Microstructure of Charcoal Produced by Traditional Technique

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ABSTRACT

Charcoal which is produced from wood, a renewable material, is potential for many engineering applications. In developing countries, charcoals are produced by traditional techniques. It is estimated that the charcoal produced by traditional techniques are inappropriate for engineering materials. This study was conducted to observe the microstructure in charcoal prepared by traditional technique by using Raman spectroscopy for further development. Thermogravimetric analysis (TGA) estimated that most of charcoals produced by traditional technique were prepared at low temperature around 300-500 ºC indicating by the weight loss above 300 ºC for charcoal from acacia wood and above 500 ºC for charcoal from mahogany and sonokeling woods. Carbonization temperature determined degree of order of graphitic crystallite and disorder and distorted structure in the microstructure of charcoal. Charcoal from mahogany and sonokeling wood which were estimated prepared at 500 ºC showed similar degree of order of graphitic crystallite and disorder and distorted structure with charcoal of Japanese cedar wood which were prepared at 700 ºC in laboratory, as showing by the similar position of the Raman G band and the width of G and D bands.

Keywords: microstructure, thermogavimetric analysis, Raman spectroscopy,

INTRODUCTION

Charcoal which is produced from wood, a renewable material, is potential for many engineering applications. The non graphitic carbon with porous structure in carbonized wood provides high reactivity in the adsorption of heavy metals from aqueous solution (Pulido et al, 1998), high reactivity for production carbide ceramics for applications such as high temperature filter, catalyst for bioengineering process (Greil, 2001), for electromagnetic shielding material (Wang and Hung, 2003), for fuel cell (Kercher and Nagle, 2002), etc. These variety applications of carbonized wood are determined by the microstructure in carbonized wood. The control microstructure in carbonized wood may lead to the proper utilization for engineering applications.

In developing countries, charcoals are mostly produced by traditional techniques. The characteristics of charcoal prepared by traditional techniques include having high contents of volatile matters and ash; and in the contrary having low content of fix carbon (Marsoem et al, 2003). The traditional techniques with low carbonization temperature are estimated to influence the inferior characteristic of charcoal produced. Therefore it is predicted that the charcoal produced from traditional techniques is inappropriate for engineering materials. It is required a study on the microstructure in the charcoal produced by traditional technique by using Raman spectroscopy.
for further developments. The carbonization condition and heating temperature in the production of charcoal by traditional technique was observed by thermogravimetric analysis.

EXPERIMENTAL

Charcoal samples produced by traditional technique were obtained from Yogyakarta area. The charcoal samples were prepared from acacia (*Acacia auriculiformis*, sonokeling (*Dalbergia latifolia*) and mahagony (*Swietenia mahagoni*) woods by mound kiln technique from different charcoal makers. Oil palm shell charcoal was obtained from the solid waste of pyrolytic liquid production at temperature 300 °C. Japanese cedar wood (*Cryptomeria japonica*) particles were carbonized at a heating rate of 4 °C/min and were then maintained constant at a temperature of 700 °C for 1 h in Argon gas flowing at a rate of 100 mL/min in a laboratory scale electric furnace.

The experiment of thermal decomposition of charcoal used thermogravimetric equipment (Mettler TGA-2050). A small sample of wood charcoal (around 15 mg) was heated from 25 to 800°C using thermogravimetric equipment under Nitrogen gas flow 200 cm³ min⁻¹.

A Raman spectroscope (Renishaw inVia, England) equipped with an air-cooled CCD detector was used to analyze the carbon structure of carbonized wood and graphite before and after the heat treatment process. An argon laser (514.5 nm) was adopted as an excitation source. The laser was focused to approximately 1 μm in diameter at a power of less than 1 mW on the sample surface in order to prevent irreversible thermal degradation. Spectra were measured in the 1,100–1,800 cm⁻¹ range. Six 30-s accumulations gave adequate signal-to-noise ratio of the spectra. The wave number was calibrated using the 520 cm⁻¹ line of a silicon wafer. Spectral processing was performed using WiRE 2 software.

RESULT AND DISCUSSION

Thermogravimetric Analysis

Thermogravimetric (TG) and derived thermogravimetric (DTG) curves of all samples of charcoal were recorded from 25 to 800 °C, as shown in Fig. 1. The curves show the non-isothermal-degradation of charcoal in nitrogen gas flow accompanied by mass losses.

![Fig. 1. TG and DTG curves of charcoals from acacia, mahagony, and sonokeling woods producing by traditional charcoal technique; from Japanese cedar wood prepared at laboratory at 700 °C; and from the solid waste of pyrolytic liquid production of oil palm shell, under dynamic conditions from 25 to 800 °C](image-url)
Charcoal from Japanese cedar wood (*Cryptomeria japonica*) shows the occurrence of two regions of weight loss in the temperature ranges 25-100 ºC and 500-800 ºC with the cumulative weight loss only 7 wt.%. The first region 30-100 ºC corresponds to desorption of water. Less weight loss in the second region of Japanese cedar charcoal indicated the less degradation of charcoal which was already carbonized at 700 ºC during the preparation in the laboratory. Charcoal from mahagony and sonokeling wood also show similar regions of weight loss. But they show slightly higher weight loss in the region 500-800 ºC with the cumulative weight loss of 13 wt.%. The weight loss of charcoal of mahagony and sonokeling wood above 500 ºC corresponds to the degradation of lignin (Byrne and Nagle, 1997). The weight loss indicated a continuation of carbonization process started from 500. The charcoal of oil palm shell prepared at 300 ºC shows three regions of weight loss in the temperature ranges 25-150 ºC and 150-700 ºC, and 700-800 ºC with the cumulative weight loss 25 wt.%. The TG and DTG curves of charcoal of acacia wood seem similarities with those of oil palm shell with the second region in the range from 300 to 700 ºC. The change in weight loss above 200 ºC until approximately 290 ºC corresponds to the decomposition of hemicellulose (Byrne and Nagle, 1997), as shown in the second region of oil palm shell charcoal. Above 290 ºC the change in weight loss corresponds to the decomposition of cellulose and lignin. The further thermal decomposition of wood component in charcoal can be evaluated from TG and DTG curves recorded in nitrogen gas flow. It is obviously that most of wood charcoals which were produced by traditional technique were prepared at low temperature around 300-500 ºC indicating by the weight loss above 300 ºC for charcoal from acacia wood and above 500 ºC for charcoal from mahagony and sonokeling wood. Improvement for traditional charcoal makers is necessary to increase the carbonization temperature up to 700-800 ºC as obtaining by the charcoal from Japanese cedar wood.

**Microstructure of Cell Wall of Charcoals**

Figure 2 shows Raman spectra of charcoals from acacia, mahagony, and sonokeling woods producing by traditional charcoal makers; from Japanese cedar wood prepared at laboratory; and from the solid waste of pyrolytic liquid production of oil palm shell. The two Raman bands corresponding to the disordered and strongly distorted structure of turbostratic carbon (D band) and stacking disorder of the basic structural units (BSU) of the aromatic layers (G band) were distinctly observed at positions around 1586 - 1603 cm⁻¹ and 1346 - 1363 cm⁻¹, respectively (Paris et al. 2005).

The position of the Raman G band, the full width at half maximum (FWHM) of the Raman G and D bands and the peak intensity ratio of G and D (I_d/I_g) are the characteristic Raman parameters for the carbon structure of carbonaceous materials (Ishimaru et al., 2007). Table 1 shows the values of these Raman parameters of charcoal of Japanese cedar wood prepared at laboratory at 700 ºC; charcoal of oil palm shell from the solid waste of pyrolytic liquid production; charcoal of acacia, mahagony and sonokeling woods produced by traditional charcoal makers.
Fig. 2. Raman spectra of charcoals from acacia, mahagony, sonokeling and Japanese cedar woods and from oil palm shell. The carbonization conditions of each charcoal refer to Fig. 1.

Table 1. Raman parameters of charcoals from acacia, mahagony, sonokeling and Japanese cedar woods and from oil palm shell. The carbonization conditions of each charcoal refer to Fig. 1.

<table>
<thead>
<tr>
<th>Wood Type</th>
<th>G band position</th>
<th>D band position</th>
<th>G band width</th>
<th>D band width</th>
<th>$I_d/I_g$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acacia</td>
<td>1586</td>
<td>1363</td>
<td>75</td>
<td>121</td>
<td>0.54</td>
</tr>
<tr>
<td>Mahagony</td>
<td>1603</td>
<td>1346</td>
<td>62</td>
<td>117</td>
<td>0.53</td>
</tr>
<tr>
<td>Sonokeling</td>
<td>1602</td>
<td>1356</td>
<td>66</td>
<td>110</td>
<td>0.58</td>
</tr>
<tr>
<td>Oil palm shell</td>
<td>1598</td>
<td>1357</td>
<td>76</td>
<td>136</td>
<td>0.64</td>
</tr>
<tr>
<td>Japanese cedar</td>
<td>1601</td>
<td>1356</td>
<td>62</td>
<td>113</td>
<td>0.63</td>
</tr>
</tbody>
</table>

There were little difference in the position of the Raman G band and the width of G and D bands observed from charcoal of Japanese cedar, mahagony and sonokeling woods. The position of the Raman G band of charcoal from acacia wood and oil palm shell shows difference with those of charcoal from Japanese cedar, mahagony and sonokeling woods. Moreover, the width of G and D bands of charcoal from acacia wood and oil palm shell were broader than those of charcoal from Japanese cedar, mahagony and sonokeling woods. The Raman parameters of charcoal from acacia wood and oil palm shell indicates that their microstructure possess a low degree of order of graphitic crystallites and less improvement on their disordered and distorted structures. The higher temperature of carbonization of Japanese cedar, mahagony and sonokeling woods influenced on the increasing degree of order of graphitic crystallites in the BSU and improving the disorder and distorted structure in the microstructure of charcoal indicating by the narrow of G and D bands width. In disordered carbon materials, the $I_d/I_g$ is inversely proportional to the development of the carbon crystallites during carbonization. In the present work, the similar values of $I_d/I_g$ between charcoal of acacia, mahagony and sonokeling and that of between charcoal of oil palm shell and Japanese cedar wood imply that the carbonization temperature did not affect on the lateral growth carbon crystallite. The opposite result reported by Karcher and Nagle (2003) by X-ray diffraction
technique that showed the increase of lateral carbon crystallites with increasing the carbonization temperature from 400 to 800 ºC. The relation between lateral crystallite size with the Raman intensity ratio might not be applicable (Paris et al., 2005).

CONCLUSION

The TGA curves in temperature range 25-800 ºC were able to estimate the carbonization temperature in the preparation of charcoal. Most of charcoal produced by traditional technique were prepared at low temperature around 300-500 ºC indicating by the weight loss above 300 ºC for charcoal from acacia wood and above 500 ºC for charcoal from mahagony and sonokeling woods. Carbonization temperature determined degree of order of graphitic crystallite and disorder and distorted structure in the microstructure of charcoal. Charcoal from mahagony and sonokeling wood which were estimated prepared at 500 ºC showed similar degree of order of graphitic crystallite and disorder and distorted structure with charcoal of Japanese cedar wood which were prepared at 700 ºC in laboratory, as showing by the similar position of the Raman G band and the width of G and D bands. Charcoal from acacia wood and oil palm shell showed less degree of order of graphitic crystallite and disorder and distorted structure in their microstructure as indicating by the position of G band and the broad width of the G and D bands.

REFERENCES