C 4.1.5 Co-operative Study on the Bio-Briquette for the Emission Control of Acid Rain Precursors in Chongqing: Research on the Biomass in Chongqing

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Abstract

Bio-briquette is a sort of composite fuel consisting of 70 to 85 percent of coal and 15 to 30 percent of biomass by weight, produced by high pressure briquetting method with compression only in the roll press technique without any binder. The biomasses works as a binder in the bio-briquette and various woody wastes and agriculture wastes such as rice straw, rice bran, sorghum stalk and wheat straw are used. As compared with raw coal, it is expected little emissions of air pollutants from combustion of bio-briquette containing slaked lime as sulfur-fixation agent and little residual matters after burning, and higher sulfur-fixation efficiency. Total yearly output of woody wastes and agriculture wastes in Chongqing amounted to ca. 18.0 million tons based on investigating data. So, it is expected enough biomass materials to produce bio-briquette in Chongqing. The water soluble chemical components of various biomass produced in one of the districts and residual matter after its combustion were measured. Most of the sulfurs in biomass were inorganic salts. The experimental results indicated that there were little emissions of air pollutants from biomass combustion and emission amounts were in the range of 0~43, 16~912 and 114~789mg for HF, HCl, and SO_2 per 1kg of biomass, respectively. The least emission was obtained for woody dust combustion. Therefore, woody dust was considered as the best suitable biomass to produce bio-briquette. The sulfur-fixation and ash-abatement efficiency of bio-briquette produced from raw coal and woody dust amounted to 82% and 25%, respectively.

Key Words: Biomass; Bio-briquette; Combustion experiment; Sulfur-fixation; Acid rain.

1. Introduction

Chongqing is well known as one of the typical regions where is suffered from the serious air pollution and acid rain caused by low graded raw coal combustion[1)]. Environmental deterioration and human damage are extremely conspicuous[2,3)]. For this reason, it becomes very urgent for the studies on integrated control techniques for precursors of acidic precipitation in Chongqing. Coal-biomass briquette is produced from pulverized-coal, biomass such as straw, and slaked lime as sulfur-fixation agent, under high roll line pressure (3~5 tons/cm) without any binder[4)]. The biomasses such as various woody wastes and agriculture wastes are circulating resources, and low heating energy fuels. For this reason, not only the biomass can be used effectively and its heating energy can be increased, but also biomass work as the binder under high pressure roll press when the biomass is added in coal-biomass briquetting process[5)]. In this paper, the characters of various biomass collected in Chongqing and Shenyang of China were investigated by the combustion experiment to choice the suitable biomass material for bio-briquette.

2. Output of biomass in Chongqing

There were large amounts of biomass from agriculture wastes because the weather was suitable for production of agriculture in Chongqing, and from woody wastes because Chongqing where lies on combination site of Jailing River and Yangzi River is a collecting and distributing center of lumber. The investigating results were shown in **Table 1**. It was known that total yearly output of woody wastes and agriculture wastes amounted to ca. 18.0 million tons based on investigating data. This data is equal to consumption of coal in Chongqing. Therefore, it is considered that biomass is enough to produce bio-briquette.

Table 1. Results of the research for biomass outputs in Chongqing.

Biomass	Output (10^6 t)
Rice straw	2.0 ~ 2.2
Wheat straw	1.0 ~ 1.2
Corn	2.3 ~ 3.0
Weeds	~ 3.2
Maize stalk and straw	2.5 ~ 2.7
Wastes of other plants	~ 5.4
Woody dust	~ 0.3
Total outputs	16.4~18.0

3. Experimental methods

3.1 Sampling

Seven types of agriculture wastes and woody wastes which are rice straw, rice bran, sorghum stalk, wheat straw, maize stalk, weeds and woody powder were collected in Jiangbei district of Chongqing where bio-briquetting model factory was being constructed. Sampling sites were shown in **Fig. 1**. Besides, rice bran was collected in Shenyang of Liaolin Province where did not occurred acid rain in order to compare their characteristics. The samples were cut finely to ca. 5mm and dried.

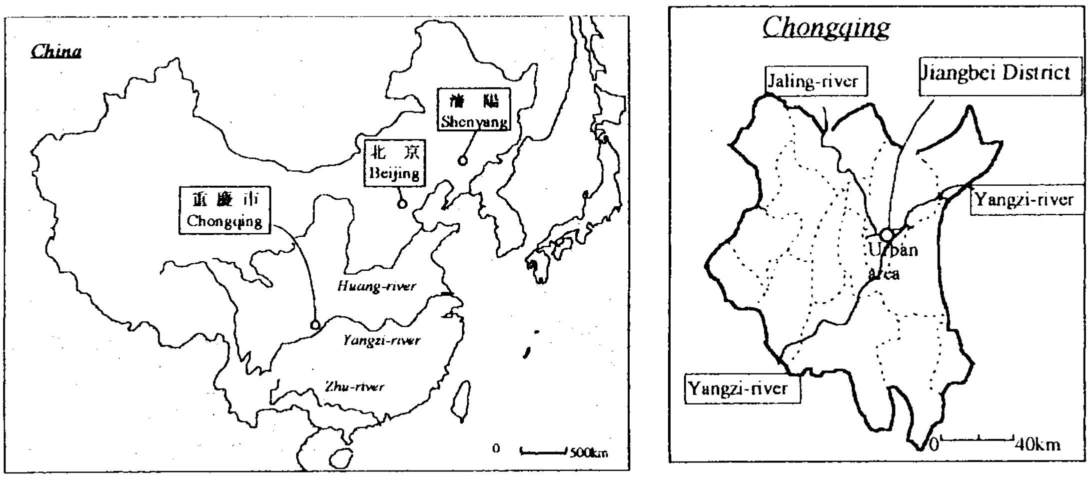

Fig. 1. Location of the sampling site for biomass.

3.2 Analysis of water soluble components

Biomasses were dried in electric stove under 107±2°C, and its moisture was calculated from decrease weight. Then, water-soluble components were extracted by distilled water, and ion concentrations in the extracted solution were measured by use of ion chromatography (DX-100, Dionex Company of U. S. A).

3.3 Combustion experiment

Experimental diagram for biomass combustion is shown in **Fig. 2.** The 0.500 grams biomass was putted in center of quartz combustion tube, then was heated to 800°C and burned for 10 minutes under 800°C. The air pollutants emitted from their combustion were absorbed in impinger filled 100ml of absorption solution (2.7mMNa_2CO_3/0.3mM$NaHCO_3$, eluent solution of ion chromatography) by the suction pump in the meantime. Then, F^-, Cl^-,

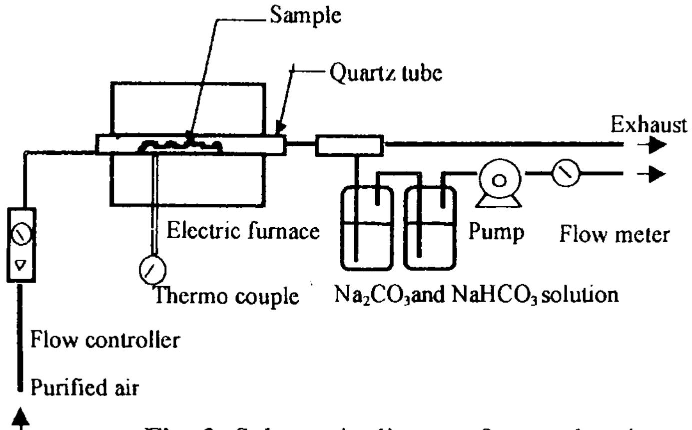

Fig. 2. Schematic diagram for combustion test.

SO_3^{2-} and SO_4^{2-} concentrations in the absorption solution were measured with an ion chromatography. Emission from biomass combustion was calculated on the basis of ion concentration measured under the above experimental condition. Besides, ash was measured from weight of residual matter after burning, and water-soluble sulfur in ash was analyzed, too.

4. Results and discussion

4.1 Water soluble components

Water soluble ion concentration and percentage of each components percent in biomass were shown in **Table 2** and **Table 3**, respectively. In the Table 2, ion balance was calculated based on the equation of $\{(\Sigma^+ - \Sigma^-)/(\Sigma^+ + \Sigma^-)\}\times 100(\%)$. The major ions were SO_4^{2-} and Cl^- for anions, and NH_4^+ and K^+ for cations in Table 2. It is considered that Cl^-, NH_4^+ and K^+ may come from the fertilizer. Water-extracted solutions were not acidic, and gave almost satisifying ion balance between anion and cation ions except woody powder. The SO_4^{2-} concentration and acidity of extracted solution in rice bran in Chongqing were higher than those in Shenyang. It may be explained that high sulfur concentrations in air pollutants and acid rain have affected agriculture and plants in Chongqing. As shown, in Table 3, the lowest

Table 2. Concentration and ion balance of water-soluble ions in the extracted solution of biomass (Dry basis).

Biomass	pH	Na^+	NH_4^+	K^+	Mg^{2+}	Ca^{2+}	Cl^-	NO_3^-	PO_4^{3-}	SO_4^{2-}	Σ^+	Σ^-	B[a)]
		meq/l											(%)
Woody dust-1	7.00	0.05	0.06	0.42	0.03	0.10	0.12	0.01	0.00	0.02	0.66	0.14	65
Woody dust-2	6.64	0.07	0.00	0.24	0.08	0.29	0.22	0.00	0.01	0.14	0.68	0.37	30
Woody dust-3	6.70	0.04	0.00	0.25	0.04	0.12	0.14	0.00	0.00	0.06	0.45	0.20	38
Average[b)]	6.75	0.05	0.02	0.30	0.05	0.17	0.16	0.00	0.00	0.08	0.60	0.24	44
Rice bran	6.00	0.03	0.52	2.11	0.18	0.11	1.60	0.01	0.17	0.40	2.95	2.18	15
Maize stalk	6.66	0.28	1.47	7.32	1.27	0.57	8.25	0.49	0.64	1.38	10.91	10.76	1
Sorghum stalk	6.63	0.34	1.70	9.55	0.75	0.56	12.96	0.13	0.61	1.64	12.90	15.34	-8
Rice straw	6.68	0.28	1.75	13.42	1.65	0.34	12.39	0.03	0.83	3.16	17.44	16.41	3
Weeds	5.94	0.46	1.98	8.43	0.88	0.37	5.93	0.03	1.94	3.26	12.12	11.16	4
Wheat straw	6.46	0.21	2.03	6.95	0.41	0.26	5.94	0.06	1.11	3.50	9.86	10.61	-3
Rice bran [c)]	7.20	0.09	0.31	2.20	0.03	0.10	2.32	0.04	0.20	0.20	2.72	2.76	-1

a) Ion balance is calculated based on the equation of $\{(\Sigma^+ - \Sigma^-)/(\Sigma^+ + \Sigma^-)\}\times 100(\%)$.

b) Average value of three woody dusts.

c) This sample was collected in Shenyang.

and highest water-soluble sulfur were observed for woody dust and wheat straw, respectively. Water-soluble sulfur in rice bran in Chongqing was higher than that in Shengyang. The biomasses were divided into three groups based on the contents of sulfur that is major resource of air pollutants, namely, woody powder with <0.01% of sulfur, rice bran, maize stalk and sorghum stalk with 0.01 ~ 0.1% of sulfur, rice straw, weeds and wheat straw with >0.1% of sulfur. Sulfur content in the third group agreed with inorganic sulfur composition in vegetation leaves (0.1 ~ 0.3%)[6]. It could be explained that there were less leaves in the first and second group.

Table 3. Water soluble chemical components of biomass (Dry basis, %).

Biomass	Moisture	Na	N	K	Mg	Ca	Cl	P	S
Woody dust-1	7.90	0.004	0.003	0.053	0.001	0.006	0.014	0.000	0.001
Woody dust-2	14.70	0.005	0.000	0.033	0.003	0.020	0.027	0.000	0.007
Woody dust-3	6.64	0.004	0.005	0.043	0.002	0.019	0.010	0.000	0.003
Woody dust ave.	9.70	0.004	0.003	0.043	0.002	0.015	0.017	0.000	0.004
Rice bran	9.10	0.002	0.025	0.272	0.007	0.007	0.188	0.006	0.022
Maize stalk	8.95	0.022	0.094	1.154	0.050	0.038	0.964	0.021	0.072
Sorghum stalk	7.86	0.025	0.082	1.213	0.029	0.036	1.416	0.020	0.086
Rice straw	8.43	0.021	0.089	1.714	0.065	0.022	1.112	0.027	0.171
Weeds	8.78	0.034	0.097	1.081	0.035	0.024	0.692	0.042	0.184
Wheat straw	9.12	0.016	0.099	0.863	0.016	0.017	0.697	0.037	0.185
Rice bran [a)]	6.60	0.006	0.015	0.289	0.001	0.006	0.090	0.008	0.011

a) This sample was collected in Shenyang.

4.2 Air pollutants from biomass combustion

HF, HCl and SO_2 emissions from biomass combustion and combustible sulfur calculated from experiment results were shown in **Table 4**. Air pollutants emitted from biomass in Chongqing were more than those in Shengyang. The least emission were observed for woody powder and the maximum for sorghum stalk. HF, HCl and SO_2 emission amounts from combustion of 1 kg biomass were in the range of 0~43, 16~912mg and 114~789mg, respectively. Compared with Table 3, the combustible sulfur contents were lower, and the order for combustible sulfur contents did not agree with water-soluble sulfur contents. For this reason, it was inferred that sulfur contained in biomass was inorganic sulfur and incombustible

Table 4. Emission of the air pollutants from biomass combustion (Dry basis).

Biomass	HF (mg/kg)	HCl (mg/kg)	SO_2 (mg/kg)	Combustible S(%)[a)]
Woody dust-1	0	16	175	0.009
Woody dust-2	0	103	64	0.003
Woody dust-3	0	112	102	0.005
Woody dust av.	0	80	114	0.006
Rice bran	2	534	181	0.009
Rice straw	4	912	220	0.011
Wheat straw	9	406	386	0.019
Weeds	16	566	485	0.024
Maize stalk	21	203	599	0.030
Sorghum stalk	43	799	789	0.039
Rice bran [b)]	5	35	52	0.003

a) Combustible S was defined as sulfur emitted from biomass combustion.
b) This sample was collected in Shenyang.

sulfur.

4.3 Ash and water–soluble sulfur in ash after combustion of biomass

Ash was calculated from weight of residual matter after burning, and water-soluble sulfur in ash was measured. The results were shown in **Table 5**. Compared with Table 3, water-soluble sulfur contents remained in ash were almost agreed with those before combustion. Ash after burning woody dust and emission from combustion were the least. For this reason, it was judged that woody dust could be the best suitable for side material of bio-briquette.

Table 5. Percentage of ash and incombustible sulfur to dry biomass after combustion.

Biomass	Woody dust-1	Woody dust-2	Woody dust-3	Woody dust ave.	Rice bran	Sorghum stalk	Rice straw	Weeds	Maize stalk	Wheat straw	Rice bran[a)]
Ash(%)	3.4	1.7	1.7	2.3	15.4	13.1	17.0	16.8	12.5	8.2	9.0
S (%)[b)]	0.004	0.005	0.005	0.005	0.029	0.141	0.158	0.155	0.169	0.214	0.012
S(%)[c)]	0.001	0.007	0.003	0.004	0.022	0.086	0.171	0.184	0.072	0.185	0.011

a) This sample was collected in Shenyang.
b) This value is water soluble and incombustible sulfur content to dry biomass after combustion.
c) This value is water soluble sulfur content to dry biomass before combustion.

4.4 Sulfur-fixation efficiency of bio-briquette

Slaked lime [$Ca(OH)_2$] as sulfur-fixation agent was added to the mixture of biomass (25%, wt.) and raw coal or refined coal produced in Chongqing (75%, wt.) based on the ratio Ca/S=1.5 or 2, then bio-briquette was compressed by twin roll press under high pressure (**Fig. 3**). Air pollutants emitted from bio-briquette[7)] and raw coal combustion, ash after burning, water-soluble sulfur in ash were measured. And, sulfur-fixation and ash-abatement efficiencies of bio-briquette were calculated from these data. These results were shown in **Table 6** and **Table 7**. Compared with raw coal, air pollutants emitted from bio-briquette combustion were reduced largely. Emission amounts for SO_2 per 1kg of raw coal and bio-briquette were 9.1~ 43.3g and 0.9 ~ 5.1g, respectively. The sulfur-fixation and ash-abatement efficiencies of bio-briquette amounted to 82% and 25%, respectively. The sulfur-fixation efficiency was calculated by equation (1).

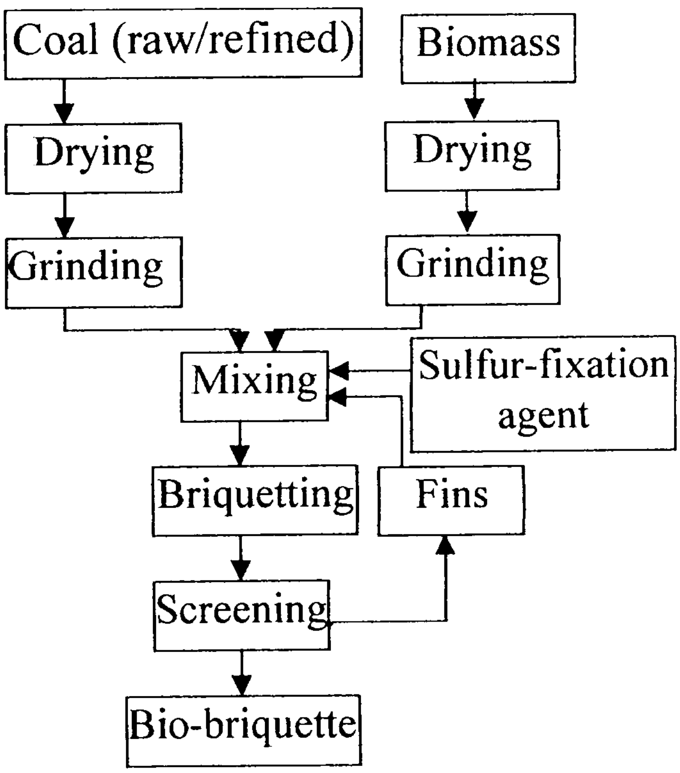

Fig. 3. Flow sheet of bio-briquette production.

$$E_{SF}(\%) = \{(0.75\times S_0+0.25\times S_B)/(1+\alpha_S\times C\times 74/32) - S_{BB}\}/\{(0.75\times S_0+0.25\times S_B)/(1+\alpha_S\times C\times 74/32)\}\times 100 \qquad (1)$$

In the equation, E_{SF} (%), S_0 , S_B , α_S , C, S_{BB} , 74, 32 represent the sulfur-fixation efficiency, sulfur emission of coal, sulfur emission of biomass, sulfur content estimated for coal, mole ratio added $Ca(OH)_2$, sulfur emission of bio-briquette, formula weight of $Ca(OH)_2$ and S, respectively.

Table 6. Emission of the air pollutants from raw coal and bio-briquette combustion (Dry basis).

Sample		HF (mg/kg)	HCl (mg/kg)	SO_2 (g/kg)	S(%)	E_{SF} (%)[a]
Chongqing	Raw coal	92	183	43.3	2.18	
	B. B.[b]	0	152	5.1	0.26	82
	Refined coal	22	149	22.0	1.11	
	B. B.[c]	0	47	0.9	0.04	94
Shengyang	Raw coal	31	131	9.1	0.46	
	B. B.[d]	0	46	0.9	0.05	85

a) E_{SF}% represents the sulfur-fixation efficiency calculated from sulfur emission difference between raw coal and bio-briquette.

b) This bio-briquette was produced by the addition of sulfur-fixation agent (molar ratio Ca/S=1.5) to the mixture of 75%- raw coal and 25% -woody dust-2.

c) This bio-briquette was produced by the addition of sulfur-fixation agent (molar ratio Ca/S=2.0) to the mixture of 75%-refined coal and 25%- bagasse.

d) This bio-briquette was produced by the addition of sulfur-fixation agent (molar ratio Ca/S=2.0) to the mixture of 75%- raw coal and 25%- rice barn.

Table 7. Percentage of ash and residual sulfur after combustion of raw coal and bio-briquette (Dry basis).

Sample	Raw coal	B. B[b].	D. A.[a]	Refined coal	B. B[c]	D. A.[a]	Raw coal	B. B[d]	D. A.[a]
Ash (%)	36.4	29.7	25	16.0	15.0	34	14.5	12.8	29
S (%)[e]	0.14	1.13		0.08	0.78		0.27	0.22	

a) D.A. represents the decreasing efficiency of residual ash after combustion of bio-briquette as compared with raw coal.

b~d) These meanings are given in Table 6.

e) This value is water soluble sulfur content in residual ash after combustion to dry raw coal or bio-briquette.

5. Conclusions

The investigation for outputs of biomass indicated that there were large amounts of biomass as agriculture wastes and woody wastes in Chongqing. Their total yearly outputs amounted to 18.0 million tons. Biomass outputs as side-material were enough to produce necessary bio-briquette in Chongqing. Therefore, biomass will be rich when briquetting of low graded raw coal is used as emission control technique for precursor causing acid rain in Chongqing.

Seven types of agriculture wastes and woody dust collected in Chongqing and rice bran collected in Shengyang were investigated for water-soluble components and air pollutants emitted from their combustion emissions. The results obtained from the above experiments were summarized as following.

1. Contents of water-soluble chemical components in various biomasses were different, water-soluble sulfur contents in all biomass were generally low. SO_4^{2-} concentration and acidity in rice bran collected in Chongqing were higher than those in Shengyang. It may

be explained that high sulfur concentrations in air pollutants and acid rain have affected agriculture and plants in Chongqing. Because, acid rain was not occurred in Shengyang.

2. Most of the sulfurs in biomass were mainly inorganic salts. There were little emissions of air pollutants from biomass combustion and emission amounts from 1kg of biomass were in the range of 0~43, 16~912 and 114~789mg for HF, HCl, and SO_2, respectively.
3. The least emission was obtained for woody dust combustion. Therefore, woody dust was considered as the best suitable biomass to produce bio-briquette.
4. Emission amounts of several air pollutants from bio-briquette combustion were reduced largely. The sulfur-fixation and ash-abatement efficiency of bio-briquette produced from raw coal and woody dust amounted to 82% and 25%, respectively.

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