EFFECT OF PYROLYSIS TEMPERATURE ON DESULFURIZATION PERFORMANCE OF HIGH ORGANIC SULFUR LOW RANK COAL

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Abstract

The sulfur in coal not only influences the coke quality but also pollutes the environment during the combustion. The desulfurization of high organic sulfur coal is a key issue in coal cleaning science. As the pyrolysis has been used in low rank coal conversion to obtain gas/liquid products and coal char, the desulfurization effects of pyrolysis on the low rank coal with high organic sulfur requires further studies. This study investigated the desulfurization performance of high organic sulfur low rank coal by the pyrolysis and the changes in the coal calorific value and sulfur forms during the pyrolysis. The XPS was applied to analyze the changing regulation of sulfur that forms on coal surface. The results indicated certain amount of FeS was newly created during the pyrolysis and high amounts of sulfate sulfur was transferred to pyrite sulfur and formed more FeS_2 when compared to the distribution of raw coal. The total sulfur content of coal was reduced from 2.32% for raw coal to 1.68% for 700 °C pyrolysis coal and then the pyrolysis temperature had little effect on the sulfur content. The net calorific value (at constant volume and air-dry basis) was increased from 17.38 kJ for raw coal to 24.35 kJ for 700 °C pyrolysis coal. The pyrolysis temperature of 700 °C may be the best pyrolysis temperature for both low sulfur content and high calorific value.

Key words: *Coal desulfurization; Pyrolysis; XPS; Calorific value; Sulphur content.*

1. Introduction

The desulphurization of coal is important for the environmental protection during the burning of coal for power generation [1 - 4]. As is known, the reserves of low rank coal are abundant around the world and majority of low rank coal is used for the power generation and gas/liquid chemical raw materials. Common coal desulfurization approaches are divided into three major types, i.e., desulfurization before utilization, sulphur-fixing during the burning, and desulfurization of flue gas [3, 5, 6]. Among these approaches, the desulphurization of coal before utilization is considered as more economic and effective [7].

Generally, gravity-based physical and flotation are used for coal desulfurization and deashing in coal preparation plants [8 – 11]. However, organic sulfur cannot be removed from coal because organic sulfur is usually bonded with coal organic materials. In laboratoral studies, organic sulfur can be partly removed from coal organic materials through chemical treatments, such as oxidation and leaching, as well as bio-desulfurization using bacterial [12 - 16]. However, these chemical- or bio-treatments cannot be well applied in industry.

In the past decades, a better utilization of low rank coal has reached an agreement that the pyrolysis treatment under lower temperature could transfer low rank coal into gaseous/liquidus chemical raw materials and coal char [17]. While gas/liquid chemical raw materials are used in chemical engineering, coal char is primarily forwarded to coal-based power generation plants for burning. The coal properties can be significantly changed during the pyrolysis. Among these changes, the sulfur forms in coal are also changed and requires in-depth studies [18 - 20]. The decomposition of organic sulfur begins with the formation of -SH radicals [21], which interact with some of the substances in the coal to produce H_2S, COS, CS_2, etc. In general, the decomposition temperature of aliphatic and aromatic thiols is about 200-300 °C, while the decomposition of fatty sulfur compounds occurs at 350-500 °C, and the

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decomposition temperature of aromatic sulfides are in the range of 700-800 °C. The decomposition temperature of thiophene compounds is usually higher than 900 °C [22, 23]. However, there is a gap in the investigation of the influence of pyrolysis on the changes of coal calorific value.

This paper aimed to study the feasibility of desulfurization of low rank coal with large organic sulfur fraction by the pyrolysis and the changes in the coal calorific value and sulfur forms during the pyrolysis. The XPS was applied to analyze the changing regulation of sulfur forms of coal surface to explain what reactions happened during the pyrolysis.

2.   Experimental material and procedure

2.1. Coal material

The coal sample was taken from Xinglinhaote of Inner Mongolia, China. Coal particles were firstly ground and then screened to 0.074 mm for subsequent use. The industrial analysis and sulfur existing form of this coal material were indicated in Table 1 [24]. The total content of sulfur on low rank coal was 2.32% and among it, the organic sulfur took up for 2.00%, suggesting that the organic sulfur was dominant in the total sulfur distribution.

Table 1 Industrial analysis and sulfur existing form of used coal samples [24]

Proximate analysis /%				Sulfur forms analysis /%			
Mad	*Ad*	*Vdaf*	*FCdaf*	$S(t,d)$	$S(p,d)$	$S(s,d)$	$S(o,d)$
14.79	13.21	65.19	34.81	2.32	0.07	0.25	2.00

Mad is the moisture of air-dry basis. *Ad* is the ash of the dry basis. *FCdaf* and *Vdaf:* fixed carbon and volatile matter contents of the dry-ash free basis. $S(t, d)$, $S(p, d)$, $S(s, d)$, and $S(o, d)$ are the total sulfur, pyrite sulfur, sulfate sulfur, and organic sulfur contents based a dry basis, respectively.

2.2. Linguistic variable

The pyrolysis treatment of low rank coal (about 24 g per treatment) was conducted in the tube furnace with purge gas of N_2 for the residence time of 1 hour. The experimental parameters were set as follows: the pyrolysis temperature was fixed at 400, 500, 600, 700, and 800 °C. The desulfurization performance was evaluated using the sulfur content and yield of the coal char.

The industrial analysis of low rank coal after pyrolysis of different temperatures is shown in Table 2. The moisture, fixed carbon, and volatile matter content of pyrolytic char decreased when heating treatment temperature increased while the ash content increased.

Table 2 Proximate analysis of low rank coal after pyrolysis of different temperatures

Coal samples	M_{ad}/%	A_d/%	V_{daf}/%	FC_{daf}/%
400 °C pyrolysis coal char	12.66	17.95	30.09	69.91
500 °C pyrolysis coal char	11.54	19.99	19.16	80.84
600 °C pyrolysis coal char	9.15	21.57	12.03	87.97
700 °C pyrolysis coal char	6.79	22.82	5.61	94.39
800 °C pyrolysis coal char	5.47	23.09	3.48	96.52

2.3. Sulfur content and calorific value measurements

Raw coal sample and pyrolytic coal char were then conducted to measure the sulfur content and calorific value employing the automatic coulomb sulfur analyzer and automatic calorimeter. Repeated tests were carried out to calculate the average sulfur content of samples to ensure the accuracy.

2.4. XPS tests

To obtain an insight observation of the sulfur existing forms variation on low rank coal surface before and after heating treatment, the XPS testing was used to quantify the chemical status. The XPS testing of raw low rank coal and pyrolysis coal were conducted under the ultra-high vacuum (UHV) system at room temperature by the surface analyzer (ESCALAB 250 Xi, USA). The raw data results were processed applying the software of XPS Peak. The binding energy should be corrected by fixing -CH$_2$-CH$_2$- bonding energy position at 284.8 eV. The S2p peaks of raw coal and pyrolysis coal were analyzed to see what have happened to the coal when pyrolyzing.

3.   Results and discussion

3.1. Effect of pyrolysis temperature on desulfurization performance

Figure 1 illustrates both the sulfur content and coal char yield reduced with higher heating temperature. The sulfur content of raw coal was 2.32%, however, it was

reduced to about 1.68% for the 700 °C pyrolysis coal char. The sulfur content of 800 °C pyrolysis coal char was similar to that of 700 °C pyrolysis coal char indicating the pyrolysis temperature over 700 °C had no significant effects on the coal char sulfur content. Therefore, the pyrolysis temperature of 700 °C was considered as an optimized temperature to release the sulfur of the low rank coal.
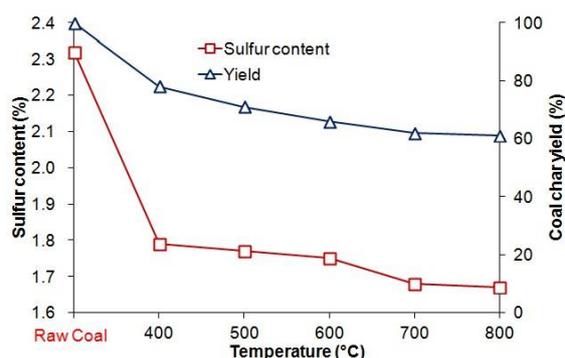
Figure 1 Changes in sulfur content and yield of coal with pyrolysis temperature

Chemical titration analysis was performed to investigate the sulfur existing forms of coal surfaces before and after pyrolysis treatment of 700 °C. Table 3 indicates that the organic sulfur content of coal decreased from 2.00% to 1.28% after the pyrolysis treatment under the 700 °C. The sulfate sulfur fraction of coal reduced from 0.25% to 0.05%, while the pyrite sulfur content of coal increased from 0.07% to 0.35% due to the migration of the sulfate sulfur to the pyrite sulfur among pyrolysis treatment [25 - 27]. The decomposition of organic sulfur occurred during the pyrolysis [22, 23], and the sulfur-containing gaseous/liquidus generated.

Table 3 Sulfur existing forms of raw coal and 700 °C pyrolysis-derived coal char

| Sample name	$S(t,d)$	$S(p,d)$	$S(s,d)$	$S(o,d)$
Raw coal	2.32	0.07	0.25	2.00
700 °C pyrolysis coal char	1.68	0.35	0.05	1.28

For the sake of revealing the changing mechanism of sulfur existing forms on the coal surface clearly, XPS was employed to confirm the sulfur existing forms of both raw coal and 700 °C pyrolysis-derived coal char. For the S2p peak fitting, the peaks near 161.2±0.2, 162.5±0.3, 163.5±0.3, 165.2±0.2, 167.0±0.2, 168.9,

170.5, and 172.2 eV bound to ferrous sulfide (FeS), ferrous disulfide (FeS_2), alkylsulphides + thiophenes + arylsulphides, sulphoxides, sulphones, and sulphates [28 - 30].

The peaks for sulphates were weakened from raw coal surface to pyrolysis coal surface while the signal strength of FeS and FeS_2 became stronger for the migration of the sulfate sulfur to the pyrite sulfur occurred when samples were pyrolyzed [25 - 27]. In addition, the area of peaks for alkylsulphides, thiophenes, arylsulphides, sulphoxides, and sulphones became smaller for pyrolysis coal surface compared with that for raw coal surface. This indicated that high amounts of organic sulfur decomposed during the pyrolysis and should be transferred into sulfur-containing gas/liquid compounds [22, 31, 32]. Thus, the sulfur composition, especially the organic fraction was significantly reduced by the pyrolysis.
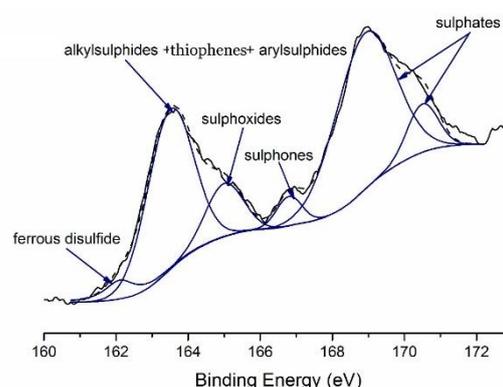
Figure 2 S2p peak fitting for raw coal surface
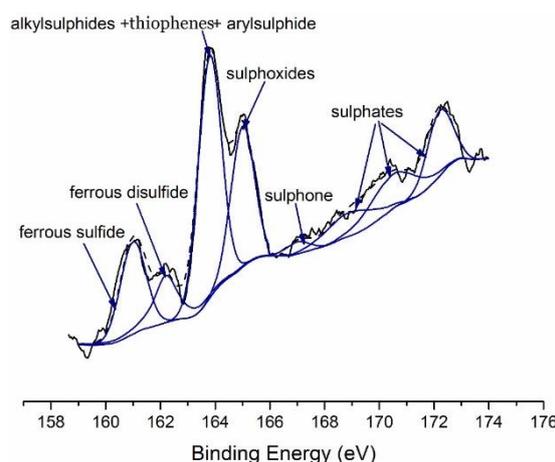
Figure 3 S2p peak fitting for 700 °C pyrolysis coal char surface

3.2. Effect of pyrolysis temperature on coal calorific value

Figure 4 shows that net calorific value (at constant volume and air dry basis) of coal increased when the heating treatment temperature rose. However, the coal calorific value did not change significantly when the heating treatment temperature raised from 700 to 800 °C. Therefore, the heating temperature of 700 °C proved to be the best temperature again related to the sulfur content changes in Figure 1.

Figure 4 also illustrates that the moisture content decreased with increasing temperature while the ash content increased. The coal char suffered from pyrolysis had lower ability to adsorb the moisture and hence had a low moisture content. Because the decomposition of organic materials from coal forming the gas/liquid compounds, the ash content significantly increased. The calorific value is usually influenced by both the ash content and moisture content. The higher moisture content needs more heating for the evaporation of moisture and hence it reduces the calorific value. For this low rank coal sample, the decrease in moisture content was more important than the increase in ash content with regard to the caloric value. Therefore, the caloric value of low rank coal sample significantly enhanced by the pyrolysis, as well as the coal desulfurization, can be achieved.
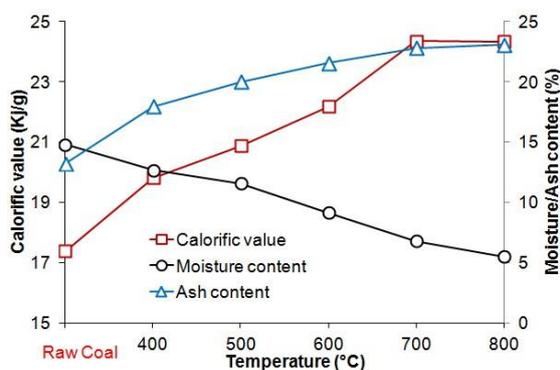

Figure 4 Changes in net calorific value of coal with pyrolysis temperature

4. Conclusion

Throughout this paper, the sulfur removal from low rank coal with high organic sulfur via the pyrolysis under low temperature was explored, and meanwhile the influence of pyrolysis treatment on the coal calorific value were investigated as well. The sulfur composition was cut down from 2.32% to 1.68% after pyrolysis of 700 °C, while the coal calorific value increased from 17.38 to 24.35 kJ/g. The optimized performance was acquired when the temperature reached 700 °C. Under this temperature, high amounts of organic sulfur decomposed and was transferred into sulfur-containing gas/liquid. The XPS results showed that the sulphates on coal surface could be transferred into FeS and FeS_2 as well as amounts of organic sulfur in coal surface, such as alkylsulphides, thiophenes, arylsulphides, sulphoxides, and sulphones were decomposed. The low temperature pyrolysis could reduce the sulfur composition of coal, also it promoted the calorific value of pyrolysis-derived char. Therefore, low temperature pyrolysis is suitable for the low rank coal conversion and better utilization.

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UTICAJ TEMPERATURE PIROLIZE NA STEPEN ODSUMPORAVANJA UGLJA NIŽEG RANGA SA VISOKIM SADRŽAJEM ORGANSKOG SUMPORA

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Izvod

Sumpor u uglju utiče ne samo na kvalitet koksa već i zagađuje životnu sredinu prilikom sagorevanja. Postupak odsumporavanja uglja sa visokim sadržajem organskog sumpora predstavlja ključno pitanje u nauci o čišćenje uglja. Kako se piroliza koristi u konverziji uglja niskog ranga za dobijanje gasnih/tečnih proizvoda i drvenog uglja, uticaj odsumporavanja prilikom pirolize uglja niskog ranga sa visokim sadržajem organskog sumpora zahteva dalja istraživanja. U ovom radu je ispitivan stepen odsumporavanja uglja niskog ranga sa visokim sadržajem sumpora, kao i promena kalorijske vrednosti uglja i oblika sumpora tokom pirolize. Za analizu promene regulacije sumpora koji nastaje na površini uglja primenjen je XPS. Rezultati su pokazali da je određena količina FeS nastala prilikom pirolize, a da su velike količine sulfatnog sumpora prešle u piritni sumpor i formirale više FeS2 u poređenju sa rovnim ugljem. Ukupan sadržaj sumpora u uglju je smanjen sa 2,32% za rovni ugalj na 1,68% za ugalj dobijen pirolizom na 700°C i tada je temperatura pirolize imala mali uticaj na sadržaj sumpora. Ukupna kalorična vrednost (pri konstantnoj zapremini i na suvom vazduhu) povećana je sa 17,38 kJ za rovni ugalj na 24,35 kJ za ugalj dobijen pirolizom na 700°C. Temperatura pirolize od 700°C se može smatrati najboljom temperaturom za ovaj postupak zbog niskog sadržaja sumpora i visoke toplotne vrednosti.

Ključne reči: *Odsumporavanje uglja; Piroliza; XPS; Kalorična vrednost; Sadržaj sumpora.*