Fuel 222 (2018) 250–257

Contents lists available at ScienceDirect

Fuel

journal homepage: www.elsevier.com/locate/fuel

Full Length Article

Mercury release characteristics during pyrolysis of eight bituminous coals

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ARTICLE INFO

Keywords:
Bituminous coal
Mercury release
Pyrolysis

ABSTRACT

The mercury release during pyrolysis of eight Chinese bituminous coals under N_2 at temperatures up to 1200 °C was studied. The pyrolysis experiment was carried out in a quartz reactor. Results show that higher than 93% of mercury release out during pyrolysis. The release of mercury from all the coals begins at about 150 °C with two or three mercury peaks at the similar temperature range. The correlation analysis shows that mercury in the coals has close relation with the mineral and the mercury released at different peaks is mainly correlated with different types of material in the coals. The first peak located at 150–400 °C is mainly correlated with carbonate mineral as well as organic material in the coals. The second peak located at 500–600 °C is mainly correlated with sulfide minerals in the coals. The third peak located at higher than 750 °C is mainly correlated with alumino-silicate mineral in the coals. A large part of mercury in coal can be removed by pyrolysis below 400 °C.

1. Introduction

Mercury is a toxic trace element in coal. The utilization of coal is the primary source of anthropogenic discharge of mercury. A large source of mercury emissions to the environment comes from coal-burning power plants. During the process of coal combustion, mercury in coal emit into atmosphere, which cause environmental and human health hazards because of its persistence, bioaccumulation and long-term contamination problems in the environment as well as serious effects on the neurological development of children. It is estimated that mercury emissions from power plants are responsible for about one-third of anthropogenic emissions [1]. Thus the emission control of mercury from coal-fired boilers has become a recent concern for the scientists and the extensive studies on removing of mercury from flue gas have been carried out [1–6].

Generally, it is more beneficial to remove the mercury in coal prior to coal combustion to protect environment. Therefore, some studies have been done about the precombustion removal of mercury from coal. Besides coal cleaning, pyrolysis of coal as a method has been carried out by some researches [6–9]. For example, Wang et al. reported that as much as 80% of the original mercury was removed by mild pyrolysis from bituminous coals [8]. Iwashita et al. studied varies types of coals and found that the removal efficiency of mercury greatly varied with coal type from 20 to 80% by mild pyrolysis [9]. Guo et al. found that more than 90% of mercury in coals could release out [10]. In summary, the work of removing mercury or mercury release behavior from coals during pyrolysis has been made some progress. However, the detailed information about the mercury release character during pyrolysis of coal is still limited, especially the correlation between the mercury release behavior and the modes of occurrence of mercury in coals. It is found that the release behavior of mercury from the coals shows a certain dependency upon coal rank and the mercury in different rank coal shows different release behavior [10]. Since bituminous coal is widely used in China, mercury release characteristics during pyrolysis of bituminous coal should be investigated intensively and deeply.

To gain information about mercury release characteristics, temperature programmed decomposition-atomic fluorescence spectroscopy (TPD-AFS) technique was used in this study to online monitor the mercury release behavior during pyrolysis of coal. This method have been proved effective in dynamic analysis of mercury release and identifying the mode of occurrence of mercury in previous work, which can provide detailed information on the mercury release during pyrolysis of coal [10,11]. In order to understand the common character of mercury release behavior during pyrolysis of bituminous coals as well as the correlation between the mercury release and the modes of occurrence of mercury in coals, eight bituminous coals produced in different areas in China have been used in this study.

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https://doi.org/10.1016/j.fuel.2018.02.134
Received 18 November 2017; Received in revised form 24 January 2018; Accepted 20 February 2018
Available online 23 March 2018
0016-2361/

Table 1
Proximate and ultimate analyses of coals, wt%.

Coal sample	Proximate analysis	Ultimate analysis, daf				
	V_{daf}	C	H	N	S	O^a
1#	31.0	82.6	5.0	0.9	2.4	9.1
2#	37.3	81.4	5.3	1.5	0.7	11.1
3#	37.5	73.9	5.7	1.5	0.6	18.3
4#	41.8	80.4	4.1	1.0	2.4	12.1
5#	44.9	81.2	5.3	1.3	3.9	8.3
6#	14.8	82.5	5.0	1.4	1.3	9.8
7#	34.6	78.8	4.6	1.6	0.7	14.3
8#	33.3	77.0	5.8	0.9	0.5	15.8

ar: as received; daf: dry and ash free; a: by difference.

2. Experimental setup

2.1. Coal sample

Eight bituminous coals produced in different areas in China have been used in this study. Proximate and ultimate analyses of the coals are shown in Table 1. The major mineral elements in the coals are shown in Table 2. The coal samples were crushed and sieved to 0.16–0.27 mm and dried before use.

2.2. Pyrolysis procedure

The TPD experiment was conducted in a fixed bed quartz tube reactor with a diameter of 20 mm, in which a quartz boat was located. The fixed-bed quartz tube reactor was directly connected to an AFS or several absorbing bottles according to the Ontario Hydro method to determine the Hg^{2+} from the tube reactor [12–14]. A thermocouple inserted into the coal sample was used to measure the temperature of the coal samples, and the data were recorded by a computer. 1 g of the coal sample was first charged into a quartz-made boat in the reactor, and than the remaining air was replaced completely with the N_2. Finally the reactor which consists of the quartz tube and the boat containing coal sample was heated from room temperature to 1200 °C at a heating rate of 20 °C/min in a stream of N_2 flow. The N_2 flow is 300 ml/min, which can swept the gas produced during pyrolysis of coal to the AFS. The intensity of mercury in the gas was recorded continually by AFS detector. At the final temperature of 1200 °C, the boat containing the coal-derived char was moved quickly to the cold end of the tube and allowed to cool with the flow of N_2. The weight loss of coal was recorded during the period of coal pyrolysis. The mercury content in the coal-derived char was analyzed. The mercury release experiments had been repeated at least twice for each coal sample and the results showed a good repeatability.

In order to determine the contents of mercury in the coal and the char, the coal or the char should be digested with an oxidizing mixture of acids in a Teflon digestion vessel [11]. And then the vessel was transferred into a microwave oven. After that, the Hg^{2+} in the digested samples from the microwave oven was reduced to Hg^0 by the addition of KBH_4. Finally the Hg^0 is determined by the atomic fluorescence technique.

To clearly show the result of the mercury release, release ratio of mercury (HgRR), release ratio of elemental mercury (Hg^0 RR) and release ratio of oxidation mercury (Hg^{2+}RR) are used to illustrate the quantity of total mercury, Hg^0 and Hg^{2+} released from coal pyrolysis and defined as the percentage ratio of total mercury released, Hg^0 released and Hg^{2+} released to the total mercury content in the coals. The volatile yield (VY) stands for the percentage of volatile matters released and is defined as the ratio of the mass of the volatile matters to the mass of the raw coals [9,15,16].

Table 2
Major mineral elements in the coals.[a]

Coal sample	Ash analysis/(g/100 g coal)									
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	TiO_2	SO_3	K_2O	Na_2O	P_2O_5
1#	1.94	1.52	0.77	1.23	0.15	0.18	0.18	0.33	0.15	0.12
2#	10.1	9.00	1.72	1.89	0.63	0.56	0.22	0.14	0.04	0.08
3#	11.1	13.61	3.99	1.34	0.34	0.41	0.64	0.16	0.15	0.05
4#	7.51	3.94	3.06	1.21	1.40	0.43	1.71	0.67	0.43	0.12
5#	5.94	2.62	3.74	1.34	0.47	0.18	3.43	0.17	0.23	0.05
6#	11.29	0.62	0.79	0.35	0.20	0.32	0.36	0.12	0.26	0.08
7#	0.66	0.29	2.74	0.55	0.43	0.12	0.61	0.19	0.27	0.02
8#	0.39	5.6	0.66	0.26	0.21	0.12	0.13	0.15	0.08	0.06

[a] Dry basis.

3. Results and discussion

3.1. Release ratio of mercury during pyrolysis of coals

As stated previously, coal samples were subjected to pyrolysis from room temperature to 1200 °C at the heating rate of 20 °C/min. At final temperature, the coal-derived char were produced and analyzed. The HgRR for each coal as well as the VY of each coal is shown in Table 3. It can be clearly seen that the HgRR for each coal is higher than 93% while the VY for each coal is less than 37%. It means that mercury in each coal has high release ability to volatile phase, which well agree with some other reports [17,18].

It is generally accepted that the mercury released may be as elemental mercury (Hg^0) or in the oxidation state (Hg^{2+}) during combustion [16,19–22]. It is reported that the mercury released also is in the form of Hg^0 or in the Hg^{2+} during pyrolysis of coal [23]. To investigate the forms of mercury released during pyrolysis of the eight bituminous coals, the measurement of the amount of Hg^0 released were made following the TPD-AFS profile as reported in previous paper [10,11]. And Hg^{2+} released were measured following the Ontario Hydro method in which the several absorbing bottles were used to adsorb the Hg^{2+} released and then it was determined by AFS [11,12,16,24,25]. The experiment results (Table 3) show that the amount of Hg^{2+} released are much less than that of Hg^0 released for the eight coals during pyrolysis. For example, the Hg^{2+} RR for 1# coal and 2# coal are 4.1% and 5.2%, respectively. However, the Hg^0 RR released is 93.1% for 1# coal and 92.3% for 2# coal. Therefore, it can be concluded that the Hg^0 is the dominant form of mercury released, and thus more attention should be paid on the Hg^0 release during pyrolysis of the eight coals.

It should be noted that the mercury content in the eight bituminous coal samples varies with coal samples and ranges from 56 to 316 ng/g coal. Among the eight samples, 3# coal sample contains the highest mercury content while 7# coal sample contains the lowest mercury content. However, there is no obvious difference between 3# and 7# coal on the proximate and ultimate analyses of coals. Actually, all the eight coals have no significant difference on the proximate and ultimate

Table 3
Basis dates of experiments.

Coal sample	Hg_{ad}, ng/g	VY, %	HgRR, %	Hg^0 RR, %	Hg^{2+}RR, %
1#	184	27.7	95.8	93.1	4.1
2#	221	30.3	94.5	92.3	5.2
3#	316	27.9	98.8	94.2	3.0
4#	129	30.8	94.1	91.8	4.7
5#	201	36.8	94.6	93.1	3.1
6#	135	28.4	95.8	92.5	5.7
7#	56	27.1	93.5	90.3	7.3
8#	72	33.0	94.1	91.1	6.4

ad: air dry.