# C-3.2.1 Studies on Utilization to Control Emission of Acid-Precursors and Evaluation of Impact of their Use on the Health Effects

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**Abstract** Chongqing city is known for the worst air pollution area in China, especially sulfur dioxides and suspended particulate matter. There are many respiratory diseases in the residents. We estimated the level of air pollutants (indoor and outdoor), and carried out physical check of the 81 families in bio-briquette group and 95 families in control group before and nine months after the start of using bio-briquette. The indoor level of $SO_2$ during using the bio-briquette decreased one of fifth compared with using of raw coal. The rate of adult female with positive nasal pharynx findings of the bio-briquette group sufficiently decreased after the using of bio-briquette compared with that of the control group. That of children of biobriquette group was also tend to decrease.

## 1. Introduction

Sulfur dioxide ($SO_2$) is one of main pollutants. Most of them come from burning coal, that is the main resource of energy in China. It is being widely consumed in industrial purpose and household use. According to the 1996 statistics of Chongqing City, that one of the famous heavy industrial cities in China, the emission of $SO_2$ was up to 54.38 million ton per year. The huge emission of coal smoke not only causes a serious environment problem and also increases incidences of respiratory diseases. In order to control air pollution, it becomes urgent to study on integrated control techniques for precursors of acidic precipitation in Chongqing distinct. In our study we introduced an effective coal-bio-briquette technique for reducing the emission of $SO_2$ and other pollutants from coal combustion source. In order to investigate the influence of bio-briquette and raw coal on human health, we carried out medical examination and measurement of both indoor and outdoor pollution at two rural areas in Chongqing, China.

## I. Studies on Evaluation of Impact of Bio-briquette Use on the Health Effects

## 1. Research Objectives

In order to evaluate the influence of bio-briquette and raw coal on human health, from March to December 1998, we questioned family hygiene status and house environment meanwhile we carried out medical examination at two rural areas. One of two areas was designed to using raw coal as domestic use and another was bio-briquette. We hope the improvement of human health will emphasize the motivation for prevalence of using bio-briquette.

## 2. Research Methods

From March to December, 1998 we conducted experimental group (Bio group) and control group (C group) in two carefully selected domestic coal use areas in countryside in Chongqing. The C group (89 families) used raw coal, and Bio group (110 families) used bio-briquette, which can reduce the emission of $SO_2$ and other pollutants. We followed up 10 months and collected medical information separately on March and December. The unit we selected individuals was a family with a child at least 7 years old.

Indexes observed included (1) general information, (2) environment indexes, such as concentration of indoor and outdoor $SO_2$, and (3) medical examination such as nasal pharynx examination and pulmonary function test. These indexes was given before and nine months after using bio-briquette. We analyzed adult female and children, respectively.

## 3. Results

### 3.1 Adult female

The mean ages of B (n=90) and C group (n=67) were 41.5±12.6 and 38.1±8.8 years old, respectively. As shown in Figure 1, positive rate of nasal pharynx in B group were all higher than in C group on March in 1988, that is before using bio-briquette, while most of them were statistical significant in two groups. B group was especially more positive findings in pharynx wall, tonsil swelling and dilation than C group. The rate of any symptoms in B or C group was 85.5% and 68.6%, respectively.

On the other hand the same positive rates of nasal pharynx in B group were all lower than in C group after nine months using bio-briquette, except nasal conchae (Figure 2). We also noticed that all positive rates between two groups were not significant on December. Actually, positive rates were greatly reduced on December contrast to on March in each group. But Quantities reduced so more in B group that those were high significant in statistics. That is rate of combined positive symptoms reduced 87.1% to 23.2% in B group, 58.5% to 32.2% in C group. Those results suggested that from March to December, positive rates in two areas had been sharply changed and the relationship of low-high contrast in two areas was up-set down.

Indexes of both pulmonary function (Forced vital capacity, Peak expiratory flow rate) were little lower in B group than in C group, though they had been little improved in B group in December.

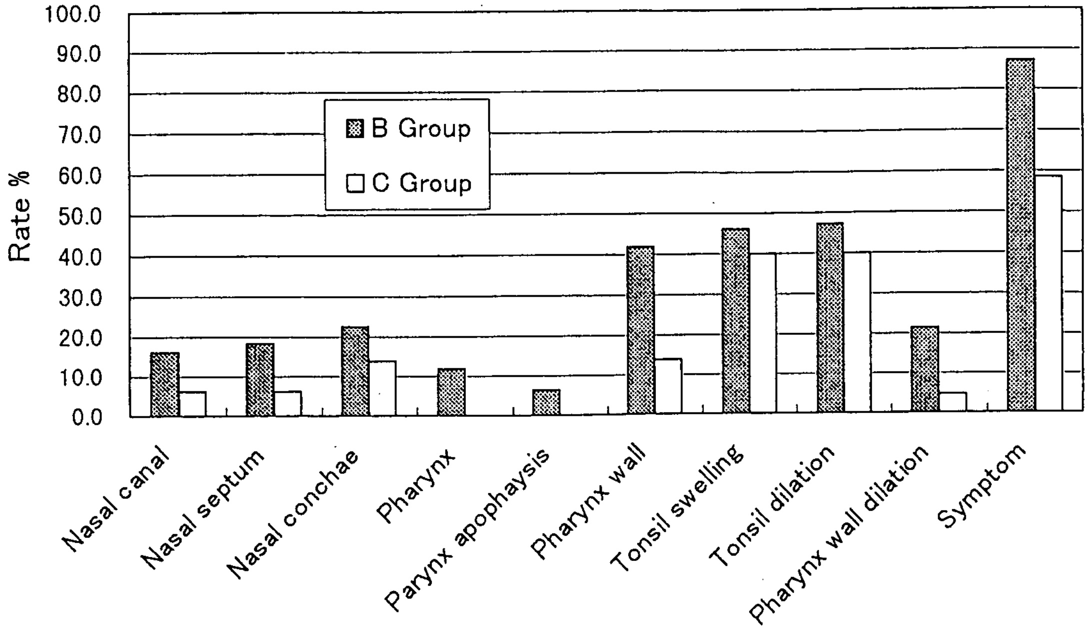

Fig. 1 The comparison nasalpharinx examination in tow groups (Before)

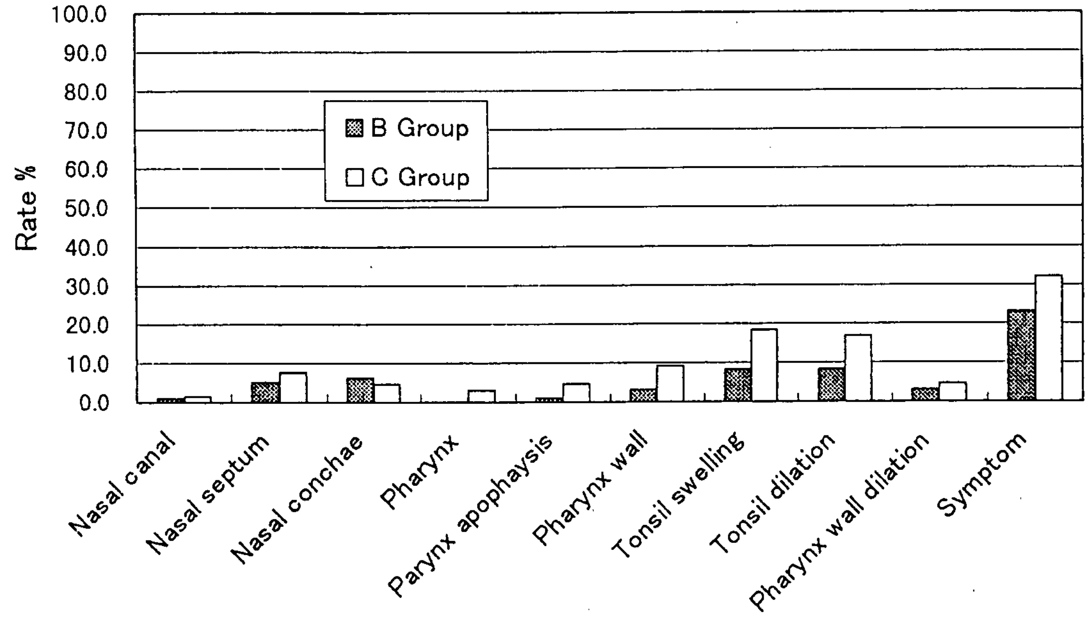

Fig. 2 The comparison of nasalpharynx examination in tow groups (After)

### 3.2 Children

The mean ages of B (n=88) and C group (n=106) were 10.0±2.7 and 12.1±2.6 years old, respectively. 4.2% of children explained continuous cough without catch a cold. As shown in Figure 3, positive rate of nasal pharynx in B group in March were all higher than those in December, that is after using bio-briquette. Similar tendency was found in C group in statistics. That is, the rate of combined positive symptoms reduced from 87.1% to 23.2% in B group, from 58.5% to 32.2% in C group. Those results suggested that from March to December, positive rates in two areas had been sharply changed and the relationship of low-high contrast in two areas was up-set down.

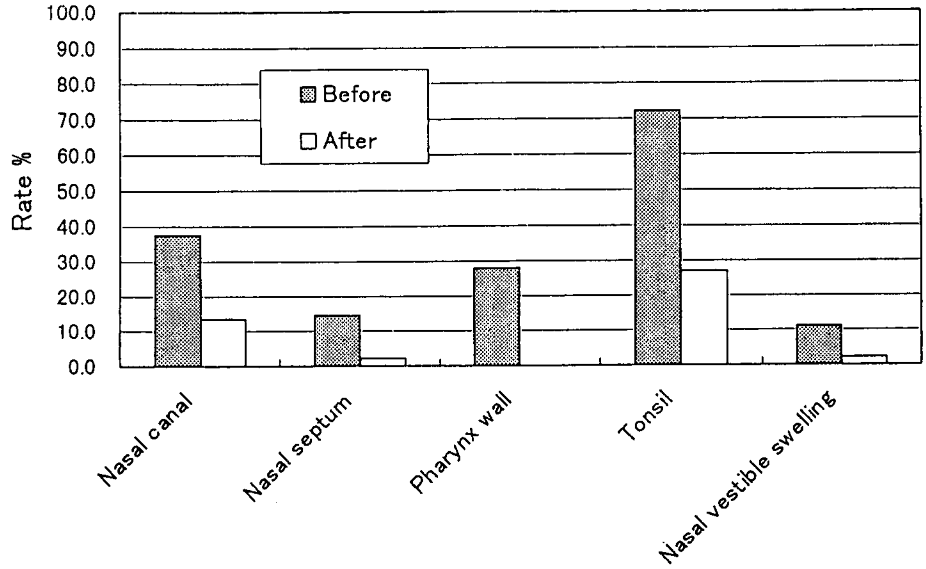

Fig. 3 The comparison of nasalpharynx examination between before and after using bio-briquettes in B group

### 3.3 Environment measurement

The concentration of sulfur dioxide and other pollution in the rooms in B group were markedly decreased during using bio-briquette (detail data will be described in section II).

## 4. Discussion

After discounting of the season effects, burning bio-briquet can significantly reduced the nasal pharynx positive symptoms in B group. Especially, adult female who spent the longer time in the kitchen was much improved. The major reason should be due to that the emission of sulfur dioxide be reduced. After burning the bio-briquette the above 90% families reported the fume status was dwindled and the odor of fume was almost grown none. So almost all families welcomed bio-briquette instead of a little high cost.

These results suggest that indoor air quality significantly affected resident health. As an effective method to reduce the emission of $SO_2$ and to improve the environment and health effects, bio-briquette is a good and simple choice. At the same time, we also should take some attention to their kitchen condition, such as correct ventilation.

## II Study on the Development for Emission Control Technique of Acid Rain Precursor and Evaluation of its Effect on the Human Health

### 1. Research Objective

In this study, the reduction efficiency of air pollutants by bio-briquetting and the evaluation methods on indoor and outdoor environment were investigated. Further, the concentrations of air pollutants such as $SO_2$, $NO_2$, 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 $NO_2$ and $SO_2$ were estimated based on these data.

### 2. Experiment methods

### 2.1 Combustion experiment

Experimental equipment for combustion test was described in detail in our previous paper1).

### 2.2 Measurement of acidic gas

The sampling filter was prepared in order to collect the acidic air pollutants. The quartz fiber filter (25 mmΦ) 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 and Exposure Chamber (two rooms: 3×1.5×2.5 m) for animals at Chongqing Medicine University in the southwest China by using the individual sampler (PS-33 type, Shibata Science Industry Crop.) in the flow rate of 1.5 l/min. The collected filter was extracted by an ultrasonic cleaner for 15 minutes, then the extraction solution filtered by the membrane filter of 0.45μm (No.5B) was measured with an ion chromatograph (Ionpac AG12A/ Ionpac AS12A, DX-100, Dionex Corp. of U. S. A.).

### 2.3 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 cartridge soused DNPH (Waters Crop.) in flow rate of 0.50 l/min. The cartridge collected was stored in cool and dark place till analysis, and extracted by acetonitrile ($CH_3CN$, 99.7%, Wakoo Crop.) 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 gas2).

### 2.4 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 chromatography. The personal exposure amounts were estimated based on these data[3,4)].

### 2.5 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 with the rolling compressor under 3~5 tons pressure. Analytical results of coal and biomass used in production of bio-briquette are shown in **Table 1**. From these results, it is known that the raw coal contained high sulfur and high ash content, which can resulted in serious air pollution due to combustion exhaust without any treading. In other side, the biomass contained lower sulfur content. Two type biomasses used in this study possessed high calorific value. The rich wastes such as woody dust and rice straw in Chongqing is enough to produce much bio-briquette. By the way, CaO content in calcined lime was 45.51%.

**Table 1.** Analytical results of coal and biomass used in production of bio-briquette (%)(dry basis).

| Sample | Ash | Volatile matter | Fixed carbon | Sulfur | Calorific value (J/g) | Moisture content |
|---|---|---|---|---|---|---|
| Coal | 38.37 | 10.46 | 48.98 | 3.13 | 19,870 | 2.19 |
| Rice straw | 17.00 | 69.59 | 12.01 | 0.019 | 14,460 | 1.40 |
| Woody dust | 2.32 | 80.99 | 15.21 | 0.006 | 17,420 | 1.48 |

## 3. Investigation of reduction efficiency of the pollutants by the bio-briquette

### 3.1 Calculation for reduction efficiency of the pollutants by the bio-briquette

The reduction efficiency of the pollutants by the bio-briquette was calculated by formula

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

(1). The denominator of formula represents sulfur emission from each raw coal and bimass combustion contained in 1.00 g bio-briquette. The numerator represents difference of sulfur emission between 1.00 g bio-briquette combustion and its raw material (raw coal and biomass) combustion. The ratio of raw coal and biomass was 75%: 25%. 74 and 32 are molecular weight of $Ca(OH)_2$ and S, respectively.

*ESF*(%) : reduction efficiency of pollutants emission

$S0$ : pollutants emission from raw coal combustion(g/g)
$SB$ : pollutants emission from biomass combustion(g/g)
$M$ : equivalent ratio of added $Ca(OH)_2$ and sulfur content
$\alpha$ S : sulfur content in coal
$SBB$ : pollutants emission from bio-briquette combustion (g/g)

### 3.2 Reduction efficiencies of air pollutants by bio-briquetting

Emission of the air pollutants from coal and their bio-briquette combustion, and reduction efficiency of pollutants by bio-briquetting were shown in **Table 2**. In Table 2, compared with raw coal, air pollutants emissions such as HCl, $SO_2$ 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 chloride in coal and biomass was decomposed easily under 800°C. It is expected that air pollutants emission such as $SO_2$ is reduced drastically with bio-briquette when it is popularly used in some districts where have been suffered from serious air pollution.

**Table 2.** 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 | Reduction efficiency (%) | | |
|---|---|---|---|---|---|---|---|
| | HCl | $SO_2$ | Dust | S% | 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).

### 4. Suggestion for the valuation 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[3,4]. 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.

### 4.1 Measurement of indoor/outdoor concentration at the real environment

The indoor/outdoor concentration of air pollutants shown in **Tables 3~4** 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 3) and detection tube (Table 4).

From Table 3 and 4, it is obvious that this area was suffering from the serious air pollution. Moreover, the indoor concentration related with human health was very high. In the case of using the raw coal, $SO_2$ indoor concentration in A and B family were 13.3 and 13.7 times of the annual average value (321 $\mu g/m^3$ (121 ppb (v/v))) of the atmosphere in 1997 at Chongqing, amounted to 65 and 67 times of annual average value (66 $\mu g/m^3$ (25 ppb (v/v))) of the atmosphere in 1997 in China, respectively. However, $SO_2$ 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 cookhouse 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, $SO_2$ 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 cookhouse should be conducted to control the indoor pollution.

Finally, ether indoor or outdoor concentration of $NO_X$ was less than annual average value ($45 \mu g/m^3$) 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.

**Table 3.** Measurements of indoor / outdoor air pollutants by passive samplers in the suburb of Chongqing.

| Sampling site | Fuel | Sampling time | Indoor | | Outdoor | |
|---|---|---|---|---|---|---|
| | | | $NO_2$ | $SO_2$ | $NO_2$ | $SO_2$ |
| | | | $\mu g/m^3$ | $mg/m^3$ | $\mu g/m^3$ | $mg/m^3$ |
| 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 2

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

| Sampling site | Fuel | Sampling time | Indoor HF | Indoor HCl | Indoor $NO_x$ [a] | Indoor $SO_2$ | Outdoor HF | Outdoor HCl | Outdoor $NO_x$ [a] | Outdoor $SO_2$ |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | µg/m³ | | | mg/m³ | µg/m³ | | | mg/m³ |
| 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]: NOx presents the sum of $NO_2$ 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 2.

µg/m³) of formaldehyde. This cause was assumed that the bio-briquette contained the biomass of about 25 % were incompletely burned. The outdoor concentrations of aldehydes were very low.

### 4.2 Estimation of the personal exposure (PE)

As expressed above, indoor concentrations in the investigated family have presented high, but they were not the personal exposure loads. Here, the personal exposure amounts were estimated as formula (2)[4] based on the data measured by Handy SONOx sampler of the portable type. The results were shown in **Table 5.**

$$PE(mg/day)=TWA \times 8(l/min) \times t\ (min) \times M/24 \times 1/10^3 \qquad (2)$$

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 $SO_2$ and $NO_2$ 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 $SO_2$ and $NO_2$ were reduced dramatically when the bio-briquette was used. However, compared with the raw coal, the personal exposure amounts of HCHO and $CH_3CHO$ 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** 5. Personal exposure to the air pollutants in Longjing of Chongqing.

| Sampling site | Fuel | Sampling time (h) | TWA | | | | PE | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | $NO_2$ | HCHO | $CH_3CHO$ | $SO_2$ | $NO_2$ | HCHO | $CH_3CHO$ | $SO_2$ |
| | | | µg/m³ | | | mg/m³ | 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 3.

## 7. Conclusion

In this study, it was obvious that the bio-briquette can reduced largely the emission of the pollutants based on the data measured at ether the laboratory or the real environment. Finally, the personal exposure amounts for $SO_2$ and $NO_2$ 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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