Article

Expedient Prediction of the Fuel Properties of Carbonized Woody Biomass Based on Hue Angle

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Abstract: Woody biomass co-firing-based power generation can reduce CO₂ emissions from pulverized coal boilers. Carbonization of woody biomass increases its calorific value and grindability, thereby improving the co-firing ratio. Carbonized biomass fuel properties depend on moisture, size and shape of feedstock, and carbonization conditions. To produce carbonized biomass with stable fuel properties, the carbonization conditions should be set according to the desired fuel properties. Therefore, we examined color changes accompanying woody biomass carbonization and proposed using them for rapid evaluation of fuel properties. Three types of woody biomasses were carbonized at a test facility with a capacity of 4 tons/day, and the fuel properties of the obtained materials were correlated with their color defined by the \( L^*a^*b^* \) model. When fixed carbon, an important fuel property for carbonization, was 25 wt % or less, we observed a strong negative correlation, regardless of the tree species, between the hue angle, \( h_{ab} \), and fixed carbon. The \( h_{ab} \) and fixed carbon were correlated even when the fixed carbon exceeded 25 wt %; however, this correlation was specific to the tree species. These results indicate that carbonized biomass fuel properties such as fixed carbon can be estimated rapidly and easily by measuring \( h_{ab} \).

Keywords: carbonization; woody biomass; color analysis; fuel properties; fixed carbon

1. Introduction

Woody biomass (WB) is an abundant, renewable, and carbon-neutral energy source that is often considered to be a suitable alternative to fossil fuels [1]. Even in Japan, a number of large pulverized-coal-fired power plants have incorporated biomass co-firing to reduce CO₂ emissions. However, compared to coal, WB has a remarkably poor grindability [2] and low calorific value. Therefore, to increase the biomass co-firing ratio in existing pulverized coal boilers, biomass modifications via pre-treatment are required.

Steam explosion and carbonization are well-known pre-treatment techniques that can be used to prepare WB for co-firing in pulverized coal boilers. The former technique features the use of high-temperature and high-pressure steam to disrupt and swell wood microstructures by rapid decompression [3]. Conversely, carbonization is a pyrolysis process used to decompose certain structural components of WB by heating in an inert (i.e., oxygen-free) atmosphere [4,5]. Although steam explosion processing does not significantly affect the caloric value, this parameter (as well as grindability) is greatly increased by carbonization [6]. In addition, carbonization was shown to reduce the chlorine content of biomass [7] and improve its hydrophobicity [8], thus allowing carbonized WB to be used in pulverized coal boilers at a high co-firing ratio [9,10].
The above-mentioned carbonization-induced property changes result from the thermal decomposition of cellulose, hemicellulose, and lignin, which are the main components of WB [11]. Moreover, numerous studies on WB carbonization [11–15] have shown that the properties of carbonized biomass strongly depend on its origin (tree species), moisture content, treatment time, and shape. Thus, the stable production of carbonized biomass with desired properties requires a rapid analysis of fuel properties, which have to be reflected in the operating conditions of the production process in a timely manner. To date, the design of rapid and expedient methods of measuring the properties of biomass-derived modified fuel has been extensively investigated. For example, Kubojima et al. [16] correlated the weight reduction of torrefied wood chips with their color change, whereas Strandberg et al. [17] used thermogravimetric and multivariate analyses for accurate elemental composition prediction. Moreover, Lestander et al. [18] showed that near-infrared spectroscopy can be used for caloric value, carbon, oxygen, hydrogen, ash, volatile matter, and fixed carbon content predictions, claiming that the production of heat-treated biomass could be controlled by spectral measurements. Lindström et al. [19] investigated the changes in appearance caused by carbonization and showed that the caloric value and chemical properties of carbonized WB can be assessed by using infrared spectroscopy. Tooyserkani et al. [20] correlated the lightness of steam-explosion-treated specimens with their carbon content, thus demonstrating that the properties of carbonized WB could be determined by weight measurements. However, despite the above methods, rapid and expedient measurement of the fuel properties of carbonized woody biomass with a high proportion of fixed carbon is still difficult. Herein, three types of WB were carbonized at 200–450 °C, i.e., in the temperature range resulting in the largest fuel property changes [21,22], and the fuel properties of the obtained carbonized WB were correlated with its color.

2. Materials and Methods

2.1. Materials and Carbonization Process

Three types of raw WB, namely, rubber tree (Hevea brasiliensis) stems, softwood (mixture of equal amounts of spruce and pine) bark, and lumber waste were selected as low-cost potential renewable energy resource, and conditioned into 20-mm particles. Figure S1 shows the outer appearance of the test facility (capacity = 4 tons/day) used for carbonization [23]; the carbonizer comprises of an externally heated rotary kiln. To obtain a wide range of different characteristics and qualities of carbonized biomass, the raw WB was treated under various conditions at a biomass feed rate of 144 kg/h, inner cylinder rotation speed of 5 rpm, and carbonization temperatures of 300–410 °C. At the exit-end of the kiln, carbonized WB was sampled and used for further experimentation.

2.2. Fuel Property Measurements

Proximate analysis (ash, volatile matter, and fixed carbon), elemental analysis (carbon, hydrogen, nitrogen, oxygen, and sulphur), and measurement of the higher heating value of raw and carbonized WB were in accordance with standard methods, namely, the JIS-M8812 (Coal and Coke—Methods for Proximate Analysis), JIS-M8813 (Coal and Coke—Determination of Constituents), and JIS-M8814 (Coal and Coke Determination of Gross Calorific Value by the Bomb Calorimetric Method, and Calculation of Met Calorific Value) methods, respectively.

2.3. Color Measurements

The color of carbonized WB was characterized by using a color meter (TES135A Plus; TES Electrical Electronic Corp, Taipei, Taiwan), and the obtained information was represented in the L’ a’ b’ color space, with L’ representing lightness and a’ and b’ expressing chromaticity. Based on the above representation, the hue angle \(h_{ab}\) was defined as \(h_{ab} = \tan^{-1}(b’/a’).\)

To measure color differences, the carbonized WB was pulverized by using a cutting mill (Wonder Blender; Osaka Chemical Co., Ltd., Osaka, Japan) and sieved to a 200-mesh size.
3. Results and Discussion

3.1. Properties of Carbonized WB

Table 1 shows the fuel properties of raw WB (i.e., specimens for carbonization treatment) and carbonized WB. Previous studies have shown that carbonization increases the fixed carbon content and calorific value while decreasing the amount of volatile matter [24,25]. Similarly, we herein observed carbonization-induced increases of the fixed carbon content, ash content and calorific value, as well as a decrease of volatile matter and oxygen contents. The carbonization temperature depended on the type of raw material that was used even in cases of those with nearly identical fuel properties. For example, No. R-8, B-9, and W-7 in Table 1 samples were obtained by carbonization at 339, 315, and 381 °C, respectively, even though all of them had a ~31 wt % of fixed carbon. Thus, the stable production of carbonized WB with desired fuel properties using carbonization temperature as an operation parameter was challenging, as it required carbonization conditions to be set according to raw material characteristics such as the tree species, chip size, and moisture content.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Moisture (wt %)</th>
<th>Ash (wt %)</th>
<th>VM (wt %)</th>
<th>FC (wt %)</th>
<th>C (wt %)</th>
<th>H (wt %)</th>
<th>N (wt %)</th>
<th>O (wt %)</th>
<th>S (wt %)</th>
<th>HHV (MJ/kg)</th>
<th>Temp. (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated rubber tree</td>
<td>R-1</td>
<td>28.9</td>
<td>1.3</td>
<td>83.6</td>
<td>15.1</td>
<td>49.9</td>
<td>6.6</td>
<td>0.4</td>
<td>41.9</td>
<td>0.02</td>
<td>19.8</td>
</tr>
<tr>
<td>R-2</td>
<td>&lt;0.1</td>
<td>14.5</td>
<td>32.0</td>
<td>47.8</td>
<td>0.5</td>
<td>0.3</td>
<td>0.1</td>
<td>0.4</td>
<td>40.5</td>
<td>0.04</td>
<td>20.2</td>
</tr>
<tr>
<td>R-3</td>
<td>&lt;0.1</td>
<td>15.0</td>
<td>33.2</td>
<td>46.0</td>
<td>0.4</td>
<td>0.2</td>
<td>0.1</td>
<td>0.4</td>
<td>39.1</td>
<td>0.04</td>
<td>20.2</td>
</tr>
<tr>
<td>R-4</td>
<td>&lt;0.1</td>
<td>13.5</td>
<td>34.0</td>
<td>47.5</td>
<td>0.6</td>
<td>0.2</td>
<td>0.1</td>
<td>0.4</td>
<td>38.0</td>
<td>0.04</td>
<td>20.2</td>
</tr>
<tr>
<td>R-5</td>
<td>&lt;0.1</td>
<td>14.5</td>
<td>32.0</td>
<td>47.8</td>
<td>0.5</td>
<td>0.3</td>
<td>0.1</td>
<td>0.4</td>
<td>40.5</td>
<td>0.04</td>
<td>20.2</td>
</tr>
<tr>
<td>R-6</td>
<td>&lt;0.1</td>
<td>12.5</td>
<td>31.0</td>
<td>48.0</td>
<td>0.5</td>
<td>0.3</td>
<td>0.1</td>
<td>0.4</td>
<td>39.0</td>
<td>0.04</td>
<td>20.2</td>
</tr>
<tr>
<td>R-7</td>
<td>&lt;0.1</td>
<td>11.5</td>
<td>30.0</td>
<td>49.0</td>
<td>0.5</td>
<td>0.3</td>
<td>0.1</td>
<td>0.4</td>
<td>38.0</td>
<td>0.04</td>
<td>20.2</td>
</tr>
<tr>
<td>R-8</td>
<td>&lt;0.1</td>
<td>10.5</td>
<td>29.0</td>
<td>49.0</td>
<td>0.5</td>
<td>0.3</td>
<td>0.1</td>
<td>0.4</td>
<td>37.0</td>
<td>0.04</td>
<td>20.2</td>
</tr>
<tr>
<td>R-9</td>
<td>&lt;0.1</td>
<td>9.5</td>
<td>28.0</td>
<td>49.0</td>
<td>0.5</td>
<td>0.3</td>
<td>0.1</td>
<td>0.4</td>
<td>36.0</td>
<td>0.04</td>
<td>20.2</td>
</tr>
<tr>
<td>R-10</td>
<td>&lt;0.1</td>
<td>8.5</td>
<td>27.0</td>
<td>49.0</td>
<td>0.5</td>
<td>0.3</td>
<td>0.1</td>
<td>0.4</td>
<td>35.0</td>
<td>0.04</td>
<td>20.2</td>
</tr>
<tr>
<td>R-11</td>
<td>&lt;0.1</td>
<td>7.5</td>
<td>26.0</td>
<td>49.0</td>
<td>0.5</td>
<td>0.3</td>
<td>0.1</td>
<td>0.4</td>
<td>34.0</td>
<td>0.04</td>
<td>20.2</td>
</tr>
<tr>
<td>R-12</td>
<td>&lt;0.1</td>
<td>6.5</td>
<td>25.0</td>
<td>49.0</td>
<td>0.5</td>
<td>0.3</td>
<td>0.1</td>
<td>0.4</td>
<td>33.0</td>
<td>0.04</td>
<td>20.2</td>
</tr>
<tr>
<td>R-13</td>
<td>&lt;0.1</td>
<td>5.5</td>
<td>24.0</td>
<td>49.0</td>
<td>0.5</td>
<td>0.3</td>
<td>0.1</td>
<td>0.4</td>
<td>32.0</td>
<td>0.04</td>
<td>20.2</td>
</tr>
<tr>
<td>R-14</td>
<td>&lt;0.1</td>
<td>4.5</td>
<td>23.0</td>
<td>49.0</td>
<td>0.5</td>
<td>0.3</td>
<td>0.1</td>
<td>0.4</td>
<td>31.0</td>
<td>0.04</td>
<td>20.2</td>
</tr>
<tr>
<td>R-15</td>
<td>&lt;0.1</td>
<td>3.5</td>
<td>22.0</td>
<td>49.0</td>
<td>0.5</td>
<td>0.3</td>
<td>0.1</td>
<td>0.4</td>
<td>30.0</td>
<td>0.04</td>
<td>20.2</td>
</tr>
</tbody>
</table>

The above table lists the results for 15 samples of raw and carbonized WB (R, rubber tree; B, softwood bark; W, lumber waste) for each type of material studied in order of the increasing carbonization temperature. All analyses were performed according to standard procedures (JIS-M8812, JIS-M8813, and JIS-M8814). VM = volatile matter; FC = fixed carbon; HHV = higher heating value; Temp. = carbonization temperature.
3.2. Color Changes of Carbonized WB

Figure 1 shows images of the carbonized WB samples. Specifically, these images show how the initially light brown raw WB became darker as the carbonization process progressed. At fixed carbon contents exceeding 30 wt %, the visual discrimination of color differences became complicated, and thus, a color meter was used to obtain quantitative data (Table S1). The results listed in Table S1 show that carbonization shifted $L^*$ from white to black, $a^*$ from red to green, and $b^*$ from blue to yellow. In addition, the numerical values of $a^*$ and $b^*$, which show the degree of color on the red–green and yellow–blue axes, respectively, decreased with increasing fixed carbon content; these results indicate that the carbonized WB was more green/blue than raw WB.

3.3. Relationship between the Color and Properties of Carbonized WB

Figure 2a,b show that the $a^*$ and $b^*$ values of carbonized WB decreased with the increasing fixed carbon content, and the above decrease was rapid at fixed carbon contents of 25 wt % or less, but the decrease gradually slowed down at values above 25 wt %; it became extremely slow when the fixed carbon content exceeded 40 wt %, with $a^*$ and $b^*$ values converging to ~3.0 and zero, respectively. Thus, fixed carbon contents of carbonized WB exceeding 40 wt % were difficult to estimate based on $a^*$ and $b^*$ measurements.

Figure 2c shows that the $L^*$ values of carbonized WB decreased with the increasing fixed carbon content, and the decrease in $L^*$ was very rapid at fixed carbon contents of 20 wt % or less, but the decrease slowed down at higher values of fixed carbon content and became extremely slow at fixed carbon contents of 30 wt % or higher, with the convergence value equaling ~20.0. Thus, the obtained results were consistent with the difficulties encountered when visually observing the differences of lightness ($L^*$) in carbonized WB samples with fixed carbon contents of 30 wt % or higher. Zhang and Cai [26] reported that during steam explosion treatment of WB, the increasing temperature induces the decomposition of cellulose and hemicellulose into a variety of low-molecular-weight polysaccharides, which results in the appearance of dark color. The decomposition of lignin at high temperatures is known to result in the formation of chromophores, i.e., functional groups that strongly absorb visible light. Herein, we observed that carbonization changed the color of WB from light to dark, similar to the trend observed for the steam explosion treatment. Additionally, the obtained results indicate that it difficult to predict the fixed carbon content of carbonized WB based on $L^*$ since this parameter stays almost constant at fixed carbon contents of 30 wt % or higher.
Figure 2. Correlation of the fixed carbon content of WB and (a) $a^*$; (b) $b^*$; and (c) $L^*$ values. Open circles = rubber tree; open triangles = softwood bark; open squares = softwood lumber waste.

3.4. Hue Angle and Fuel Properties

Figure 3 shows that the $h_{ab}$ decreased with the increasing fixed carbon content of WB. At a fixed carbon ratio of 25 wt % or less, a raw material type-independent negative correlation was observed strongly, but it became material type-dependent at higher fixed carbon contents. During the production of carbonized WB with under 25 wt % of fixed carbon, carbonization temperatures ranged between 310 and 390 $^\circ$C and varied with the raw material type. Since this temperature range was slightly higher than that of the thermal decomposition of hemicellulose (220–235 $^\circ$C) and matched that of the thermal decomposition of cellulose (315–400 $^\circ$C) [27], the thermal decomposition of the above constituents probably contributed to the increase of fixed carbon content and decrease of $h_{ab}$. In comparison to the aforementioned correlations ($a^*$, $b^*$, and $L^*$ values vs. FC), the rate of $h_{ab}$ change remained significant even when the fixed carbon content exceeded 30 wt %. These results indicate that the fuel properties of carbonized WB (such as the fixed carbon content and caloric value) can be estimated from $h_{ab}$ if correlations between $h_{ab}$ and such properties are determined in advance for each raw material.
4. Conclusions

The ability to rapidly ascertain the fuel properties of carbonized WB is indispensable during its production process from raw WB. In this study, three types of woody biomasses were carbonized, and the fixed carbon of the obtained materials was correlated with their color defined by the $L^*a^*b^*$ model. When fixed carbon was 25 wt % or less, we observed a strong negative correlation, regardless of the tree species, between the hue angle, $h_{ab}$, and fixed carbon. The $h_{ab}$ and fixed carbon were correlated even when the fixed carbon exceeded 25 wt %; however, this correlation was specific to the tree species. Therefore, $h_{ab}$ shows good potential for operation control during the carbonization processes to rapidly and easily estimate fuel properties such as the fixed carbon content of carbonized woody biomass.

Supplementary Materials: The following are available online at http://www.mdpi.com/1996-1073/11/5/1191/s1, Figure S1: Outer appearance of the carbonization test facility, Table S1: Color differences of raw and carbonized WB samples.

Author Contributions: Y.S., K.S., T.S. and M.O. designed and performed the experiments. All authors analyzed the data, discussed the results, and contributed to writing the paper. All authors have read and approved the final manuscript.

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References


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