Available online at www.sciencedirect.com
SCIENCE DIRECT®
Fuel 84 (2005) 1874–1878
FUEL
www.fuelfirst.com

The volatilization behavior of chlorine in coal during its pyrolysis and CO_2-gasification in a fluidized bed reactor

Wen Li*, Hailiang Lu, Haokan Chen, Baoqing Li

State Key Laboratory of Coal Conversion, Institute of Coal Chemistry, Chinese Academy of Sciences, Taiyuan 030001, People's Republic of China

Received 15 October 2004; received in revised form 14 March 2005; accepted 15 March 2005
Available online 21 April 2005

Abstract

The volatilization behavior of chlorine in three Chinese bituminous coals during pyrolysis and CO_2-gasification in a fluidized bed reactor was investigated. The modes of occurrence of chlorine in raw coals and their char samples were determined using sequential chemical extraction method. The Cl volatility increases with increasing temperature. Below 600 °C the Cl volatility is different, depending on the coal type and the occurrence mode of Cl. Above 700 °C, the Cl volatilities for the three coals tested are all higher than 80%. About 41% of the chlorine in Lu-an coal and 73% of that in Yanzhou coal are organic forms, and most of them are covalently-bonded organic chlorine, which shows high volatile behavior even at low pyrolysis temperatures (below 500 °C), while the inorganic forms of chlorine in two coal samples are hardly volatilized even at low pyrolysis temperatures (below 400 °C). The restraining efficiency of addition of CaO on chlorine volatility is greatly dependent on pyrolysis temperature. The optimal restraining efficiency can be obtained at temperature range from 450 to 650 °C during pyrolysis of Lu-an coal. The volatile behavior of Cl is mainly dependent on temperature. Above 700 °C high volatility of Cl is obtained in both N_2 and CO_2 atmospheres.

Keywords: Coal; Chlorine; Mode of occurrence; Fluidized-bed reactor; Volatility; Pyrolysis; Gasification

1. Introduction

It is well known that there are many kinds of harmful trace elements in coal, which can cause environmental and technological problems during coal utilization. Chlorine is one of the harmful trace elements easily volatilized. A large amount of chloride is present in the gas phase in coal utilization process. Clean air legislation in many countries imposes emission limits on chlorine due to its environmental impact. Meanwhile, high concentration of chlorine in coal can create corrosion and deposition damage in equipment, which leads to a huge cost for solving the technological problems. Information about the modes of occurrence of chlorine in coal and its volatile behavior is important when measures are adopted to control the emission of chlorine during coal conversion. Because of the restriction of determination method and coal complexity, general agreement has not been reached about the modes of occurrence of chlorine in coal. Several forms of chlorine in coal have been reported, such as covalently-bonded Cl, the Cl bound to organic cations in ion exchangeable form, and the Cl ions present in inorganic salts or in water within micropores of coal [1–4]. Literatures show that chlorine is mainly released as hydrogen chloride during heat-treatment of coal in an inert atmosphere or under combustion conditions [5,6]. However, the modes of occurrence of chlorine are much different from coal to coal. Most previous work [5,7–9] about the behavior of chlorine in coal during pyrolysis was performed in a fixed-bed reactor, i.e. in a programmed heating system. The volatilization behavior of chlorine in coal during fluidized bed pyrolysis, moreover, and in gasification is not clear. The purpose of this work is to examine the volatilization behavior of chlorine in coal during fluidized-bed pyrolysis and gasification, and to identify the modes of occurrence of chlorine in coal. In addition, the restraining efficiency of the added CaO on chlorine volatility was studied.

* Corresponding author. Tel.: +86 351 4044335; fax: +86 351 4050320.
E-mail address: liwen@sxicc.ac.an (W. Li).

0016-2361/$ - see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.fuel.2005.03.017

2. Experimental

2.1. Coal samples

Three Chinese coal samples, Lu-an, Pingshuo and Yanzhou, were used in the experiments. They are selected because the chlorine content in them is high and the volatile matter content is different. The chlorine contents of Lu-an, Pingshou and Yanzhou coal are 369, 347 and 434 μg g^{-1} on a dry basis, respectively. And the volatile matter content (daf basis) is 15.85, 45.23 and 39.19%, respectively. The coal samples were crushed and sieved to 147–246 μm for use. The coal property is given in Table 1.

2.2. Pyrolysis and gasification tests

Pyrolysis tests were performed in a quartz tube fluidized-bed reactor (length of 600 mm and inner diameter of 25 mm) under nitrogen at temperatures ranging from 300 to 900 °C for Lu-an and Pingshuo coal, and from 300 to 600 °C for Yanzhou coal. There is a porous quartz disk located at 360 mm from the top of the reactor to support the coal samples and as a gas distributor. At a predetermined temperature, about 3.0 g coal sample was quickly placed into the quartz tube reactor. The nitrogen flow was 500–1000 ml/min corresponding to the different temperatures. After duration for 30 min, the char sample was cooled down to room temperature by removing the quartz tube reactor from the tube furnace. The chars were collected, weighted and analyzed. To clarify the restraining efficiency of addition of calcium-based mineral matter on chlorine volatility, CaO was added in several runs during Lu-an pyrolysis with the molar ratio of Ca/S equal to 2.8. Gasification tests were carried out under CO_2 atmosphere (300 ml/min) at temperature range from 800 to 950 °C. The other conditions are same as those in pyrolysis tests.

2.3. Sequential chemical extraction

It is difficult to determine the species of chlorine in coal directly, and no reliable analytical methodology has been generally accepted. The modes of occurrence of chlorine in Lu-an and Yanzhou coal and their pyrolysis chars were roughly determined by sequential chemical extraction method suggested by Cox et al [1]. Several associated forms of chlorine were separated in the following order: (1) water soluble inorganic chlorine: first the samples were dissolved into deionized water and stirred for 3 h, and then further extracted by dimethyl sulphoxide (DMSO) for 1 h; (2) chlorine bound to organic cations: the samples was extracted by 0.1 M KNO_3 in 100% DMSO; (3) covalently-bonded organic chlorine: obtained by difference. The amount of chlorine from (2) and (3) is the whole organic chlorine in the sample.

Table 1
Proximate and ultimate analysis of coal samples

Sample	Proximate analysis (wt%)			Ultimate analysis (wt%, daf)				
	M_{ad}	A_d	V_{daf}	C	N	H	S	O[a]
Lu-an	0.87	12.94	15.85	88.27	1.23	3.93	0.15	6.42
Yanzhou	2.31	9.99	45.23	78.28	1.14	5.04	2.66	12.88
Pingshuo	4.80	19.88	39.19	78.76	1.46	5.39	0.49	13.90

[a] By difference.

2.4. Determination of chlorine and its volatility

Chlorine contents in coal and char were determined by combustion-hydrolysis/potential titration method based on Chinese standard method (GB/T 3558-1996). The basic theory of this method is as follows: the sample (coal or char) is combusted and hydrolysed in a mixed stream of oxygen and steam during which chlorine in the sample is converted into chloride and dissolved quantitatively in water; the chlorine contents in condensate were determined by potential titration with silver nitrate. A standard sample with chlorine content of 570 μg g^{-1} was used to analyze the precision of the present method using which 565 ± 10 μg g^{-1} was obtained. This indicates that the combustion–hydrolysis/potential titration method is effective and exact in determining the chlorine content in the samples.

Chlorine volatility during coal pyrolysis and gasification was calculated by the following equation:

$$V\% = \left(1 - \frac{C_{1,d} m_{1,d}}{C_{0,d} m_{0,d}}\right) 100 \left(1 - \frac{C_{1,d} Y}{C_{0,d}}\right) 100 \qquad (1)$$

where V is the volatility of chlorine, %; $C_{1,d}$, the content of the chlorine in char, (g g^{-1}; $C_{0,d}$, the content of chlorine in coal, (g g^{-1}; $m_{1,d}$, the mass of char, g; $m_{0,d}$, the mass of coal, g; and Y, the yield of char, %. The difference of chlorine volatility with and without CaO addition is defined as the restraining efficiency.

3. Results and discussion

3.1. Chlorine volatility during pyrolysis

3.1.1. Effect of temperature

Figs. 1 and 2 show the effect of temperature on chlorine contents in char and its volatility during pyrolysis. With increasing temperature, chlorine contents in the chars decrease greatly, which indicates that a large amount of chlorine has volatilized. As shown in Fig. 2, chlorine volatility increases from 4 to 89% for Lu-an coal and from 25 to 82% for Pingshuo coal when raising temperature from 300 to 900 °C; that of Yanzhou coal increases from 14% at 300 °C to 80% at 600 °C. This clearly shows that chlorine volatility of Yanzhou is obviously higher than that of Lu-an and Pingshuo in the temperature range from 300 to 600 °C,