Fuel 215 (2018) 446–453

Contents lists available at ScienceDirect

Fuel

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

Full Length Article

Effects of atmospheres on sulfur release and its transformation behavior during coal thermolysis

Nuannuan Yang[a], Huiqing Guo[a,b], Fenrong Liu[a,*], Hao Zhang[a], Yongfeng Hu[c,*], Ruisheng Hu[a]

[a] College of Chemistry and Chemical Engineering, Inner Mongolia University, Hohhot 010021, China
[b] College of Pharmaceutical Science, Inner Mongolia Medical University, Hohhot 010110, China
[c] Canadian Light Source, Saskatoon, SK S7N 2V3, Canada

ARTICLE INFO

Keywords:
Sulfur release
Sulfur transformation
Py-GC
XANES
Coal thermolysis

ABSTRACT

In this study, Pinshuo (PS) coal with high organic sulfur content was selected to investigate the effects of atmospheres on sulfur release and its transformation during thermolysis. Pyrolysis connected with gas chromatography (Py-GC) was used to analyze the sulfur containing gases of H_2S, COS and SO_2. Sulfur K-edge XANES was carried out to study the sulfur transformation after thermolysis. For PS raw, deashed and depyrited coals, the order of effect of atmospheres on sulfur removal is 3% O_2-Ar > CO_2 > 85% CO_2-Ar > 75% CO_2-Ar > Ar. The trends about the effects of 3% O_2-Ar atmosphere on sulfur removal and char yield are similar to CO_2 atmosphere, but desulfurization rate is slightly higher under 3% O_2-Ar atmosphere than that under CO_2 atmosphere, while the char yield is much lower under 3% O_2-Ar than that under CO_2. This indicates that CO_2 atmosphere is a moderate atmosphere for sulfur removal. SO_2 release concentration, its maximum peak temperature and its release amount is the highest under 3% O_2-Ar atmosphere. Meanwhile, most of sulfurs in the gas phase is SO_2 under 3% O_2-Ar atmosphere and H_2S under 85% CO_2-Ar, 75% CO_2-Ar and Ar. However, H_2S, COS and SO_2 are all relatively high under pure CO_2 atmosphere. Based on the analysis of sulfur K-edge XANES, more thiophenes are easily gathered in the chars after thermolysis under those atmospheres. Thiophenes peak in the char under 3% O_2 - Ar atmosphere are lower than other atmospheres, which indicates some stable thiophenes are relatively easier to decompose under this atmosphere. This is also in agreement with the higher sulfur removal under 3% O_2 - Ar atmosphere. According to the similar XANES spectra of thiophenes, the effects of those three CO_2 atmospheres on sulfur transformation in the chars are almost the same, but desulfurization rate is the highest under pure CO_2 atmosphere.

1. Introduction

Coal, as the primary energy, has been playing an important role in economic development in China. Middle low sulfur coal and middle sulfur coal are proximate about 33% total coal reserves, most of which is also directly combusted in China. In recent years, the haze occurs in many areas of China, and one of the major causes is SO_x and NO_x released from direct combustion of coal [1,2]. Therefore, the rational and efficient use of coal resources to reduce the release of sulfur and nitrogen and other toxic atoms during coal utilization remains to be an important research topic [3,4].

Pyrolysis is an important intermediate stage of many coal conversion processes, such as coking, gasification and liquefaction. During coal pyrolysis, most of organic sulfur and inorganic sulfur can be removed with a part of sulfur escaping into the gas phase in the form of H_2S, SO_2 and COS [5–10]. Thus, pyrolysis could be an effective method for sulfur removal with optimized pyrolysis conditions. There are many factors affecting pyrolysis process, such as coal ranks, minerals and atmospheres. In this study, effects of the atmospheres on sulfur removal, releasing and transformation behaviors will be investigated. In an inert atmosphere, desulfurization rate is very low, as only unstable organic sulfur and pyrite can be removed. In addition, FeS_2 is only converted to FeS and FeS decomposition requires much higher temperatures. Sometimes, only a small amount of organic sulfur can be removed during rapid pyrolysis desulfurization in N_2 atmosphere [11]. Compared with inert atmosphere, CO_2 atmosphere is favorable for H_2S, COS and SO_2 releasing into gas phase as the temperature of the maximum evolution curves of those gases decreases drastically [12,13]. Carbon dioxide atmosphere is more effective on the organic sulfur removal at high temperature, as the thermal transfer coefficient of CO_2 is greater than that of N_2 [14]. Under low oxygen content atmosphere, when the temperature is higher than 400 °C, the C—S bond in organic

* Corresponding authors.
E-mail addresses: fenrongl@163.com (F. Liu), Yongfeng.Hu@lightsource.ca (Y. Hu).

https://doi.org/10.1016/j.fuel.2017.11.099
Received 25 September 2017; Received in revised form 20 November 2017; Accepted 24 November 2017

sulfur bases can react with oxygen to produce SO_2, so the amount of SO_2 is higher than that under Ar atmosphere [15].

Most of the above literatures only investigated the sulfur release and transformation behaviors by GC or by MS, or the sulfur forms in the char determined only by classic methods. Thus, sulfur in coal can only be broadly divided into pyrite (FeS_2), sulfate and organic sulfur. X-ray absorption spectroscopy (XAS) is a synchrotron radiation based technique that is elementally and chemically sensitive to the absorbing sites. It has been shown to be a powerful method for the direct, non-destructive and quantitative determination of all major sulfur forms in coal, including pyrite, ferrous sulfide, mercaptans, thioethers, disulfides, thiophenes sulfones, sulfoxides and sulfate [8]. A few reports have used sulfur K-edge XANES to study sulfur transformation under inert atmosphere during pyrolysis [16–18]. In this study, sulfur release and transformation behavior of PS raw, deashed and depyrited coals will be revealed by Py-GC combined with sulfur K-edge XANES under pure Ar, pure CO_2, 85% CO_2-Ar, 75% CO_2-Ar and 3% O_2-Ar atmospheres. Thus, a thorough understanding of sulfur release and transformation behavior can be obtained under different atmospheres. This can provide theoretical basis for clean and efficient use of coal by thermolysis combined with pre-desulfurization.

2. Experimental

2.1. Sample

In this study, Pingshuo (PS) coal (containing higher organic sulfur) was selected, crushed and sieved to a particle size range of 0.154–0.258 mm. Its deashed coal and depyrited coal were obtained by HCl - HF - HCl method [19] and Accolla introduction [20], respectively. FTIR spectra of PS raw, deashed and depyrited coals are shown in Fig. 1, and it is clear that the deashing process has no significant effect on the organic matrix of coal. But the process can affect the inorganic part, like the Si—O—Si or Si—O—C bonds at 1023 cm^{-1} and dissociation - OH at 3684 cm^{-1}. The proximate and ultimate analyses of PS raw, deashed, depyrited coal samples are shown in Table 1. Sulfur forms analyses of those samples are shown in Table 2, where it can be clearly seen that the organic sulfur content is 89.72% together with very little pyrite. The ash composition analyses of PS raw coal are shown in Table 3.

2.2. Py-GC equipment

Thermolysis experiments [12,21] were carried out in a quartz tube fixed bed reactor (I. D. 35 mm, length 60 cm). About 1.0 g sample was

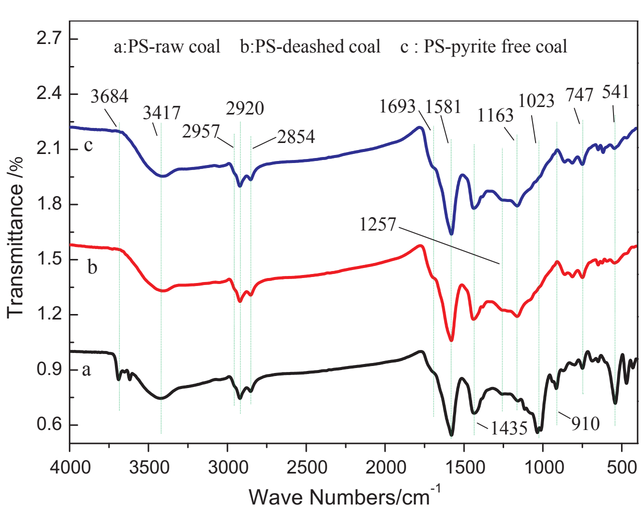

Fig. 1. FTIR spectra of PS raw, deashed and depyrited coals.

pyrolyzed under pure Ar, pure CO_2, 85% CO_2-Ar, 75% CO_2-Ar and 3% O_2-Ar atmospheres at the temperature range from room temperature to 900 °C at a flow rate of 300 mL/min and a heating rate of 10 °C/min. H_2S, COS and SO_2 concentration (ppm) were analyzed by gas chromatography (SP-7800) with flame photometric detector (GC -FPD, SP - 7800) every 50 °C, off-line. The column and detector temperatures were 80 °C and 250 °C, respectively. After thermolysis, quick cooling and collection of char, the sulfur content of raw coal and its chars was determined by XK - 5000 microcomputer - sulfur - analyzer.

2.3. Calculating methods

The char yield (Y) was obtained according to the following equation:

$$Y = \frac{m_{char}}{m_{coal}} \times 100\% \tag{1}$$

where m_{char} is the weight of char after thermolysis; and m_{coal} is the weight of raw sample.

The desulfurization rate (DR) can be obtained according to the equation:

$$DR = \frac{C_{s,coal} - YC_{s,char}}{C_{s,coal}} \times 100\% \tag{2}$$

where $C_{s,\ coal}$ and $C_{s,\ char}$ are the sulfur content in the raw coal and the char, respectively, Y is char yield. According to Eqs. (1) and (2), desulfurization rates and char yields are listed in Table 4.

The sulfur ratio in the gas phase can be obtained according to gas chromatography results. For example, the sulfur ratio in the form of H_2S (

R_{S,H_2S}

) was obtained according to the Eq. [21]:

$$R_{S,H_2S} = \frac{V \times A_{H_2S}}{R \times 22.4 \times 10^6} \times \frac{M_s}{W_s} \tag{3}$$

where R is the heating rate 10 °C/min, V is the flow rate of 0.3 L/min, M_S is the atomic weight of sulfur (unit: g/mol), W_S is sulfur weight of in the raw, deashed and depyrited coal (unit: g), and

A_{H_2S}

is integrated area of H_2S (unit: $\frac{mL}{mL}$·°C). Similarly, $R_{S,\ COS}$ and $R_{S,\ SO2}$ can be calculated using Eq. (3). For example, Fig. 2 presents H_2S release concentration (ppm) of PS raw, de-ashed and depyrited coals during thermolysis under different atmospheres. Sulfur release content (ppm), A_{H2S} for H_2S, was then obtained by integrating over the temperature range. The integrated areas A_{COS} and A_{SO2} of COS and SO_2 can be obtained by the same procedure. The sulfur weight of different sulfur-containing gases is shown in Table 5.

The total sulfur rate (S_{gas}) in the gas phase is the sum of sulfur ratio in the forms of H_2S, COS and SO_2.The equation is:

$$S_{gas}(\%) = R_{S,H_2S}(\%) + R_{S,COS}(\%) + R_{S,SO_2}(\%) \tag{4}$$

The sulfur present in the char (S_{char}) was obtained by the equation:

$$S_{char}(\%) = 100\% - DR(\%) \tag{5}$$

The sulfur present in the tar (S_{tar}) was obtained by the following equation:

$$S_{tar}(\%) = 100(\%) - S_{gas}(\%) - S_{char}(\%) \tag{6}$$

2.4. FTIR spectra analysis

The FTIR spectra of samples were measured by BRUKER VERTEX 70 FT-IR spectrophotometer. The coal samples were placed in a vacuum oven at the temperature of 60 °C for 7 h before analysis, in order to