (up to 24%), which also contain more silica (Raveendran *et al.*, 1995). Manures produce high-ash biochars, with ash contents up to 45% (Koutcheiko *et al.*, 2007).

The different properties of those biochars seem to be associated with the nature of the chemical constituents in the feedstock biomass. Brown, 2009; Chan and Xu, 2009; Hammes *et al.*, 2006, have confirmed that the different nature of biochar products are typically influenced by wide range of factors including different types of materials being used or feedstock quality and also different charring condition. Chan *et al.* (2007) showed that biochar made from manure like cow dung will have a higher
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nutrient content than biochar made from wood materials. According to Sukartono et al., (2011) the nutrient of the cow dung biochar is derived from the fodder biomass which was fed by the animal and this implies the fact that the basic biochar characteristics are of the basic biomass features.

6.4.2 Elemental composition

![EDS spectra showing elemental concentration of different biochars](image-url)

**Fig. 6.4** EDS spectra showing elemental concentration of different biochars
## Table 6.2 Elemental concentration (weight %) of various biochars.

<table>
<thead>
<tr>
<th>Biochar</th>
<th>C</th>
<th>Al</th>
<th>Si</th>
<th>K</th>
<th>O</th>
<th>Mg</th>
<th>P</th>
<th>Ca</th>
<th>Na</th>
<th>Cl</th>
<th>S</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rice husk</td>
<td>15.9</td>
<td>0.23</td>
<td>18.96</td>
<td>0.43</td>
<td>64.40</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Coconut husk</td>
<td>26.7</td>
<td>-</td>
<td>-</td>
<td>0.96</td>
<td>71.84</td>
<td>0.08</td>
<td>0.09</td>
<td>0.20</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Coconut shell</td>
<td>26.9</td>
<td>-</td>
<td>0.05</td>
<td>0.38</td>
<td>72.09</td>
<td>-</td>
<td>-</td>
<td>0.35</td>
<td>0.11</td>
<td>0.06</td>
<td>-</td>
</tr>
<tr>
<td>Cow dung</td>
<td>23.1</td>
<td>0.04</td>
<td>-</td>
<td>0.20</td>
<td>72.39</td>
<td>0.11</td>
<td>0.04</td>
<td>0.10</td>
<td>-</td>
<td>-</td>
<td>0.03</td>
</tr>
<tr>
<td>Rubber seed shell</td>
<td>26.5</td>
<td>5.37</td>
<td>-</td>
<td>-</td>
<td>70.10</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td><em>Eichhornia</em></td>
<td>23.4</td>
<td>1.90</td>
<td>7.61</td>
<td>32.69</td>
<td>18.15</td>
<td>1.62</td>
<td>-</td>
<td>9.16</td>
<td>1.62</td>
<td>28.61</td>
<td>-</td>
</tr>
</tbody>
</table>

The Fig. 6.4 and Table 6.2 represent the distribution of various elements in different biochars. The C concentration varies between 15.9 and 26.9 % by weight. This difference can be explained on the basis of variation of ash content. This is an important observation as biochars are commonly regarded as OC-rich materials. Presence of Si was noted only in rice husk, coconut shell and *Eichhornia* biochars. Amorphous Si is of particular interest as it is typically in the form of phytoliths that contain and protect plant C from degradation (Wilding, 1967; Krull et al., 2003; Smith and White, 2004; Parr and Sullivan, 2005; Parr, 2006). Two factors, mainly feedstock and process conditions control the amount and distribution of mineral matter in the biochar.

### 6.4.3 C functional groups

The 13C NMR spectral pattern of various biochar (Fig. 6.5) revealed prominent peaks between 120-130 and 180-190 ppm. These peaks indicate that most of this biochar is distributed in aromatic structures. In 0 - 50ppm, weak signals represent the low occurrence of aliphatic structures. This speculation has merit because the high pyrolysis temperature explains the lack or low occurrence of alkyl C (0-50 ppm), as volatile material such as oils, fatty acids, and alkyl alcohols would be lost (Antal and Gronli, 2003). Carboxyl-containing structures were present in the NMR spectra possibly because of their structural decomposition resistance during pyrolysis. The NMR spectra indicate that these biochars are composed of a mixture of organic structural groups reflecting the chemistry of the feedstock and reactions occurring
during both pyrolysis and after pyrolysis on exposure of the biochar to oxygen and water (Schmidt and Noack, 2000; Novotny et al., 2007).

Fig 6.5 NMR spectra of different biochars
6.4.4 Morphological features

Scanning electron microscopy (SEM) is a potential technique for studying morphology and surface properties. SEM analysis has been especially used to evaluate the structural variations in biochar particles after different thermal treatments and SEM images are very useful to obtain accurate details about pore structure of biochars (Ozçimen & Mericboyu, 2010). Some surface properties of biochar samples such as porosity, total pore volume and surface area are presented in Table 6.3. It can be seen that porosity values of biochar samples change from 0.13 to 0.17 (%), total pore volume values are in the range of 0.67–14.68 (m²/g), 0.12–0.18 (m³), respectively.

Table 6.3 Porosity of different biochars

<table>
<thead>
<tr>
<th>Biochar</th>
<th>Porosity (%)</th>
<th>Total pore Volume (m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Eichhornia</td>
<td>0.17</td>
<td>0.18</td>
</tr>
<tr>
<td>Cow dung</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Coconut husk</td>
<td>0.17</td>
<td>0.18</td>
</tr>
<tr>
<td>Coconut shell</td>
<td>0.18</td>
<td>0.15</td>
</tr>
<tr>
<td>Rubber seed shell</td>
<td>0.16</td>
<td>0.13</td>
</tr>
<tr>
<td>Rice husk</td>
<td>0.13</td>
<td>0.12</td>
</tr>
</tbody>
</table>

The SEM analysis (Fig. 6.6) shows the presence of micro-pores with a surface area of 750 - 1360 m² g⁻¹ and a volume of 0.2 - 0.5 cm³ g⁻¹ and macro-pores with a surface area of 51 - 138 m² g⁻¹ and a volume of 0.6 - 1.0 g⁻¹. Here the maximum porosity was achieved by coconut shell followed by coconut husk and *Eichhornia*. Coconut husk and *Eichhornia* biochars provided maximum pore volume.
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Rubber seed shell

Rice husk

Cow dung

A study on carbon and green house gas dynamics of wetland rice soils with special reference to biochar application
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Fig. 6.6 SEM images of different biochars

Eichhornia

coconut husk

Coconut shell

Fig. 6.6 SEM images of different biochars
All these biochars are prepared under considerable temperature ranges of 350-400°C and this high temperature generally causes greater condensation of aromatic structures (Chan et al., 2007). Hence these chars expected to be more resistant to chemical oxidation and microbial degradation. Therefore a longer half life in soil environment than soil organic matter was also expected. NMR spectra revels the presence of recalcitrant aromatic C functional group in all biochars prepared and this recalcitrance would be a desirable property if the primary goal was to remove atmospheric CO₂ and sequester carbon in soil for millennia (Harris et al., 1966). The ash content and residue of biochars contains different proportions of carbonates of alkali and alkaline earth metals, amounts of silica, heavy metals, sesquioxides, phosphates and small amounts of organic and inorganic N (Sharma et al., 1968) as observed in EDS spectra and this explains the preferable variation in the pH and CEC of different chars. The SEM images show the variations in the porous structure of morphology. These variations will result in different capacity to adsorb soluble inorganic matter, gases and inorganic nutrient and habitat suitability for microbes to colonize, grow and reproduce, particularly for bacteria (Sainju et al., 2006) The positive effect of biochar on SOC levels was expected due to their high carbon content and this content varies between biochars as observed in the elemental analysis and is greatly dependent on the feedstock properties. The structural composition of the biomass feedstock relates to the chemical and structural composition of the resulting biochar and, therefore, is reflected in its behaviour, function and fate in soils.

Thus the characteristic features of the prepared biochar revealed their chemical, physical and morphological features. It can be inferred that certain factors like the nature of feedstock, pyrolysis temperature etc. determine these characteristic features and hence make every biochar distinct from each other. Based on these qualities, the nature of biochar on application to soil also differs. The fate of the biochar in the soil to a larger extent is determined by these basic characteristic features.

6.5 Conclusion

Biochar is comprised of stable carbon compounds created when biomass is heated to temperatures between 300 to 1000°C under low (preferably zero) oxygen concentrations. The structural and chemical composition of biochar is highly
heterogeneous, with the exception of pH, which is typically > 7. Some properties are pervasive throughout all biochars, including the high C content and degree of aromaticity, partially explaining the high levels of biochar’s inherent recalcitrance. Nevertheless, the exact structural and chemical composition, including surface chemistry, is dependent on a combination of the feedstock type and the pyrolysis conditions (mainly temperature) used. These same parameters are key in determining particle size and pore size (macro, meso and micropore distribution in biochar. Biochar's physical and chemical characteristics may significantly alter key soil physical properties and processes and are, therefore, important to consider prior to its application to soil. Furthermore, these will determine the suitability of each biochar for a given application, as well as define its behaviour, transport and fate in the environment. Dissimilarities in properties between different biochar products emphasise the need for a case-by-case evaluation of each biochar product prior to its incorporation into soil at a specific site. Further research aiming to fully evaluate the extent and implications of biochar particle and pore size distribution on soil processes and functioning is essential, as well as its influence on biochar mobility and fate.