

C-3.2.2 Co-operative Study on the Evaluation of Emission Control on the Indoor and Outdoor Environment in the Model Area

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Total Budget for FY 1997-1999 5,995,000 Yen (FY1999; 1,995,000 Yen)

Abstract In this study, the low and stable concentration of the hydrogen fluoride gas was got by using porous polytetrafluoroethylene (PPTFE) tube, which HF gas generated from reaction of NaF and H₂SO₄ solution can diffuse through the membrane. Then, it is considered that the simple sampling (passive sampler and detection tube) could be used in measuring the concentration of the air pollutants emitted from the raw coal and the bio-briquette combustion instead of alkaline solution since the results of two methods were approximately agreement. And, the aldehydes emitted from the raw coal and the bio-briquette combustion were collected by cartridge sampler and their concentrations were analyzed by HPLC-UV.

The reduction efficiencies of air pollutants by bio-briquetting and the evaluation methods for indoor and outdoor pollution were investigated. Further, the personal exposure amounts of NO₂ and SO₂ were estimated based on the concentration of air pollutants determined at the real environment in Chongqing of China. Concentration of SO₂ in indoor air amounted to 13 times of annual average of Chongqing outdoor-air when the raw coal was burned, but they dropped to 1/2~1/3 of raw coal combustion in case using the bio-briquette. It is known that the reduction efficiencies of air pollutants by bio-briquetting were high based on the comparison of the human exposure amounts. The human exposure amounts of SO₂ and NO₂ were 15.66 mg/day and 0.23 mg/day for the bio-briquette combustion, 37.01 mg/day and 0.34 mg/day for the raw coal combustion, respectively.

Keywords: coal combustion; bio-briquette; personal exposure amounts, aldehydes.

1. Introduction

With the economic development in China, the air pollutants emitted from the combustion of the raw coal with high sulfur and high ash content without any treating have become the source of the serious air pollution^{1,2)}. And, the human effect has been reported recently³⁾. In the southwest areas such Chongqing and Guiyang, there is the fear of human's health damage caused by the air

pollution since the respiratory disease is commonly occurred along with the economic loss such as the forest decline, the agricultural damage and the corrosion of building³⁾. Thus, it becomes very urgent for the studies on integrated control techniques for acid-precursors from the domestic coal consumption which could largely contribute the environmental concentration of sulfur dioxide, VOC, dust and the fluorides in the residential area considering the environmental measure and residents' health protection. Coal-biomass briquette (bio-briquette) which is little emissions of air pollutants from the combustion and little residual matters after burning, and higher sulfur-fixation efficiency as compared with the raw coal, is expected to be a better emission control technique. The establishment of an evaluation method for the reduction of air pollutants by bio-briquetting of raw coal in real environment is an urgent task in order to encourage the use of the bio-briquette. Namely, considering the spread to a general family, it needs to make obvious the reduction efficiency of the pollutants in real environment (indoor), and it is important to establish an evaluation method for indoor and outdoor exposure amounts.

The reduction efficiency of air pollutants by bio-briquetting and the evaluation methods on indoor and outdoor pollution were investigated. Further, the concentrations of air pollutants such as SO₂, NO₂, aldehydes in indoor and outdoor environment using the raw coal and the bio-briquette were measured in Chongqing of China. Thus, the reduction efficiency of the exposure amounts by bio-briquetting was investigated by comparison of the exact concentration in indoor environment between raw coal and bio-briquette combustion. Finally, the human exposure amounts of NO₂ and SO₂ were estimated based on these data.

2. Experiment methods

2.1 Generation of low concentration of HF gas

In Fig. 1^{4,5)}, HF gas from the reaction of H₂SO₄ and NaF solution shown in Table 1 is generated through PPTFE tube maintained in common temperature (35 ± 1°C), which is a special membrane for diffusing the gas. The generated gas was introduced to impinger, which was filled with the absorption solution (2.7 mM Na₂CO₃ / 0.3 mM NaHCO₃ (eluent solution for anion analyses in an ion chromatograph)). Then, F⁻ concentrations in the absorption solution was measured with an ion chromatograph (DX-100, Dionex Corp. of U. S. A.) and calculated to the gas concentration.

Table 1. Conditions of HF gas generation.

Item	Condition
Concentration of H ₂ SO ₄	0.18 M
Concentration of NaF	0.018~0.036 M
Flow rate of H ₂ SO ₄ and NaF solution	80 ml/min ^{a)}
Flow rate of purified air	2.5~3.0 L/min
Temperature	35 ± 1 °C

^{a)} Flow rate of H₂SO₄ to NaF solution is constant.

2.2 Combustion experiment

In Fig. 2⁶⁾, 1.000 g of the sample in the quartz boat was put in the center of quartz combustion tube maintained at 500°C. Then, 1.0 l/min of burning gas was flowed from a flow controller to electric furnace, electric furnace was heated from 500°C to 800°C and the experimental sample was burned for 20 minutes at

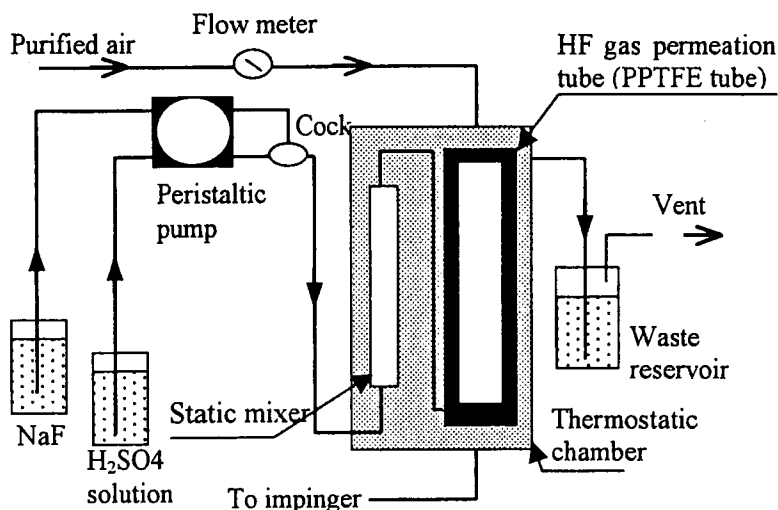


Fig. 1. Schematic diagram of continuous HF gas generating apparatus.

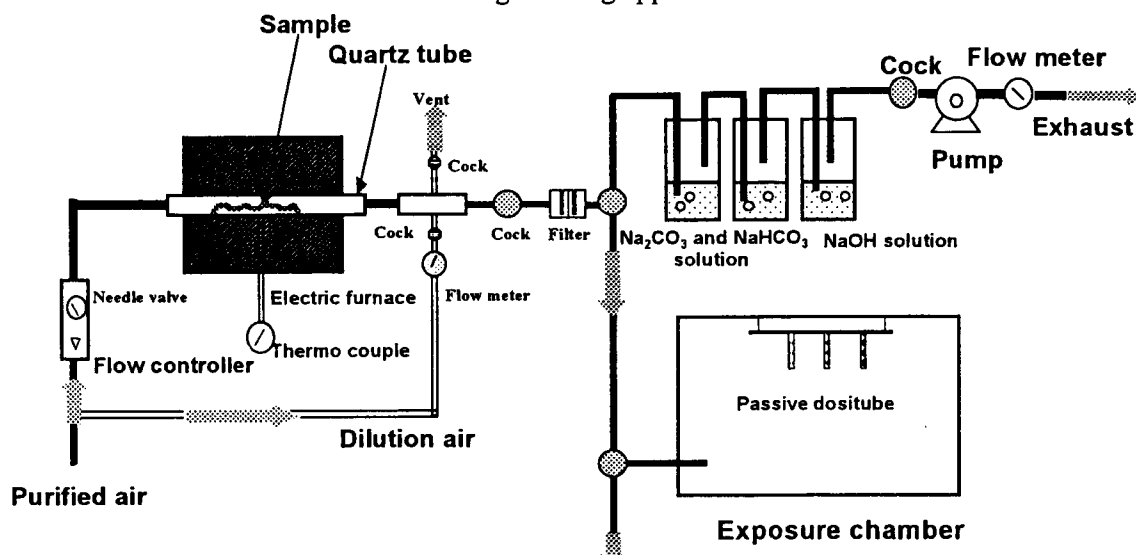


Fig. 2. Experimental equipment for combustion test.

800°C. Temperature in combustion tube was monitored by a thermo-couple. The exhaust gas from combustion was diluted by 4.0 l/min of purified air. The particles emitted from the sample combustion were collected with a quartz filter (2500QAT-UP, Pallflex Co.). A part of diluted gaseous exhaust (1.0 l/min) was introduced to impinger, which was filled with 150 ml of absorption solution (2.7 mM Na_2CO_3 / 0.3 mM NaHCO_3 (eluent solution for anion analyses)). A part of the filter collected aerosols and residual ash is extracted by an ultrasonic cleaner. Then, F concentrations in the absorption solution and the extraction solution were measured with an ion chromatograph (DX-100, Dionex Corp. of U. S. A.).

2.3 Measurement of acidic gas

The sampling filter was prepared in order to collect the acidic air pollutants. The quartz fiber filter (25 mm ϕ) was put in 2% KOH solution (1:1 MeOH/ H_2O) for the time enough to souse in

the solution. Then, the filter was put into a vacuum desiccator for 48 hours. The prepared filters were stored in the bag with the slide fastener.

During Sep. 21~26 in 1999, acidic gas was collected in Longjing village of Chongqing in the southwest China by using the personal sampler (PS-33 type, Shibata Science Industry Corp.) in the flow rate of 1.5 l/min. The collected filter was extracted by an ultrasonic cleaner, then the extraction solution filtered by the membrane filter of 0.45 μ m (No.5B) was measured with an ion chromatograph (Ionpac AG12A/ Ionpac AS12A, DX-100, Dionex Corp. of U. S. A.).

2.4 Measurement of aldehydes

The exhaust gas from the raw coal and the bio-briquette combustion after removing the particles by Teflon filter was collected by using the DNPH cartridge impregnated (Waters Corp.) in flow rate of 0.50 l/min. The cartridge collected was stored in cool and dark place till analysis, and extracted by acetonitrile (CH₃CN, 99.7%, Wakoo Corp.) with using the hydrazone method in the opposition direction of sampling. The concentrations of the hydrazone derivative in the extraction solution measured with HPLC-UV (LC-9A, Shimadzu Seisakusho Ltd.) were calculated into RCHO concentration in the exhaust gas.

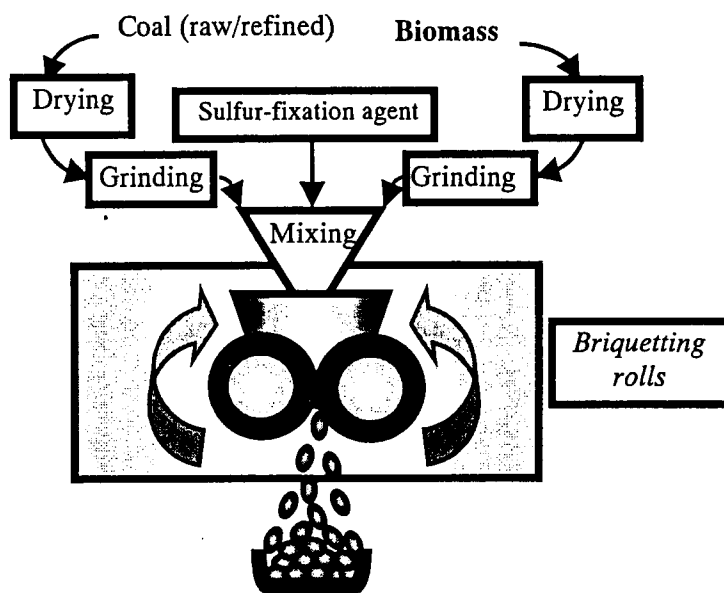


Fig. 3. Flow sheet of bio-briquette production.

2.5 Measurement of personal exposure concentration and amounts

The pollutants measurer (Handy SONOx sampler, Green Blue Corp.) were put on the breast pocket of two housewives in A and B family who using the bio-briquette and the raw coal. They were carrying for 24 hours. The filter after the exposure was taken out from the measurer, then oxidized by 0.3% hydrogen peroxide. Anion concentrations in the oxidized solution were analyzed by an ion chromatograph. The personal exposure amounts were estimated based on these data^{7,8}.

2.6 Production of bio-briquette

The mixtures of the coal (75%) and the biomass (25%) added the sulfur fixation agent Ca(OH)₂ (Ca/S=2) were produced to the bio-briquettes by the manufacturing procedure in Fig. 3

with the rolling compressor under 3~5 tons/cm² pressure.

3. Time till reaching stable concentration of HF gas and stable concentration

The time till reaching stable concentration of HF gas from 0.036 M and 0.018 M NaF was investigated under extra H₂SO₄ (0.18 M) condition. The time to stabilize HF gas concentration depended on the concentration of reactant NaF, was long with low concentration of NaF, and the generated HF concentration was low. In the above reaction condition, the time until becoming stable took 8 hours and 5 hours, respectively. Long time to stabilize could be caused by the stabilization of HF generation and the adsorption equilibrium existed on the wall of the tube.

4. Comparison of the integration measurement

As a sampling method of the acidic gas from the emission source, absorption with the alkaline solution is generally used, then ion concentrations are analyzed by an ion chromatograph (IC method). However, there were several faults in the transportation and the preservation of the sampler during the outdoor sampling with this solution. So as to overcome those faults, in this experiment, SO₂ concentration in the exhaust gas from the standard coal combustion was measured with using simple sampling methods, namely, using the passive sampler and the detection tube.

It is found that the SO₂ concentration in the exhaust gas from the standard coal combustion measured by IC method and the passive sampler was almost in accordance with the one obtained in an error of 7%. Detection tube is an analysis method based on the integration measurement, related with the read method of the coloring part. The compensation of the temperature, the humidity and the pressure should be conducted in order to calculate correctly the concentration of air pollutants. It is possible that the simple sampling is used as measuring the concentration of acidic gas instead of IC method since two methods gave high degree of correlation with the slope 1.06 and the correlation coefficients 0.98 (n=5).

The measurement data of SO₂ between by the detection tube and the passive method were almost agreement. Two methods was high degree of correlation with the slope 0.97 and the correlation coefficients 1.00 (n=6). Therefore, if the measurement on the real environment uses 2 methods alternately, it is considered that an instant value and the average value of the pollutants could be got at the same moment.

5. Investigation of reduction efficiency of the pollutants by bio-briquetting

5.1 Fundamental analysis and the combustion characteristics of the coal

The fixed carbon, the ash content, volatile matter content and the sulfur content of the standard coal sample and the raw coal produced in various parts of China, and the concentration of air pollutants from their combustion were shown in **Table 2**. The standard coal samples used in this experiment were prepared by China Institute of Coal Science Study. Taixi coal with high fixed

carbon and low sulfur content emitted a little pollutants, has good quality as known a famous coal production center of China. However, all of the coal produced in Chongqing and Chengdu of southwest China contained high sulfur and ash, which can result in the serious air pollution. And, the most of sulfur was the combustible sulfur, which will be emitted when burning. It was known that the serious air pollution have occurred at Chongqing of southwest China due to the coal combustion with high sulfur and ash without any treating in addition to the complicated terrain and an unfavorable meteorological condition for diffusion of air pollutants.

Table 2. Emission of the air pollutants and basic analysis of coal (dry basis).

Sample	Emission (mg/g-coal)			Sulfur (%)		Ash	Volatile matter (%)	Fixed carbon
	HF	HCl	SO ₂	Combustible	Total			
GBW11101c ^{a)}	0.01	0.17	5.77	0.29	0.30	9.18	32.72	58.1
GBW11102c ^{b)}	0.02	0.12	22.16	1.11	1.43	40.48	23.17	36.4
GBW11108b ^{a)}	0.03	0.11	16.06	0.80	0.87	11.13	33.25	55.6
GBW11109b ^{a)}	0.02	0.17	49.38	2.47	2.59	13.81	34.27	51.9
GBW11110b ^{b)}	0.03	0.21	73.98	3.70	3.79	11.14	10.97	77.9
Sichuan ^{a)}	0.07	0.05	8.01	0.40	0.51	23.01	8.70	66.5
Chengdu raw coal 1 ^{a)}	0.06	0.20	40.62	2.03	2.70	29.24	15.90	48.1
Chengdu raw coal 2 ^{a)}	0.06	0.15	52.83	2.64	2.95	28.60	11.91	55.3
Chongqing raw coal 1 ^{b)}	0.10	0.10	55.33	2.88	3.03	35.63	9.73	51.6
Chongqing raw coal 2 ^{a)}	0.12	0.39	49.49	2.47	2.73	29.81	12.71	53.0
Chongqing refined coal 3 ^{b)}	0.09	0.30	15.81	0.79	0.90	13.34	19.10	65.5
Chongqing raw coal 4 ^{b)}	0.03	0.22	31.97	1.60	1.97	37.30	20.91	39.6
Heijinju raw coal ^{a)}	0.03	0.06	32.38	1.62	1.68	12.76	13.36	73.9
Huanglitan raw coal ^{b)}	0.05	0.03	102.51	5.13	5.30	35.02	11.47	53.5
Taixi raw coal ^{a)}	0.01	0.03	1.19	0.06	0.22	4.30	8.06	87.7
Shenyang ^{b)}	0.10	0.05	8.54	0.53	0.68	10.40	30.50	50.8

^{a)} Anthracite coal; ^{b)} Bituminite

And in Table 2, hydrogen fluoride was also emitted from the coal combustion. It is thought that the fluorides is one of the air pollutants and may lead to big damage to human health, the animals and the plants. Recently, it is reported that an adverse effect on the human health (the bone, the tooth and the woman reproduction function) caused by the fluorides have occurred in the various parts of China^{9, 10)}. High concentration of the fluorides was measured in the atmospheric particle, cloud water and fog water^{11, 12)}. For these reasons, considering the environmental measure and citizen's health protection, it is very urgent for the studies on integrated control techniques for air pollutants such as sulfur dioxide, dust and fluorides emitted from the coal combustion in southwest China.

5.2 Reduction efficiencies of air pollutants by bio-briquetting

In Table 3, compared with raw coal, air pollutants emissions such as HCl, SO₂ and dust from bio-briquette combustion were reduced largely, their reduction efficiency ranged 26~61%, 82~88% and 55~83%, respectively. From these results, it is known that the reduction efficiency of

dust for bituminite coal was more excellent than anthracite coal. While, the reduction efficiency for HCl was lower because HCl emission from biomass combustion was higher, and chlorides in coal and biomass were decomposed easily under 800°C. It is expected that emissions of air pollutants such as SO₂ are reduced drastically by bio-briquetting when it is popularly used in some districts where have suffered from serious air pollution.

Table 3. Emission of the air pollutants from coal and their bio-briquette combustion, and reduction efficiency of pollutants by bio-briquetting (dry basis).

Sample	Emission (mg/g-coal)			Combustible S%	Reduction efficiency (%)		
	HCl	SO ₂	Dust		HCl	SO ₂	Dust
Chengdu raw coal 1 ^{a)}	0.05	8.01	0.69	0.40			
B.B ^{c)} (coal +sawdust)	0.04	1.02	0.31	0.05	30	83	55
Chengdu raw coal 2 ^{a)}	0.20	40.62	2.37	2.03			
B.B ^{c)} (coal +sawdust)	0.10	4.16	0.90	0.21	35	85	62
Chengdu raw coal 3 ^{a)}	0.15	52.83	2.82	2.64			
B.B ^{c)} (coal +sawdust)	0.06	6.65	1.02	0.33	49	82	64
Chongqing raw coal 1 ^{b)}	0.39	49.49	2.25	2.47			
B.B ^{c)} (coal +sawdust)	0.11	5.48	0.79	0.27	61	84	65
Chongqing refined coal 2 ^{b)}	0.30	22.20	8.93	1.11			
B.B ^{c)} (coal +sawdust)	0.12	2.06	2.18	0.10	54	87	76
B.B ^{c)} (coal+rice bran)	0.28	1.93	1.60	0.10	26	88	82
B.B ^{c)} (coal+maize stalk)	0.12	2.67	1.59	0.13	31	83	82
B.B ^{c)} (coal+tofu dregs)	0.14	2.99	1.51	0.15	50	82	83

^{a)}Anthracite coal; ^{b)} Bituminite coal, ^{c)} Bio-briquettes (B. B.) were produced from 75 wt% of raw coal and 25 wt% of biomass by the addition of sulfur-fixation agent (Ca(OH)₂) (Ca/S=2.0).

6. Suggestion for the evaluation methods on indoor and outdoor pollutants

Recently, the epidemiological survey on the relationship between the human health and air pollution have been scheduled for since the various damages caused by the serious air pollution have occurred^{13, 14)}. For these studies, it is important to measure correctly the exact concentration of the air pollutants at the human's existence place, in other words, to investigate the indoor/outdoor concentration and personal exposure.

6.1 Measurement of indoor/outdoor concentration at the real environment

The indoor/outdoor concentration of air pollutants shown in Tables 4~6 were measured by the active sampling and passive sampling (passive sampler and detection tube) at two families where were using the raw coal and the bio-briquette in Longjing village of Chongqing suburb. There was a little difference of the data measured between passive sampler (Table 4) and detection tube (Table 5).

From Table 4 and 5, it is obvious that this area suffered from the serious air pollution. Moreover, the indoor concentration relating with human health was very high. In the case of using the raw coal, SO₂ indoor concentrations in A and B family were 13.3 and 13.7 times of the annual average value (321 µg/m³ (121 ppb (v/v)))¹⁾ of the atmosphere in 1997 at Chongqing, amounted to

65 and 67 times of annual average value ($66 \mu\text{g}/\text{m}^3$ (25 ppb (v/v)))¹⁾ of the atmosphere in 1997 in China, respectively. However, SO₂ outdoor concentration in the both of A and B family were lower than the annual average value of the atmosphere in 1997 at Chongqing. The sampling time in this study was midwinter, and furthermore there were no chimneys in the stove and the windows at the kitchen were closed. For these reasons, it is assumed that the combustion exhaust gas has become a state which diffused over the interior of the room, and its indoor concentration became much higher than outdoor. On the other hand, in the case of using bio-briquette, SO₂ indoor concentrations in A and B family were reduced largely, dropped to 1/2~1/3 of the raw coal, were 5.2 and 4.2 times of the annual average value of the atmosphere in 1997 in Chongqing, amounted to 25 and 21 times of China, respectively. Thus, not only the fuel conversion but also the usage of the stove and the remodeling of the kitchen should be conducted to control the indoor pollution.

Table 4. Measurements of indoor / outdoor air pollutants by passive samplers in the suburb of Chongqing.

Sampling site	Fuel	Sampling time	Indoor		Outdoor	
			NO ₂ μg/m ³	SO ₂ mg/m ³	NO ₂ μg/m ³	SO ₂ mg/m ³
A	Coal	24 hours (1999,12,21,10:00~22, 10:00)	31.2	5.08	13.8	0.03
	B.B ^{a)}	24 hours (1999,12,22 15:00~23, 15:00)	10.4	0.79	10.6	0.07
B	Coal	/	/	/	/	/
	B.B ^{a)}	24 hours (1999,12,22 15:00~23, 15:00)	11.0	0.60		

^{a)}: Refer to Table 3

Table 5. Measurements of indoor / outdoor air pollutants in the suburb of Chongqing.

Sampling site	Fuel	Sampling time	Indoor				Outdoor			
			HF μg/m ³	HCl μg/m ³	NO _x ^{a)} μg/m ³	SO ₂ mg/m ³	HF μg/m ³	HCl μg/m ³	NO _x ^{a)} μg/m ³	SO ₂ mg/m ³
A	Coal	Breakfast ^{b)}	9.5	9.1	1.5	4.40	4.5	5.4	3.7	0.13
		Lunch ^{b)}	21.1	14.0	2.8	4.40	nd	nd	5.6	0.21
		Dinner ^{b)}	26.6	33.2	11.0	4.00	/	/	/	/
		Average value	19.1	18.8	5.1	4.27	2.2	2.7	4.6	0.17
	B.B ^{c)}	Breakfast	4.3	6.4	1.2	1.68	3.3	3.0	2.5	0.09
		Lunch	9.8	12.8	0.6	1.70	1.6	7.6	0.5	0.10
		Average value	7.0	9.6	0.9	1.69	2.4	5.3	1.5	0.10
B	Coal	Breakfast	2.9	6.2	1.5	4.09	/	/	/	/
		Lunch	13.0	15.0	5.2	5.08	/	/	/	/
		Dinner	23.5	25.1	5.1	4.02	nd	5.7	1.0	0.22
		Average value	13.1	15.4	3.9	4.40		5.7	1.0	0.22
	B.B ^{c)}	Breakfast	2.0	12.8	1.2	1.60	4.7	nd	1.0	0.08
		Dinner	1.6	17.6	0.5	1.12	nd	2.3	0.8	0.08
		Average value	1.8	15.2	0.8	1.36	2.3	4.0	0.9	0.08

^{a)} NO_x presents the sum of NO₂ and NO. ^{b)} Breakfast time is 8:00~10:00, lunch time is 10:00~13:00, and dinner time is 16:00~19:00 in this study. ^{c)}: Refer to Table 3.

Finally, either indoor or outdoor concentration of NO_x were less than annual average value (45µg/m³) of the atmosphere in 1997 in China, under the 2 level of national standard. Meanwhile, outdoor was a little higher than indoor since A and B family in the side of highway could be affected by the exhaust gas from the car and the heavy-duty truck.

From Table 6, the formaldehyde indoor concentration in A house was high, exceeded WHO standard 0.08 ppm (96 µg/m³)¹⁵⁾, while the formaldehyde indoor/outdoor concentration of B house were pretty lower than the standard. The reason is assumed that the structure of the stove and the ventilation condition used at A and B house was different.

Table 6. Indoor / outdoor concentration of aldehyde using coal and B.B in Chongqing.

Sampling point		Indoor (µg/m ³)			Outdoor (µg/m ³)		
		HCHO	CH ₃ CHO	CH ₃ CH ₂ CHO	HCHO	CH ₃ CHO	CH ₃ CH ₂ CHO
A	Coal	165.6	239.5	118.0	40.5	59.3	8.8
	B.B ^{a)}	134.8	180.3	77.9	27.5	42.6	8.1
B	Coal	55.4	67.2	12.8	45.3	54.9	12.2
	B.B ^{a)}	64.3	88.1	58.3	17.4	43.8	9.5

^{a)} Refer to Table 3

6.2 Concentration of air pollutants in the exposure chamber for animals

In Chongqing area with a high incidence of respiratory disease, it is worried about that the generation of the lung cancer may entangle complicatedly with air pollution also. In order to understand the relationship between the disease and air pollution, it is important to conduct the exposure experiments of the animals (rabbits) to the exhaust emitted from the raw coal and the bio-briquette combustion in same condition 2 rooms (floor area 4.5 m² and height 2.5 m). In this study, the concentrations of air pollutants in these two rooms were measured (Tables 7, 8).

Table 7. Indoor / outdoor concentration of air pollutants from coal and bio-briquette combustion exhausts in chamber for exposure experiment of animals.

Sampling time	Coal (Control room)				Bio-briquette (Test room)			
	HF	HCl	NO _x	SO ₂	HF	HCl	NO _x	SO ₂
	µg/m ³		mg/m ³		µg/m ³		mg/m ³	
Breakfast time ^{a)}	32.0	35.5	1.3	7.49	17.2	92.7	48.9	4.40
Lunch time ^{a)}	18.0	52.8	9.0	7.35	14.4	205.0	83.2	1.75
Dinner time ^{a)}	8.1	30.8	20.7	3.36	4.1	80.6	17.1	1.59
Average value	19.4	39.7	10.3	6.07	11.9	126.1	49.7	2.58
Outdoor								
	HF	HCl		NO _x	SO ₂			
		µg/m ³			mg/m ³			
Breakfast time	5.8	9.0		12.0	0.28			
Lunch time	8.6	10.6		36.4	0.37			
Dinner time	3.1	1.4		13.5	0.29			
Average value	5.8	7.0		20.6	0.31			

^{a)} Refer to Table 5.

Compared with Test room, SO₂ indoor concentration in Control room was 2 times higher, ranged 3.36~7.49 mg/m³ and with average value 6.07 mg/m³. The outdoor concentration ranged 0.28~0.37 mg/m³ and was almost similar with the annual average of the atmosphere in Chongqing. On the other side, the indoor concentration of aldehyde in Test room was higher than that of Control room, exceeded the WHO indoor standard 0.08 ppm (96 µg/m³) of formaldehyde. This cause was assumed that the bio-briquette contained about 25 % of the biomass were incompletely burned. The outdoor concentrations of aldehydes were very low.

Table 8. Indoor / outdoor concentrations of aldehyde in chamber for exposure experiment of animals from coal and bio-briquette combustion (µg/m³).

Sampling time	Coal (Control room)			Bio-briquette (Test room)		
	HCHO	CH ₃ CHO	CH ₃ CH ₂ CHO	HCHO	CH ₃ CHO	CH ₃ CH ₂ CHO
Breakfast time ^{a)}	48.0	19.1	19.2	215.2	222.1	95.1
Lunch time ^{a)}	28.3	30.0	21.8	303.4	452.9	204.3
Dinner time ^{a)}	69.2	31.2	28.4	127.2	178.5	110.9
Outdoor						
	HCHO	CH ₃ CHO	CH ₃ CH ₂ CHO			
Breakfast time	1.0	1.8	26.5			
Lunch time	6.3	35.7	37.9			
Dinner time	4.1	11.7	15.4			

^{a)} Refer to Table 5.

6.3 Estimation of the personal exposure (PE)

As shown above, indoor concentrations of major pollutants in the investigated family were high, but they were not the personal exposure loads. Here, the personal exposure amounts were estimated as follows^{6, 7)} based on the data measured by the portable type of Handy SONOx sampler. The results were shown in **Table 9**.

$$PE(\text{mg/day}) = \text{TWA} \times 8(\text{l/min}) \times t(\text{min}) \times M/24 \times 1/10^3$$

Here, TWA (ppm): personal exposure concentration; 8(l/min): personal respiratory amount per minute; t: personal exposure time per day (min); M: molecular weight of pollutant.

In case of using the raw coal, the personal exposure amounts of SO₂ and NO₂ between A and B families were almost similar, amounted to 40 mg/day and 0.4 mg/day, respectively. It is clear that the personal exposure amounts of SO₂ and NO₂ were reduced dramatically when the bio-briquette was used. However, compared with the raw coal, the personal exposure amounts of HCHO and CH₃CHO were increased fractionally while in case of the bio-briquette, but did not exceed the WHO standard 0.08 ppm (96 µg/m³). It is considered that that there is no fear which leads to the health effect from those exposure amounts also. Therefore, the reduction efficiency of the pollutants by the bio-briquette was made obvious in the areas where are using the raw coal with high sulfur and high ash content. As the developing countries such as China, especially at the

suburbs and the village area, it is difficult to change fundamentally the energy composition due to the restrictions of the resources and the finances. It is thought that the briquetting techniques should be encouraged as one of the main transitional measure in the present stage.

Table 9. Personal exposure to the air pollutants in Longjing of Chongqing.

Sampling site	Fuel	Sampling time (h)	TWA				PE			
			NO ₂	HCHO	CH ₃ CHO	SO ₂	NO ₂	HCHO	CH ₃ CHO	SO ₂
			μg/m ³			mg/m ³	mg/day			
A	Coal	24 ^{a)}	14.8	/	/	1.24	0.31	/	/	38.09
	B.B	24 ^{a)}	10.4	/	/	0.79	0.22	/	/	24.26
B	Coal	24 ^{a)}	18.0	6.9	4.9	1.17	0.38	0.10	0.1	35.94
	B.B	24 ^{a)}	11.5	34.6	30.1	0.23	0.24	0.50	0.64	7.06

^{a)} Refer to Table 4.

7. Conclusion

In this study, low concentration hydrogen fluoride standard gas from the mixture solutions of H₂SO₄ and NaF was got by using a hydrogen fluoride generation device to establish an evaluation method of the pollutants. And, it is possible that the passive sampler and detection tube could collect the air pollutants instead of the traditional alkaline solution. It was obvious that the bio-briquette can reduced largely the emission of the pollutants based on the data measured at either the laboratory or the real environment. Finally, the personal exposure amounts for SO₂ and NO₂ estimated based on the concentration from combustion exhaust were 37.01 mg/day and 0.34 mg/day for the raw coal, 15.66 mg/day and 0.23 mg/day for the bio-briquette, respectively.

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