THE ANALYSES OF POLLUTANTS EMITTED FROM BURNING COAL AND THEIR MUTAGENICITIES

Weixi YAO, Xiaobai XU

Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences,
P.O. Box 934, Beijing 100083, P.R. China.

Abstract The pollutants emitted from industrial boilers fired with coal and its mutagenicities were analyzed and evaluated by dual-detector high performance liquid chromatography (HPLC), atomic absorption spectrometry (AAS) and Ames test. When coal briquettes were used instead of raw coal in boilers, the total suspended particles (TSP) emitted decreased approximately by 60% in weight. SO_2 decreased approximately by 40%, and the Ames mutagenicities of emissions from burning coal briquettes are lower than that by raw coal.

Key words coal briquettes, HPLC, polycyclic aromatic hydrocarbons (PAHs), AAS, Ames mutagenic test.

Coal combustion is the major air pollution source in China. A Lot of pollutants were emitted from industrial boiler fired with coal, such as, SO_2 , TSP, PAHs and inorganic elements etc. This paper introduces a method of controlling and abating air pollution by burning coal briquettes which were made from raw coal and 8% binding material, 3-5% SO_2 fixation agents by pressure and heat. When coal briquettes are used instead of raw coal in boiler, approximately 10-15% of coal can be saved. Meanwhile, there is also an apparent reduction in particulates, SO_2 and mutagenicities. Hence the coal briquettes combustion technology for the boilers will form an important interim measure that can reduce air pollution.

EXPERIMENTAL

Sampling The amount of SO_2 in stack flue was measured by SO_2 analyzer. For TSP, PAHs and inorganic elements, we designed a sampler which is based on the modified U.S.A. EPA method 5 in order to collect not only pollutants on TSP surfaces, but also those in a vaporform smoke effectively (Fig.1).

Fig.1 Schematic diagram of the sampler
(1) Stack flue (2) Pitot manometer (3) Sampling probe (4) Dustfall collector
(5) Thermometer (6) Filter holder (7) Cooling tube (8) Flask (9) Adsorbent tube
(10) Active carbon (11) Silica gel (12) Flowmeter (13) Manometer (14) Safety bottle (15) Sampling pump.

Analysis The samples collected by the above mentioned sampler were divided into two parts: one was used to analyze PAHs by dual-detector HPLC (Shimaduz LC-3A), and the other was used to measure the inorganic elements by AAS (PE 4000 U.S.A.). Protocol suggested by Ames with strains TA98 and TA100 was followed without changes. The ultra-violet-fluorescence detector HPLC have good sensitivity for most of PAHs because those of small number rings are stronger absorbers of UV light while the others of large number rings yield intense fluorescence (fig. 2).

Fig. 2 HPLC chromatogram of 16 PAHs standards with dual-detectors (UVD 254 and FLD 296/427nm) Zorbax-ODS Φ 4.6x250mm CH₃OH/H₂O=85/15 for 35min, then to 100% CH₃OH (2%/min.)

RESULTS AND DISCUSS

1). SO₂ and TSP emissions from boiler fired with coal (Table 1):

TABLE 1 SO ₂ and TSP emissions from coal fired boilers				
boilers	KZL-2-8 (2T/h)		UG-35/39M (35T/h)	
coal yield area	Beijing soft coal		Datong soft coal	
dust remover	cyclolone-dust remover		water-dust remover	
binding materials	asphaltic residue		soda-lime	
coal type	raw-coal	coal-briquettes	raw-coal	coal-briquettes
SO ₂ (g/Nm ³)*	0.994	0.500	0.686	0.315
TSP (g/Nm ³)*	1.404	0.584	1.081	0.301

* g/Nm³: quantity of pollutants emitted per standard cubic meter stack gases

Table 1 shows that when coal briquettes are used instead of raw coal in boilers, SO₂ reduction is about 40-50%, while TSP reduction is about 60-70%.

2). PAHs and inorganic elements emitted (Table2 and 3):

TABLE 2 PAHs emitted from coal-fired boilers					
boilers		KZL-2-8 (2T/h)		UG-35/39M (35T/h)	
Name	(number of rings)	raw coal (μ g/Nm ³)	coal-briq. (μ g/Nm ³)	raw coal (μ g/Nm ³)	coal-briq. (μ g/Nm ³)
Naphthalene	NA (2)	1.28	1.44	26.7	28.0
Biphenyl	BP (2)	2.05	2.23	27.6	15.1
Fluorene	FL (3)	0.04	ND	5.58	21.4
Phenanthrene	PH (3)	1.59	2.58	8.86	6.65

Fluoranthrene	(4)	3.8	1.1	95.2	0.9	1.4	97.7
Pyrene	(4)	24.1	24.2	51.7	10.8	14.4	74.8
Benz(a)anthracene*	(4)	15.5	5.7	79.3	2.2	12.0	85.5
Benz(k)fluoranthene*	(5)	6.5	47.2	46.3	3.6	69.6	26.8
Benzo(a)pyrene	(5)	13.9	38.9	47.2	2.9	45.7	51.4
Dibenz(a,h)anthracene	(5)	29.2	19.1	51.7	5.3	57.4	37.3
Benzo(ghi)perylene	(6)	34.4	40.9	24.7	4.6	91.9	3.5
Coronene	(7)	17.2	65.5	17.2	1.7	96.6	1.7

* DF= dustfall, FD= floating dust, VS= vaporform smoke.

TABLE 5 The contribution of inorganic elements emission from UG-35/39M type boilers

\	Coal	Raw coal			Coal briquettes		
		D F	F D	V S	D F	F D	V S
Name	(atomic weight)	(%)	(%)	(%)	(%)	(%)	(%)
Aluminium	(27)	83.6	15.9	4.5	22.4	75.4	2.2
Arsenic	(75)	60.3	39.7	0.0	0.0	100.0	0.0
Barium	(137)	75.9	24.1	0.0	21.3	78.0	0.7
Cadmium	(112)	80.0	12.9	7.1	21.4	61.3	17.3
Calcium	(40)	20.1	70.8	9.1	0.7	97.8	1.5
Chromium	(52)	72.8	24.6	2.6	9.6	88.3	1.1
Copper	(64)	40.2	42.7	17.1	2.2	92.0	6.8
Iron	(56)	71.6	28.0	0.4	34.5	64.6	0.9
Manganese	(55)	71.9	23.3	4.8	20.5	73.8	5.7
Nickel	(59)	64.0	31.5	4.5	5.9	90.5	3.6
Lead	(207)	30.7	0.0	7.3	1.3	86.2	12.6
Selenium	(79)	58.2	41.8	0.0	1.9	98.1	0.0
Zinc	(65)	12.9	52.9	34.2	0.7	68.8	30.5

Table 4 and 5 show that the PAHs in the vaporform smoke are mostly of small number rings, while existed on the floating dust are mostly of large number rings. the inorganic elements existed on dustfall and floating dust are main.

4). mutagenicities:

The TSP collected from the sampler were extracted by ultrasonic wave with the solvent benzene. And mutagenicities of the extracts were measured by Ames test (Table 6)

TABLE 6 Mutagenicities of emissions from UG-35/39M type boilers

\	Coal	Raw coal				Coal briquettes			
		D F	F D	V S	tatol	D F	F D	V S	tatol
strains		(Rev/Nm ³)				(Rev/Nm ³)			
TA98		2584	5015	4384	11983	783	4958	936	6676
TA100		643	644	1746	3033	278	1044	884	2206

Table 6 indicates that the mutagenicities of organic extracts emitted from coal briquettes are 25-40% lower than those from raw coal.

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Anthracene	AN (3)	79.5	9.40	0.82	0.37
Fluoranthene	FA (4)	48.1	16.8	31.9	34.9
Pyrene	PY (4)	12.5	20.8	4.30	3.74
Benz (a) anthracene*	BaA (4)	3.10	1.90	2.25	3.12
Benz (k) fluoranthene*	BkF (5)	0.48	0.52	0.11	0.06
Benzo (a) pyrene	BaP (5)	0.20	0.12	0.04	0.04
Dibenz (a, h) anthracene	DBA (5)	0.52	0.28	0.18	0.38
Benzo (ghi) perylene	BPE (6)	0.76	0.31	0.09	0.48
Coronene	COR (7)	0.61	0.06	0.06	0.06
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nitro-pyrene**	NO ₂ -PY (5)	0.31	1.85	NA	NA

*: the benz (a) anthracene = Benz (a) anthracene + Chrysene,
 the Benz (k) fluoranthene = benz (k) fluoranthene + Perylene
 **: microgram of nitro-pyrene per gram of TSP.
 NA = not analyzed for

TABLE 3 Inorganic elements emitted from coal-fired boilers

\ boilers		KZL-2-8 (2T/h)		UG-35/39M (35T/h)	
		raw coal (μ g/Nm ³)	coal-briq. (μ g/Nm ³)	raw coal (μ g/Nm ³)	coal-briq. (μ g/Nm ³)
Name \	(atomic weight) \				
Aluminium	(27)	89.3	70.9	8140	6530
Arsenic	(75)	25.5	34.4	32	86
Barium	(137)	6.0	1.4	744	71
Cadmium	(112)	41.8	96.5	1080	1380
Calcium	(40)	4.2	7.8	5	5
Chromium	(52)	31.3	45.0	237	67
Copper	(64)	142	142	144	72
Iron	(56)	676	668	4680	4040
Manganese	(55)	8.9	6.1	178	31
Nickel	(59)	24.2	37.5	85	69
Lead	(207)	608	443	372	286
Selenium	(79)	2.4	5.3	100	74
Silver	(108)	2.1	1.4	ND	ND
Zinc	(65)	887	1109	678	1290

Table 2 and 3 indicated some of PAHs and inorganic elements emitted from raw coal-fired boiler are higher than those from using coal briquettes, while others are lower. When the raw coal only were burned in the boilers, the emissions of some inorganic elements are large different, such as, Aluminium, Cadmium and Iron etc, it may be relative to the coal yield area.

3). The contribution of PAHs and inorganic elements emitted in stack:
 The stack gases were collected separately to give dustfall (5-20 μ m), floating dust (0.2-5 μ m) and the vaporform smoke (<0.2 μ m), PAHs and inorganic elements were emitted together with stack gases from boilers. Their contribution in it will show table 4 and 5.

TABLE 4 The contribution of PAHs emitted from UG-35/39M type boilers

\ Coal		Raw coal			Coal briquettes		
		D F (%)	F D (%)	V S (%)	D F (%)	F D (%)	V S* (%)
Name \	(number rings) \						
Naphthalene	(2)	14.5	10.8	74.7	5.4	12.5	82.1
Biphenyl	(2)	10.3	9.7	80.0	9.2	1.8	89.0
Fluorene	(3)	2.7	4.6	92.8	0.5	5.1	94.5
Phenanthrene	(3)	4.9	3.4	91.8	2.5	2.7	94.8
Anthracene	(3)	3.2	9.2	87.6	3.5	13.8	82.7