Fuel 165 (2016) 484–489

Contents lists available at ScienceDirect

Fuel

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

Effects of CO_2 on sulfur removal and its release behavior during coal pyrolysis

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ARTICLE INFO

Article history:
Received 11 April 2015
Received in revised form 11 October 2015
Accepted 14 October 2015
Available online 23 October 2015

Keywords:
Sulfur removal
Sulfur release
Coal pyrolysis
CO_2 atmosphere
Py-MS
Py-GC

ABSTRACT

In this study, two Chinese coals, Jiexiu (JX) and Yanzhou (YZ) raw coals, their deashed coals and depyrited coals, were used to investigate the effects of CO_2 on sulfur removal and its release behavior during coal pyrolysis by pyrolysis with mass spectrometer (Py-MS) and pyrolysis connected with gas chromatogram (Py-GC). It is found that the sulfur removal ratio of YZ and JX coals under CO_2 atmosphere is higher than that under Ar atmosphere. Most sulfur removal of JX coal is distributed in tar under Ar atmosphere, while it is distributed in gas phase under CO_2 atmosphere. The CO_2 atmosphere is very beneficial to H_2S, COS and SO_2 release into gas phase. That is the maximum evolution peak temperature of H_2S and SO_2 decreases, and their evolution amount all increase remarkably, especially for COS evolution. The COS evolution of each coal increases with temperature increasing after 850 °C under CO_2 atmosphere. This further validates COS formation is related to CO at higher temperatures, while it is unrelated to CO at lower temperatures.

1. Introduction

Coal, main energy and chemical raw materials, plays an important role in the energy structure of China. In recent years, there is an increasing demand for clean coals [1–3]. But large-quantity use of coal in China has caused great damage to the environment [4]. The SO_2 and CO_2 release from coal combustion has led to a series of air pollution related problems, such as acid rain and global warming [5,6]. Therefore, the clean coal utilization has become the urgent topic.

Sulfur in coal occurs in both inorganic and organic forms [7–9]. The inorganic sulfur is mostly pyrite and small amounts of sulfates. The organic sulfur is usually categorized as mercaptans, sulfones, aliphatic and aryl sulfides, sulfoxides, disulfides and thiophenes [6,10]. Pyrolysis is a frequent step in various conversion processes, and it is also a simple and effective way for rational utilization of coal and environmental protection [11]. During pyrolysis, both pyrite sulfur and partial organic sulfurs can be removed, a part of sulfurs goes into the gas phase in the form of H_2S, COS, SO_2, etc., which can be easily recovered [12]. During pyrolysis, sulfurs and minerals or sulfurs and organic matter can interact each other, the sulfur-containing gases also can react with char and retain in the char [13,14]. The interaction between organic matter and pyrite shows that the behavior of sulfur evolution during pyrolysis may be different in raw coal, deashed coal and pyrite-free coal [15,16]. Therefore, the behavior of sulfur evolution during pyrolysis should be discussed separately.

Previous studies have mainly paid attention to desulfurization under inert atmospheres and hydrogen atmosphere, however desulfurization under inert atmospheres during pyrolysis is very low, and hydro-desulfurization still needs higher cost [4,17,18]. Semra's study [15] shows that pyrolysis under CO_2 atmosphere has higher organic sulfur removal ratio at higher temperatures. Pyrolysis under CO_2 atmosphere can not only effectively improve desulfurization ratio, but reduce the release of CO_2.

Due to the very complex presence of sulfur forms in coal, the mechanism of sulfur release and its transformation behavior are still not very clear under CO_2 atmosphere, as well the effect of pyrite and mineral matter on them. In this study, the sulfur release and transformation behavior during pyrolysis of two Chinese raw coals, their deashed coals and pyrite-free coals were investigated by Py-MS and with Py-GC under Ar and CO_2. This can provide theoretical basis for comprehensive use of coal by pyrolysis connected with pre-desulfurization.

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http://dx.doi.org/10.1016/j.fuel.2015.10.047
0016-2361/

2. Experimental

2.1. Coal samples

Jiexiu (JX) and Yanzhou (YZ) raw coals, their deashed coals and pyrite-free coals were used in this study. Organic sulfur content of JX coal is the highest compared with its sulfate sulfur and pyrite, about 92.11%. Pyrite of YZ coal is higher than that in the JX coal, about 34.21%. The deashed coal and pyrite-free coal (thus depyrited dashed coal) were obtained according to the procedures described in literature [14], respectively. Their proximate and element analyses, sulfur forms and ash analyses are shown in Tables 1–3, respectively. The ratio of basic oxides to acid oxide is obtained according to the formula: $R_{B/A} = \frac{Al_2O_3+Fe_2O_3+CaO+MgO+TiO_2+K_2O+Na_2O}{SO_3+P_2O_5+SiO_2}$.

2.2. Py-MS equipment

Py-MS equipment can be seen elsewhere [19]. About 1.5 g coal sample was placed into a quartz tube fixed-bed reactor (i.d. 30 mm, length 610 mm) and heated from room temperature to 1000 °C at a heating rate of 10 °C/min in a continuous flow of pure Ar or pure CO_2 atmosphere at a flow rate of 300 mL/min. A mass spectrometer (QIC-20) was used to measure H_2S, COS, SO_2, CO, etc. online, about once every 1 min.

2.3. Py-GC equipment

Pyrolysis experiments were carried out in quartz tube fixed bed reactor (i.d. 35 mm, length 700 mm). About 1.0 g coal was pyrolyzed under pure Ar or pure CO_2 atmosphere at the temperature range from room temperature to 1000 °C at a flow rate of 180 mL/min at heating rate of 10 °C/min. H_2S, COS and SO_2 contents (ppm) were analyzed by gas chromatography (GC) with flame photometric detector (FPD) every 50 °C from 50 °C to 1000 °C, off-line (SP-7800). The column and detector temperatures were 80 °C and 250 °C, respectively. After pyrolysis, the sample was cooled and collected for further analyzing its weight and sulfur content. And the sulfur content in coal char was measured by automatic sulfur determination analyzer (XK-5000).

2.4. Calculating methods

The char yield (Y) was obtained according to the following formula: $Y = \frac{W_{char}}{W_{coal}} \times 100\%$, where W_{char} is the weight of char after pyrolysis and W_{coal} is the weight of raw sample. The desulfurization ratio (DR) can be obtained according to the formula: $DR\% = \frac{W_{s,coal} - W_{s,char} \times Y}{W_{s,coal}} \times 100\%$, where $W_{s,coal}$ and $W_{s,char}$ is the sulfur content in the raw coal and char, respectively [20], the desulfurization ratio and char yield are shown in Table 4.

The sulfur weight in the form of COS ($m_{s,COS}$) obtained according to the formula: $m_{s,COS} = \frac{V \times A_{COS}}{R \times 22.4 \times 10^6} \times M_s$, where R is the heating rate 10 °C/min, V is the flow rate of 180 mL/min, M_s is the atomic weight of sulfur, and A_{COS} is integrated area of COS. And m_{S,H_2S} and m_{S,SO_2} can also be obtained according to the formula. For example, Fig. 1 shows the COS evolution content (ppm) of JX raw coal obtained by Py-GC under CO_2 atmosphere. After integration with temperature, the integrated area can be obtained from this figure as A_{COS}. A_{H_2S} for H_2S and A_{SO_2} for SO_2 can be also obtained accordingly. The sulfur weight in different form of sulfur-containing gases is shown in Table 6. The sulfur presence in the gas (S_{gas}) is the sum of the sulfur weight in the form of H_2S, COS and SO_2 to the one of sulfur in the raw coal, the formula is: $S_{gas}\% = \frac{m_{S,H_2S} + m_{S,COS} + m_{S,SO_2}}{W_{s,coal}} \times 100\%$; the sulfur presence in the char (S_{char}) was obtained by the formula: $S_{char}\% = 100\% - DR(\%)$; the sulfur presence in the tar (S_{tar}) was obtained by the following formula: $S_{tar}\% = 100\% - S_{gas}\% - S_{char}\%$.

Table 2
Sulfur forms analysis of coal samples.

Sample	Sulfur forms in coal (wt%)				Sulfur form ratio in total S (%)		
	$S_{t,ad}$	$S_{s,ad}$	$S_{p,ad}$	$S_{o,ad}$[a]	S_s	S_p	S_o[a]
YZ raw coal	3.04	0.08	1.04	1.92	2.63	34.21	63.16
YZ deashed	2.48	0.06	0.69	1.73	2.42	27.82	69.76
YZ pyrite-free	1.67	0.04	0.02	1.61	2.40	1.20	96.40
JX raw coal	2.28	0.07	0.11	2.10	3.07	4.82	92.11
JX deashed	2.27	0.04	0.21	2.02	1.76	9.25	88.99
JX pyrite-free	2.19	0.03	0.03	2.13	1.37	1.37	97.26

Note: S_t is the total sulfur; S_s is the sulfate sulfur; S_p is the pyrite sulfur; S_o is the organic sulfur.
[a] By difference.

3. Results and discussion

3.1. Effects of CO_2 on sulfur removal during pyrolysis

Table 4 shows the desulfurization ratio of different coals and their char yield during pyrolysis under Ar and CO_2 atmospheres. Generally speaking, under Ar atmosphere sulfur removal ratio is related to the volatile content and the stability of organic sulfur in the coal. That is the higher the volatile content is, and the less stable the organic sulfur is, thus the higher sulfur removal ratio is. Under Ar atmosphere, for those two raw coals, the sulfur removal ratio is YZ > JX. This order is very consistent with the volatile content shown in Table 1. This indicates, for JX coal, the organic sulfur is very stable, which can hardly decompose during pyrolysis. For YZ coal with higher pyrite, the desulfurization ratio is deashed coal > depyrited coal > raw coal, this suggests that the deashed treatment and depyrited treatment is helpful for sulfur removal. The reason may be that heat transfer and mass transfer can increase sharply for their deashed and depyrited coals during pyrolysis. This may be also caused by the basic mineral of raw coals

Table 1
Proximate and ultimate analyses of coal samples (wt%).

Sample	Proximate analyses				Ultimate analyses				
	M_{ad}	A_{ad}	V_{daf}	FC_{daf}	C_{ad}	H_{ad}	O_{ad}[a]	N_{ad}	S_{ad}
YZ raw coal	3.19	12.09	42.85	57.15	67.03	4.63	7.98	1.32	3.76
YZ deashed	3.40	2.02	38.92	61.08	73.80	4.83	11.96	1.51	2.48
YZ pyrite-free	3.55	0.93	39.71	60.29	75.05	4.94	12.33	1.53	1.67
JX raw coal	0.55	10.25	20.75	79.25	76.52	4.04	5.04	1.32	2.28
JX deashed	0.90	0.33	19.82	80.18	84.39	4.33	6.34	1.44	2.27
JX pyrite-free	0.99	0.15	20.39	9.61	84.26	4.35	6.64	1.42	2.19

Note: ad is air-dried basis; daf is dried and ash-free basis.
[a] By difference.