Effect of Biomass Carbonization on the Grinding of Coal/Biomass Mixtures

Kiyoshi Sakuragi* and Maromu Otaka

ABSTRACT: To increase the co-firing ratio of biomass in existing pulverized coal-fired power plants, biomass should be pulverized to obtain a particle size suitable for combustion. However, evaluation of the particle size distribution of each coal and biomass mixture via traditional fuel analysis is difficult. Because coal does not contain neutral sugars, the particle size distribution of biomass in the mixture can be estimated based on its neutral sugar content. The current study was conducted to evaluate the effect of biomass carbonization on the grinding process via neutral sugar analysis. Mixtures of coal and carbonized pine chips with three different degrees of carbonization were prepared and ground using a Hardgrove grindability index mill. In the pulverized mixtures of low carbonized biomass and coal, the biomass content at all particle size ranges was nearly the same as that of the input feedstock. As the degree of biomass carbonization increased, the biomass content in the mixture of large particle sizes was decreased, whereas it was increased in the mixture of small particle sizes. The current study indicated that particle size distribution of coal and biomass in the pulverized mixture depends on the degree of carbonization of biomass.

INTRODUCTION

Co-firing of biomass is conducted in pulverized coal-fired power plants to reduce CO₂ emissions. However, in existing pulverized coal-fired power plants, the maximum achievable co-firing ratio is limited by the design of the coal mill and grindability of the biomass fuel. Because biomass is more difficult to pulverize than coal using a roller mill,1 a high ratio of biomass in the feedstock remains unpulverized. Therefore, in most cases, co-firing of the biomass in pulverized coal-fired power plants is only possible up to a maximum mass percent.

The fuel properties of coal and biomass, such as grindability, ash content, flow properties, and calorific value, are vastly different.2-4 Therefore, recent studies have investigated methods for improving the fuel properties of biomass via upgrading technologies, such as torrefaction and carbonization.5,6 Carbonization technology involves thermochemical treatment, which thermally decomposes a part of the biomass in an inert atmosphere and removes its oxygen.7 Following carbonization, the calorific value per weight of the biomass is increased, water repellency is improved, and grindability is markedly improved.1,3,8-10 In pulverized coal-fired power plants, the particle size of the pulverized mixture is an important parameter affecting combustion efficiency, unburned ash content, and combustion stability.11,12 Thus, biomass co-firing requires the efficient operation of coal-fired power plants leading to the pulverization of coal and biomass to sizes corresponding to the combustibility of each of these entities.

The Hardgrove grindability index (HGI)13,14 and Bond work index (BWI)15,16 are two well-known methods used to evaluate the grindability of coal. Reportedly, HGI and BWI are closely correlated in some biomass samples.17 HGI, the most common index for grindability, is widely used as the accepted
specification for pulverized coal in coal-fired power plants. In the HGI test, 50 g of air-dried coal containing particle sizes ranging from 600 μm to 1.18 mm is pulverized using an HGI mill, and the weight (W) of the pulverized product passing through a 75 μm sieve is quantified (HGI index = 13 + 6.91W). Samples with high HGI index values are easy to grind, whereas those with low HGI values are difficult to grind. The HGI index of a mixture of several types of coals is not the same as the average HGI index of each individual type of coal.19,20 The HGI test assumes that a single type of coal with a constant composition is being analyzed. The weight-based measurement of the HGI index is generally adopted for coal samples. Because the bulk density of biomass and coal are vastly different, a volume-based method has also been proposed for biomass samples.19,20

As it is more difficult to pulverize biomass than coal, biomass in the pulverized mixture has a larger particle size than coal. Because of its higher volatility and reactivity, biomass does not need to be pulverized to the same extent as coal.21 To appropriately increase the biomass co-firing ratio, it is necessary to separately evaluate the particle size distributions of coal and biomass in order to be able to pulverize each of these into particle sizes corresponding to the reaction rate of each material. However, evaluation of the distribution of individual particles of coal and of biomass in the pulverized mixture on the basis of analytical data of traditional fuel analysis values applied to coal, such as ash, fixed carbon, and calorific value, is difficult. To evaluate the particle size distributions of individual particles of coal and biomass, tracer components should be measured. As a tracer component, unique components of coal or biomass and isotopes22,23 are considered. It is preferable that the tracer component is associated with a high rate and is easier to measure.

Plant biomass is mainly composed of polysaccharides, such as cellulose and hemicellulose, and phenolic compounds, such as lignin. Cellulose contains glucose as a sole sugar unit, whereas hemicellulose is a heterogeneous molecular compound mainly composed of sugars, such as arabinose, galactose, glucose, mannose, and xylose. Cellulose and hemicellulose are connected to each other via hydrogen bonds, whereas hemicellulose and lignin are chemically bonded.24−26 These components are present in the cell wall of plants and together form strong structures. In this study, the quantification of neutral sugars, which are only present in biomass, was used as a method to estimate the carbonized biomass content in a pulverized coal mixture. Mixtures of coal and carbonized biomass were pulverized using an HGI mill, and the neutral sugar content corresponding to each particle size range in the pulverized samples was quantified. The effect of the degree of biomass carbonization on the particle size distribution after milling was studied in the pulverized mixture.

**MATERIALS AND METHODS**

**Carbonization and Sample Preparation.** Carbonization was performed in a pilot plant (maximum supply rate of feedstock = 4 tons/day) located in the Central Research Institute of Electric Power Industry (CRIEPI, Kanagawa, Japan).27 Japanese red pine wood chips (Pinus densiflora) collected from the Akagi area of CRIEPI (Japan) were used as the feedstock (RP). The size of RP was smaller than 40 × 40 × 2 mm. RP was air-dried prior to carbonization. In order to obtain a wide range of carbonized samples, RP was treated under various conditions at a biomass feed rate of about 100 kg h−1, an inner cylinder rotation speed of 3 rpm, a residence time of about 30 min, and carbonization temperatures from 310 to 335 to 342 °C. Carbonization temperature was measured at the surface of the kiln using a radiation thermometer (RAYTXTJ3M, Fluke Process Instruments, Everett, WA, USA), near the outlet. The temperature shows the average value within the collection time. At the exit end of the kiln, carbonized pine chips (CP) were sampled and named as CPL, CPM, and CPH in order of increasing fixed carbon content. Bituminous coal (collected in Warkworth, Australia) was used as the coal sample.

**Fuel Property Measurement.** Proximate analysis (ash, volatile matter, and fixed carbon) and elemental analysis (carbon, hydrogen, nitrogen, oxygen, and sulfur) were conducted in accordance with Japanese Industrial Standard (JIS) methods as follows: the JIS-M8812 (Coal and Coke—Methods for Proximate Analysis) and JIS-M8813 (Coal and Coke—Determination of Constituents). Measurement of the tapped density of coal, RP, and CP (a size range of 600−1180 μm) was performed according to Japanese pharmacopoeia (JP 16th Edition 3.01, Bulk Density and Tapped Density of Powders). For the measurement of tapped density, a 250 mL graduated cylinder (readable to 2 mL) with a sample mass of 100 g was used. The measuring cylinder was mechanically tapped, and volume readings were taken until little further volume change was observed.

**Neutral Sugar Analysis.** The neutral sugar content was determined using the two-stage sulfuric acid hydrolysis method28 with slight modifications.29 For neutral sugar analysis, approximately 0.25 g of each dried sample was dissolved in 1 mL of 72% sulfuric acid for 1 h in a 30 °C water bath. Each mixture was quantitatively diluted by adding 28 mL of distilled water (final sulfuric acid concentration, 4%), and each solution was incubated for 1 h at 121 °C. The resulting hydrolysate was filtered through a 0.2 μm high-performance liquid chromatography (HPLC)-certified filter (GE Healthcare, Little Chalfont, UK). The neutral sugars obtained via acid hydrolysis were analyzed by HPLC (Prominence, Shimadzu Corporation, Kyoto, Japan) on SP0810 columns (Showa Denko K. K., Kanagawa, Japan), with a charged aerosol detector (Corona Veo RS; Thermo Fisher Scientific, Waltham, MA, USA). Neutral sugars were eluted with acetonitrile/water 13.0/87.0 (v/v) at a flow rate of 0.5 mL min−1. Analytical grade l-arabinose, d-galactose, d-glucose, d-mannose (Wako Pure Chemical Industries, Ltd., Osaka, Japan), and d-xylose (Tokyo Chemical Industry Co., Ltd., Tokyo, Japan) were used as standards to quantify the neutral sugars. Since a coal sample does not contain neutral sugar and only a biomass sample contains neutral sugar, the content of biomass in the mixture can be estimated from the following equation.

\[
\text{the content of biomass in the mixture \%} = \left( \frac{\text{neutral sugar content of the mixture}}{\text{neutral sugar content of the biomass sample}} \right) \times 100
\]

**Grinding Tests.** The coal and CP samples were premilled (Wonder Blender; Osaka Chemical Co., Ltd., Osaka, Japan) and sieved to a size range of 600−1180 μm. Grinding tests for coal and the mixture of coal and 20 wt % CP were performed using a Hardgrove testing machine (1134-S, Yoshida Seisakusho Co., Ltd., Tokyo, Japan) (Table 1). Next, 50 ±
are consistent with those of previous studies, which indicated carbon caused the volatile content to decrease. These results and content. Biomass-derived samples, RP, and CP had lower ash compared to those of coal. RP showed a higher oxygen content among the three carbonized samples. As carbonization progressed, the oxygen content decreased. These results indicate that the elemental composition of biomass was closer to that of coal as carbonization progressed.

RESULTS AND DISCUSSION

Proximate Analysis and Ultimate Analysis. The results of proximate and elemental analyses are shown in Table 2.

Table 2. Analytical Data of Coal and Biomass Samples

| parameter          | coal   | RP     | CPL    | CPM    | CPH    |
|--------------------|--------|--------|--------|--------|--------|
| moisture [wt %]    | 3.9    | 27.8   | 0.7    | 0.3    | 0.4    |
| ash [wt %]         | 13.1   | 0.2    | 0.3    | 0.3    | 0.4    |
| volatile matter [wt %]a | 33.0   | 89.4   | 84.5   | 78.8   | 69.2   |
| fixed carbon [wt %]a | 53.9   | 10.4   | 15.2   | 20.9   | 30.4   |
| ultimate analysis  |        |        |        |        |        |
| carbon [wt %]b    | 72.3   | 50.2   | 52.8   | 55.3   | 59.3   |
| hydrogen [wt %]b  | 4.6    | 6.5    | 6.5    | 6.2    | 5.8    |
| nitrogen [wt %]b  | 1.6    | 0.1    | 0.1    | 0.1    | 0.1    |
| oxygen [wt %]b    | 8.0    | 43.0   | 40.3   | 38.2   | 34.4   |
| total sulfur [wt %]b | 0.4    | <0.1   | <0.1   | <0.1   | <0.1   |

*Dry basis. b As received.

Compared to those of coal, RP showed a higher oxygen content. Biomass-derived samples, RP, and CP had lower ash and fixed carbon contents than coal. In addition, RP and CP had lower nitrogen and sulfur contents than coal. In CPL, which had the lowest fixed carbon among the three carbonized samples, the oxygen content was lower than that with RP. When fixed carbon was further increased, the oxygen content of the carbonized sample decreased. Increasing the fixed carbon caused the volatile content to decrease. These results are consistent with those of previous studies, which indicated that carbonization removes low-temperature volatile components from biomass samples. As carbonization progressed, the carbon content of CP increased, and the hydrogen and oxygen contents decreased. These results indicate that the elemental composition of biomass was closer to that of coal as carbonization progressed.

Neutral Sugar Analysis of Coal and Biomass Samples. The results of neutral sugar analysis of the biomass and coal samples are shown in Table 3. Only the biomass sample contained neutral sugar; neutral sugar was not detected in the coal sample. The neutral sugar content of RP was 59.4% as most components of RP were derived from neutral sugar. The main neutral sugar of RP was glucose at 38.5%, although high contents of mannose and xylose were also detected. The glucose content decreased from 38.5% in RP to 28.0% in CPL.

Table 3. Neutral Sugar Analysis of Coal and Biomass Samples

| name                | coal   | RP     | CPL    | CPM    | CPH    |
|---------------------|--------|--------|--------|--------|--------|
| glucose [wt %]a     | N.D.b  | 38.5   | 28.0   | 30.1   | 35.4   |
| xylose [wt %]a      | N.D.b  | 6.5    | 2.9    | 1.2    | 0.5    |
| galactose [wt %]a   | N.D.b  | 1.9    | 1.2    | 0.5    | 0.4    |
| arabinose [wt %]a   | N.D.b  | 1.4    | 0.4    | 0.2    | 0.1    |
| mannose [wt %]a     | N.D.b  | 11.1   | 7.9    | 4.3    | 0.6    |
| total [wt %]a       | 59.4   | 40.4   | 36.3   | 37.0   |

*Neutral sugars are presented as the weight percentages contained in each sample. b N.D., not detected.

With increasing fixed carbon levels, the glucose content of CPM and CPH also increased to 30.1 and 35.4%, respectively. In addition to glucose, RP contained approximately 21% other neutral sugars including xylose, galactose, arabinose, and mannose. The neutral sugar content of CP gradually decreased with increasing fixed carbon. The neutral sugar content, except for that of glucose, was approximately 1.6% in CPH. Thus, the hemicellulose content appeared to gradually decrease as biomass carbonization progressed, whereas the glucose content decreased in CPL and gradually increased in CPM and CPH. As described previously, the neutral sugar content of biomass decreases because of carbonization. In softwood biomass, such as that of Japanese red pine, glucose is mainly derived from cellulose and hemicellulose, such as glucomannan. In the thermal treatment process, hemicellulose is preferentially decomposed after which cellulose is decomposed. Therefore, the glucose content in the carbonized biomass decreased with the decomposition of glucose from hemicellulose in CPL. Because glucose in cellulose is thermally stable compared to that in hemicellulose, the content of glucose in CPM and CPH was relatively increased.

Grinding Test. The particle size distribution of the mixture of pulverized coal and biomass is shown in Figure 1. The particle size distribution of all pulverized products exhibited a two-peak distribution with high weight yields of <75 μm (Pan) and 250−500 μm. The yield of Pan in coal alone was 15.7 g. A comparison of the yield of Pan with coal alone indicated decreases of 29.9, 20.4, and 5.7% for CPL (11.0 g), CPM (12.5 g), and CPH (14.8 g), respectively. The yield of the product in the 75−500 μm range decreased as the carbonization degree of the biomass increased. A yield of 5.5 g was obtained for the <500 μm range in the coal alone. In the pulverized coal and biomass mixture, almost the same yield of >500 μm was observed for all the degrees of biomass carbonization samples (11.4−11.6 g). These results indicated that the intensive carbonization process of biomass leads to a higher yield of Pan but a slightly lower yield of 75−500 μm, while the >500 μm biomass was not affected in the coal mixture. Therefore, it is confirmed that the grindability of the mixture of coal is increased with the progress of biomass carbonization. However, the suitable particle size for coal and biomass on co-firing is different. The particle size distribution of coal and biomass cannot be evaluated from the weight yield of each sieve of the grinding product. To evaluate the particle size distribution of coal and biomass, it is necessary to quantify the tracer components specific to coal or biomass for each range of grinding products.

Analysis of Neutral Sugars in Grinding Products. The neutral sugar content for each particle size range of the mixture of coal and biomass is shown in Figure 2. Regardless of the...
degree of carbonization, the distribution of neutral sugar content showed two peaks for Pan and 250–500 μm. In the pulverized mixture, the neutral sugar content of Pan was 0.8 g in CPL (approximately 19 wt % of the total neutral sugar content in the pulverized mixture of 20% CPL), 1.4 g in CPM (approximately 41 wt % of the total neutral sugar content in the pulverized mixture of 20% CPM), and 3.0 g in CPH (approximately 67 wt % of the total neutral sugar content in the pulverized mixture of 20% CPH) (Figure 2). Previous studies have reported that the xylose content is not dependent on the particle size, and the glucose content tends to be slightly underestimated in a sample having a small particle size in this analysis method. Therefore, it is confirmed from the neutral sugar content that the grindability of the mixture of coal is increased as the biomass carbonization progresses.

**Estimation of Biomass Content in Mixtures with Coal.**

The respective particle size distributions of coal and biomass for each particle size range in the mixture, which were estimated using the neutral sugar content, are shown in Figure 3. In the mixture of pulverized coal and low carbonized biomass, the biomass contents for all particle size ranges were similar to those of a coal. The biomass content of Pan increased, and the content of biomass in the >500 μm range decreased as carbonization progressed. These results indicate that whereas carbonization increased the neutral sugar content of the small particle size region, it decreased the neutral sugar content of the large particle size region. Therefore, it is confirmed from the neutral sugar content that the grindability of the mixture of coal is increased as the biomass carbonization progresses.

**Figure 1.** Particle size distribution of the pulverized mixture of coal and biomass. Each graph represents the mean of the three measurements with the standard deviation.

**Figure 2.** Neutral sugar content for each particle size range of the mixture of coal and biomass. Ground samples were sieved to <75 (collected in a pan), 75–106, 106–150, 150–250, 250–500, and >500 μm. The neutral sugar content is the sum of arabinose, galactose, xylose, mannose, and glucose contents. Each graph represents the mean of the three measurements with the standard deviation.
known for carbonized biomass. Compared with the tapped
density of coal (0.75 g cm\(^{-3}\)), the tapped density of CP was
lower. The tapped density of biomass was decreased as
carbonization progressed in 0.23 g cm\(^{-3}\) (CPL), 0.22 g cm\(^{-3}\)
(CPM), and 0.20 g cm\(^{-3}\) (CPH). In addition, while the actual
roller mill is equipped with a rotary classifier, the HGI mill is
not equipped with the discharging system of grinding products.
Thus, the easily grindable carbonized biomass with small
tapped density may be a cause of the decrease of the
grindability of coal using the HGI mill in the mixture.

Despite many attempts to use carbonized biomass in
pulverized coal-fired power plants, relatively little attention
has been given to the respective particle size distributions of
carbon is burned in pulverized mixtures. Although an HGI mill
was used as grinding equipment in this study, the actual roller
mills used in coal-fired power plants are equipped with rotary
classifiers. The pulverized biomass passes through the classifier
with a particle size larger than that of coal due to the difference
in terminal velocity. However, our results demonstrated that
carbonization pretreatment noticeably improved the grind-
ability of biomass in the coal mixtures.

**CONCLUSIONS**

Carbonization is effective for improving the grindability of
biomass even in a mixture of coal. The addition of carbonized
biomass to coal, particularly low carbonized biomass,
decreased the yield of the low-sized fraction (<75 \(\mu m\)),
whereas highly carbonized biomass is preferentially milled to
carbon. To achieve efficient co-firing of coal and biomass, the
mixture of coal and biomass should be milled to particle sizes
suitable for each combustion. Our findings demonstrate that
the detection of neutral sugar, which is only contained in
biomass, showed the effect of the degree of biomass
carbonization on the particle size distribution in the pulverized
mixture.

**AUTHOR INFORMATION**

**Corresponding Author**

Kiyoshi Sakuragi — Energy Engineering Research Laboratory,
Central Research Institute of Electric Power Industry, Yokosuka
240-0196, Japan; orcid.org/0000-0002-8384-7578;
Phone: +81-70-6638-2037; Email: sakuragi@
criepi.denken.or.jp; Fax: +81-46-856-3456

**Author**

Maromu Otaka — Energy Engineering Research Laboratory,
Central Research Institute of Electric Power Industry, Yokosuka
240-0196, Japan

Complete contact information is available at:
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**ABBREVIATIONS**

HGI: Hardgrove grindability index
BWI: Bond work index
HPLC: high-performance liquid chromatography
JIS: Japanese Industrial Standard

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**Figure 3.** Particle size distribution estimated by the content of neutral sugar. The biomass content in the mixture was estimated using eq 1. The particle size distribution of coal was calculated by subtracting the biomass particle size distribution.
RP: Japanese red pine wood chips
Pan: ground samples collected in a pan

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