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Study on Emission Control for Precursors Causing Acid Rain (VI) : Suitability of Aquatic Plant Biomass as a Co-combustion Material with Coal

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ABSTRACT

In China, energy and environmental problems are becoming serious owing to rapid economic development. Coal is the most problematic energy source because it causes indoor and outdoor air pollution, acid rain, and global warming. One type of clean coal technology that has been developed is the coal-biomass briquette (or bio-briquette, BB) technique. BBs, which are produced from pulverized coal, biomass (typically, agricultural waste), and a sulfur fixation agent (slaked lime, $Ca(OH)_2$) under high pressure without any binder, have a high sulfur-fixation effect. In addition, BB combustion ash, that is, the waste material, can be used as a neutralization agent for acidic soil because of its high alkalinity, which originates from the added slaked lime. In this study, we evaluated the suitability of alternative biomass sources, namely, aquatic plants, as a BB constituent from the perspective of their use as a source of energy. We selected three types of aquatic plants for use in BB preparation and compared the fuel, handling, and environmental characteristics of the new BBs with those of conventional BBs. Our results showed that air-dried aquatic plants had a higher calorific value, which was in proportion to their carbon content, than agricultural waste biomass; the compressive strength of the new BBs, which depends on the lignin content of the biomass, was high enough to bear long-range intracontinental transport in China; and the new BBs had the same emission control capacity as the conventional BBs.

Key words: Aquatic plant biomass, Ash amendment, Co-combustion, Low-grade coal, Sulfur dioxide

1. INTRODUCTION

China is one of the most coal-dependent countries of the world. China was first in coal production and consumption in the world in 2005, and 70% of its primary energy is still supplied by coal (Fig. 1) (British Petroleum, 2006). Most of the coal used in China is low grade, that is, high in ash and sulfur and of low calorific value. This coal is an environmentally problematic energy source, and its use causes indoor and outdoor air pollution, acid rain, and global warming. These environmental problems are expected to become more and more serious with China's rapid economic development. Although the development of new, clean energy sources that do not use fossil fuel (e.g., solar, hydrogen, and fuel-cell technologies) has recently been much studied, these new technologies cannot be expected to rapidly replace conventional coal-dependent technologies, especially in rural areas of China (Isobe *et al*., 2005). Therefore, for several years or decades, it is important that we minimize the negative impacts of fossil fuels.

Various types of clean coal technology (CCT), focusing on pre-, mid-, and postcombustion processes, have been studied (U.S. DOE FE, 1999). One CCT, intended to control sulfur emission, is the coal-biomass briquette (bio-briquette, BB). Bio-briquettes are pillow- or almond-shaped solid fuel pellets produced from pulverized coal, biomass waste, and a sulfur fixation agent (slaked lime, $Ca(OH)_2$) under high pressure without any binders. This fuel has a high sulfur-fixation effect, and its use effectively reduces sulfur dioxide (SO_2) emission. Typically, agricultural or forestry wastes are used as the biomass. The use of biomass, a carbon-neutral energy source, makes it possible to reduce carbon dioxide (CO_2) emissions, which contribute to global warming. Bio-briquettes are suitable

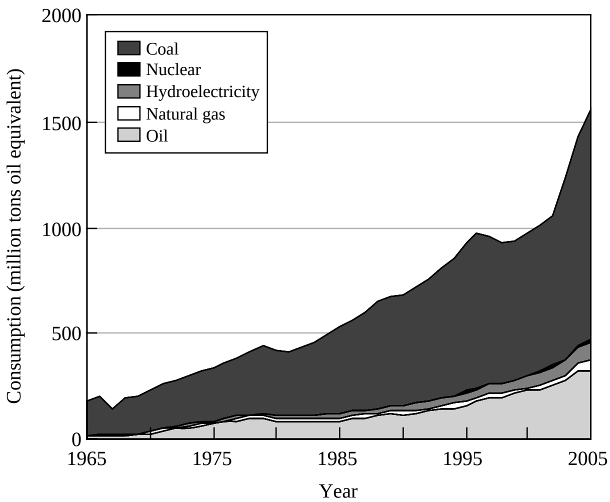

Fig. 1. Transition of primary energy consumption in China from 1965 to 2005; the data was given from BP Statistical Review of World Energy 2006.

for use in rural areas, where their introduction is comparatively easy. In fact, test and pilot plants are currently operating in some areas of China, such as Chongqing, Chendo, and Anshan (Sakamoto, 2002).

In addition, as with coal or biomass burning, BB combustion leads to the generation of residue ash. Numerous reports discuss coal ash treatment techniques, for example, landfill disposal or recycling as a building or road base material, a desulfurization agent, an alternative soil material for planter cultivation, or a soil amendment (e.g., Reijnders, 2005). Effective recycling of the waste is most desirable. For civilian use of BB fuel in rural China, waste ash from BB fuel is most suitably used as an acid soil reclamation agent, particularly in southern China, which suffers from soil acidification owing to deposition of acidic components resulting from coal combustion (Gao *et al*., 2001a; Larssen *et al*., 1999). Soil acidification can inhibit the growth of field crops (Zhou, 1998), not only directly by lowering pH but also indirectly by raising the concentrations of potentially toxic metals (e.g., aluminum, manganese) in the soil solution.

Many research papers about acid soil improvement using coal combustion byproducts (CCBs) have been published. Coal ash is often alkaline, depending on the chemical composition of the coal (Adriano *et al*., 1980), and other alkaline materials are often used as desulfurization agents during combustion so that the generated CCBs will have high acid-neutralization capacity.

BB incinerator ash also has high alkalinity because of the added slaked lime. Therefore, BB ash can be used as a neutralization agent in acidic soil (Dong *et al*., 2004; Sakamoto *et al*., 2001). Agricultural waste biomass, for example, wheat straw, rice straw, and sawdust, has generally been used as the biomass for producing BBs. BBs prepared with these types of biomass maintain a high compressive strength without any binding agents being required (Gao *et al*., 2001b). If we can also use aquatic plants, which absorb more plant nutrient salts (such as N and P compounds) from river or lake waters than terrestrial plants, as the biomass in BBs, the BB combustion ash should serve both as a neutralization agent for acidic soil and as a fertilizer. Moreover, the use of aquatic plants can help improve eutrophic wetlands and rivers (Fujita *et al*., 2001). On the whole, it is anticipated that the use of BBs made with aquatic plant biomass would simultaneously address four problems: indoor and outdoor air pollution, soil acidification, waste disposal, and water pollution.

Therefore, in this study, we evaluated the use as fuel of BBs prepared with three types of aquatic biomass. The fuel characteristics evaluated were higher heating value (HHV), handling properties for intracontinental transportation in China, and the desulfurization effect. These characteristics were compared with those of conventional BBs.

2. MATERIALS AND METHODS

2.1 Fuel Samples and Sulfur Fixation Agents

The selected plants, the common reed (*Phragmites australis*), common cattail (*Typha latifolia*), and water hyacinth (*Eichhornia crassipes*), were collected from various water systems in late autumn. Sampling was in autumn with the objective of recovering absorbed nutrients before they were returned to the water body by die-back processes. At the same time, mowing of emergent plants such as reeds and cattails at the right time forces the growth of new shoots (Karunaratne *et al*., 2004). Harvested biomass samples were divided into shoots and roots (root were also collected about 30 cm below ground to research its metal content), and sun-dried. Each part was then cut more finely, oven-dried, and crushed to pass through a 2-mm-mesh sieve. The habitat soil and water were also sampled and the samples refrigerated until element analysis. Wheat and rice straw were selected as the conventional agricultural biomass for comparison with aquatic plant biomass. Wheat straw was harvested in Chongqing, China, and rice straw was sampled at a ricefield site near that at which the aquatic plants were harvested. These straw samples were prepared in the same

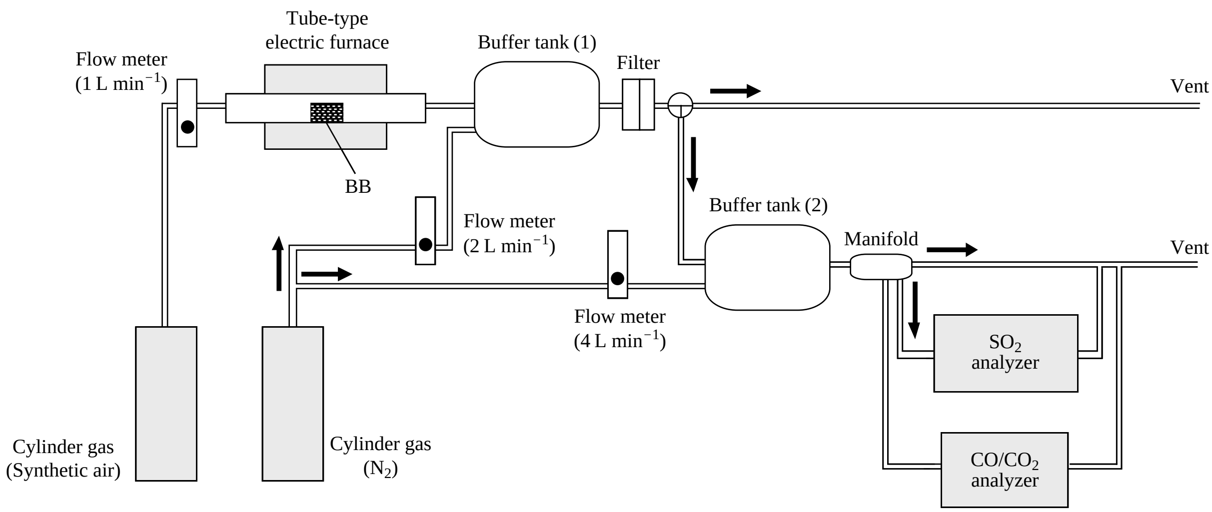

Fig. 2. Combustion experimental apparatus for measurement of sulfur fixation ratio.

way as the aquatic plant samples.

The selected coal sample, bituminous Foo-yong coal mined at Chongqing, China, was crushed mechanically and screened through a 2-mm-mesh sieve. Slaked lime (reagent-grade calcium hydroxide) was used as the sulfur fixation agent.

2. 2 Preparation of the Coal-biomass Briquettes

Test samples of coal-biomass briquettes (BBs) were prepared by mixing the pulverized coal and each type of biomass at the mass ratio of 3 : 1, adding slaked lime to the mixture at the molar ratio Ca/S=2, and compacting the mixture with a hydraulic press-type high-pressure jack (model J-15; Iuchi, now As One, Osaka, Japan) to small tablets (7×12 mm, about 1 g each), using a pressure of 4 t cm^{-2}.

2. 3 Fundamental Analyses of BBs and Their Raw Materials

Each biomass and coal sample was analyzed in accordance with JIS M 8812 (JIS, 1993) procedures for the proximate analysis, and by the Eschka method (JIS M 8813; JIS, 1994) for total sulfur determination. Calorific value was measured with an adiabatic bomb calorimeter (IKA C7000, Staufen, Germany). Carbon content was measured with a CHN recorder (Yanaco MT-3, Kyoto, Japan).

Prepared BB samples were subjected to pressure tests investigate whether this solid fuel had enough compressive strength to bear intracontinental transport in China. This experiment was done using an unconfined compression apparatus (S-56A MARUTO Testing Machine Company, Tokyo, Japan). Lignin contents of all biomass types were also measured in accordance with JIS P 8008 procedure (JIS, 1976).

2. 4 Combustion Experiments for BB

To check that the sulfur dioxide emission-reduction capacity of the BBs was not altered when aquatic plants were used as the biomass instead of the conventional biomass sources, the desulfurization effect was investigated by a combustion experiment with test BB samples. The experimental setup is shown in Fig. 2. Synthetic air and nitrogen gas were used for the co-combustion gas and dilution gas, respectively. A two-step dilution was performed using acrylic buffer tanks with a capacity of about 1.3 L, and the dilution ratio was determined by monitoring the O_2 level with an infrared gas analyzer (CGT-7000, Shimadzu, Kyoto, Japan). The furnace temperature profile was maintained at 873 K. Emitted sulfur dioxide was monitored using the gas analyzer (SOA-7000, Shimadzu, Kyoto, Japan). The end point of combustion was judged by the return of a reduced CO_2 concentration peak, monitored with another infrared gas analyzer (CGT-7000). The desulfurization ratio was calculated by using equation (1):

$$DR\,(\%)=100\,(S_{coal}-S_{BB})/S_{coal} \tag{1}$$

where DR (%) is the desulfurization ratio, S_{coal} (g/g) is the amount of emitted sulfur dioxide per unit weight of coal during the coal combustion process, and S_{BB} (g/g) is that emitted during the BB combustion process.

Table 1. Proximate analysis of a coal and some biomasses.

Sample	Moisture (%)	Ash (%)	Volatile matter (%)	Carbon (%)
Foo-yong coal	2.01	23.97	13.47	60.55[b]
Common reed	5.59	5.56	*n.m.*	44.18[c]
Common cattail	8.45	4.80	*n.m.*	44.50[c]
Water hyacinth	6.00	14.08	*n.m.*	39.05[c]
Wheat straw	*n.m.*[a]	8.37	*n.m.*	*n.m.*
Rice straw	6.35	15.25	*n.m.*	37.02[c]

[a]: Not measured. (air-dried basis)

[b]: Fixed carbon (%) calculated by subtracting moisture, ash, and volatile matter from 100.

[c]: Carbon contents (%) measured using CHN analyzer.

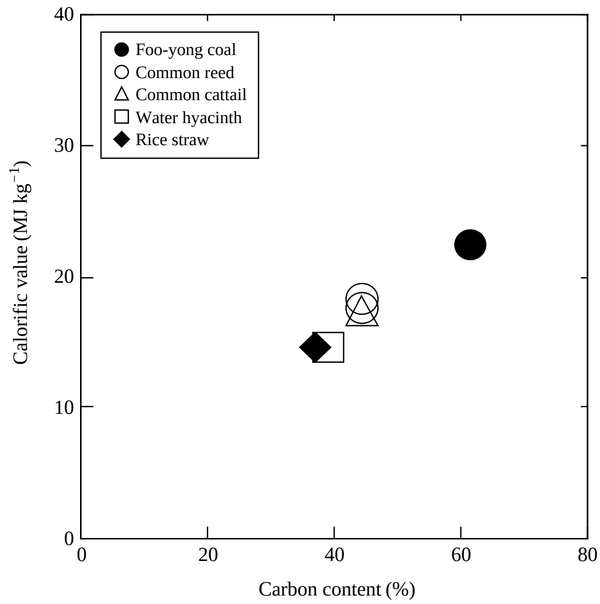

Fig. 3. Carbon content and calorific value of selected coal and aquatic biomasses.

3. RESULTS AND DISCUSSION

3.1 Selection of the Aquatic Biomass

The kind of aquatic biomass selected for BB use is very important. We consider appropriate plants to be those (1) for which the maintenance of a stable supply for use as an energy resource is anticipated, (2) that contain much lignin, for BB strength (Gao *et al*., 2001b), and (3) that contain many plant nutrient salts (nitrogen, phosphorus, and potassium) so that the ash will act as a fertilizer when amended to soil.

For there to be a stable supply, an aquatic plant should be fast-growing. In a database of aquatic plants available for water purification, constructed by Fujita *et al*. (2001), the fastest growing species is common reed, followed by water hyacinth and common cattail. These plants are all perennial macrophytes that grow about 30 g-dw m^{-2} day^{-1}, so a stable supply can be anticipated. Reeds and cattails are both poaceous emergent plants that were expected to contain a large quantity of lignin because of their fibrous characteristics. On the other hand, the floating water hyacinth (family Pontederiaceae) contains less lignin than reeds or cattails, but because it accumulates more nitrogen and phosphorus, it is often used for water purification. For these reasons, these three aquatic plant species were selected for this study.

Results of the proximate analysis of the coal and various biomass types are shown in Table 1. The fixed carbon value of Foo-yong coal was about 61% (air-dried basis). On a dry, mineral-matter-free basis, it corresponds to about 82%. This coal is classified as a low-volatility bituminous coal, as defined by the coal classification system proposed by American Society for Testing and Materials (ASTM, 1992). However, this coal is low grade because of its ash and sulfur content, 23.97% and 4.07%, respectively; on the basis of these values, it is categorized as a high-ash (total ash $>$15%) and high-sulfur coal (total sulfur $>$3%).

3.2 Combustibility and Potential CO_2 Reduction

The chemical energy content, that is, the calorific value, of the biomass is one of the most important parameters in biomass selection. The relationship between carbon content and calorific value for the selected coal and the various types of biomass are shown in Fig. 3.

All of the biomass types had a HHV of 15-20 MJ kg^{-1} on a dry weight basis. The aquatic plants exhibited carbon contents and calorific values equal to or greater than those of wheat straw, an agricultural waste biomass. Among the aquatic plants, the emergent plants, common reed and common cattail, had a higher capacity than the floating plant, water hyacinth. The high calorific value of all selected hydrophytes indicates that those biomass sources are in no way inferior to the conventional biomass sources for energy use.

On the basis of the calorific values measured in this experiment, we estimated the greenhouse gas reduction effect that would result from the adoption of BBs for fuel. The use of a carbon-neutral biomass instead of coal would lead to a reduction in net CO_2 emissions corresponding to the reduction of coal mass. For example, to produce 1 GJ energy from BBs instead of coal, 8-10 kg of coal is replaced by 12 kg of biomass, which is an 18-22% reduction in the amount of coal used;

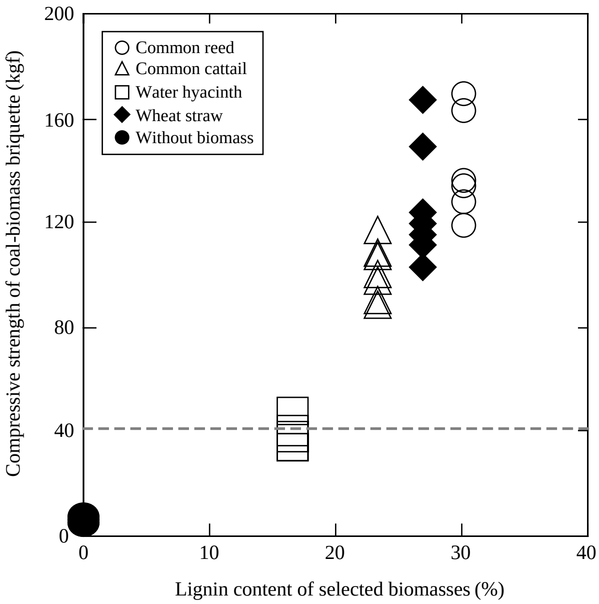

Fig. 4. Lignin content of selected biomasses and compressive strength of coal-biomass briquettes prepared using these biomasses; dotted line in this figure is threshold value of compressive strength which is bearable for vibration of intracontinental transportation.

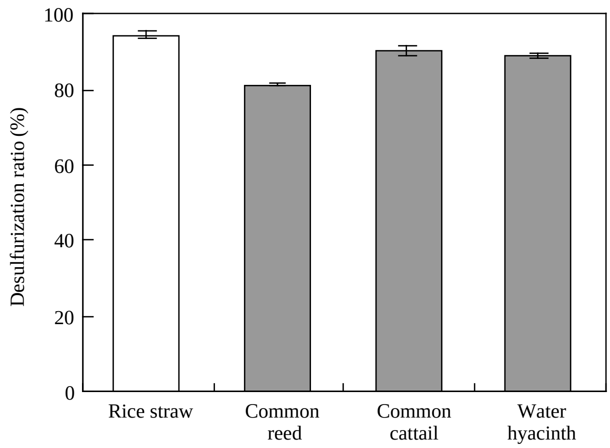

Fig. 5. Desulfurization ratio of BB prepared using rice straw and three aquatic biomasses (n=2, the error span marker on each bar means max-minimum range).

thus, the use of BB fuel can reduce net CO_2 emissions effectively.

3. 3 Compressive Strength

The compressive strength of BBs is known to depend on the binding effect, called the "lignin-induced strength effect," derived from the softening of lignin materials in the biomass (Gao *et al.*, 2001b).

When the lignin contents of the selected hydrophytes and wheat straw were compared with the compressive strength of the BBs prepared with each type of biomass (Fig. 4), the lignin content and the compressive strength of the BBs were found to be positively correlated. This result supports the suggestion that lignin content is a major factor controlling the strength of BBs prepared with plant biomass. Previously, Gao *et al.* (2001b) reported that the critical strength of BB solid fuel necessary to bear intracontinental transport in China is 40 kgf ($\approx$392 N). BBs prepared with water hyacinth biomass were at about this threshold level, but the BBs prepared with the other two hydrophytes were well above this threshold. Although there are little differences among lignin content value for each biomass (RSD: 1-2%, n=4), as the lignin content increased, the variation in strength became larger, owing to differences in the fibrousness of the different biomass sources. These results show that emergent plants are suitable as a raw materials for preparation of BB fuel. However, water hyacinth is also suitable if used in combination with emergent plants having a high lignin content such as reed and cattail.

3. 4 Emission Inhibition of Sulfur Dioxide

The desulfurization ratios achieved during BB combustion using hydrophyte biomass were slightly lower than those achieved with conventional types of biomass, but the ratios were still 80% or higher (Fig. 5). This result demonstrates that the new BBs also have a high sulfur-fixation effect. In contrast to the compressive strength data, there was little repetitive variation (~1.5%). The relatively lower desulfurization ratio of BBs made with common reed was probably due to its being more fibrous than the other biomass types, which may have affected the accessibility of the desulfurization agent to the coal. When examined in detail, the difference in sulfur emission among the different biomass types is negligible, on the order of 0.01-0.001 wt%.

4. CONCLUSIONS

The suitability of aquatic plants used as biomass (i.e., as an energy crop) in BBs depends on whether these plants perform similarly to conventional agricultural biomass. Determination of their suitability requires a comprehensive assessment of their (i) productivity, for the maintenance of a stable supply, (ii) handling properties, (iii) fuel performance, (iv) waste management, and (v) environmental impact. In this research, we focused on points (ii), (iii), and (v). We found that the selected hydrophytes were similar to agricultural waste biomass in their suitability for use as fuel. With regard to (i), productivity, the many reports on the planting and utilization of aquatic plants for water purification would serve as useful references. The target area, Chongqing, is a city by the Changjiang (Yangtze) River, that contains many shallow eutrophic lakes and marshes of all sizes (NIES, 2001), so this area is favorable for the planting and harvesting of emergent plants. In addition, water hyacinths, which require open water, can also be grown in this area despite their harmful characteristics, because even lakes and marshes near the main stream are completely segmentized by floodgates constructed for flood disaster prevention. In the catchment area of the Changjiang, eutrophication of water bodies has been progressing rapidly in recent years owing to economic development and the delay in implementing environmental policies regarding water quality (Shindo *et al*., 2006). Therefore, a technology that simultaneously addresses energy problems and water purification is powerful. As for (iv), waste management, it has been suggested that BB ash can be used effectively as a soil amendment to improve crop productivity (Sakamoto *et al*., 2001). The construction of a locally sustained cyclic system on the basis of these findings would thus contribute to the resolution of environmental problems in China.

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