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Transformation of nitrogen and sulphur impurities during hydrothermal upgrading of low quality coals

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ABSTRACT

The influence of hydrothermal upgrading on the configuration of nitrogen and sulphur species in coal was investigated in this paper. Hydrothermal modification of three typical Chinese lignite was performed at 200 °C, 250 °C and 300 °C. It was found that hydrothermal modification reduced the moisture content of coal and therefore increased the heating value. X-ray photoelectron spectroscopy (XPS) was used to analyze the speciation of nitrogen and sulphur in coal samples before and after the hydrothermal modification. XPS peak fitting analysis was performed by using the XPSPEAK points-peak software. Results showed that the hydrothermal treatment destroyed micro-structures and altered the functional groups of nitrogen and sulphur in coals. Nitrogen, which originally detected as a pyrollic peak (N-5), was converted to pyridic (N-6) or quaternary nitrogen (N-Q) species after the hydrothermal upgrading. Quaternary nitrogen associated with polycyclic aromatic hydrocarbon was converted to N-6 while N-Q molecules located at the coal edge transformed to nitrogen oxides (N-X). Sulphoxides, sulphones and sulphides were converted to thiophenes; alternatively, sulphides transformed to pyrite. These changes could result in a decrease in SO_2 emission. Furthermore, there may be the transformation form sulphoxide and sulphone to sulphonates. Organic sulphur, to some extent, transformed to inorganic sulphur during the hydrothermal process.

1. Introduction

Energy development in the last century has grown under the influence of two dominant factors. Universal demand for increased energy availability has pushed for ever greater production capacity. Constraining this is the desire to reduce the environmental impact of energy production. Among fuel sources currently used, coal always plays an important role in energy generation. However, the content of NO_x and SO_x precursors that are naturally occurring in the coal amalgam, affects the coal quality making its utilization problematic. Specifically, excessive combustion of high N- and S-containing coal generates high levels of NO_x and SO_2 emissions, which leads to acid rain and various adverse health effects. Unsurprisingly, the study of desulphurization and denitrogenation of coal is a significant topic for energy development. With the amount consumption of high quality coals, the reserves shortage and high price push the usage of low qualities coals like sub-bituminous and lignite become more and more important.

Due to the high moisture content of sub-bituminous and lignite, the low qualities coal's upgrade or dehydration treatment become essential for the amount usage. One method to upgrade lignite is dehydration and conversion by hydrothermal modification (also called hydrothermal upgrading, hydrothermal treatment). Hydrothermal upgrading for dehydration is a type of non-evaporative drying technology and has been applied in lignite utilization [1,2]. This treatment is usually performed in an airtight high-pressure reaction vessel where lignite and water are heated to the operative temperature. Water that is located in the lignite pore volume is removed by the compression force exerted on the coal particle by the high pressure steam. This treatment was initiated by Graff and Brandes [3] in 1987 to improve the yields of liquids. After the hydrothermal upgrading, the processed lignite has an increased carbon ratio, decreased moisture, an increased heating value and a higher rank than the raw lignite [4]. Favas and Jackson [5] reported that moisture in Australia lignite decreased by 72% and its quality improved to a large degree after hydrothermal treatment. A large amount of sodium was detected in the used process water, indicating that alkali metal reduction

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occurs simultaneously. According to Mursito [6], the final temperature of hydrothermal treatment had a great influence on the modification process.

In coal, sulphur and nitrogen conformation can be probed by various non-destructive analytical methods. Among these, a frequently used alternative is X-ray photoelectron spectroscopy XPS [7]. Kelemen [8] used XPS to investigate nitrogen migration during a coal pyrolysis process and found that pyrrolic (N-5) was the most common form of coal-N. Moreover, quaternary nitrogen (N-Q) content decreased and pyridinic nitrogen (N-6) content increased with coal rank. Pietrzak [9] used XPS to study activated carbon and found that the nitrogen introduced by the ammoxidation process mainly took the form of pyridic (N-6), pyrrolic (N-5), amides, amines and imines, no matter which processing stage at which it is applied.

However, up to now, a detailed investigation into the effect of hydrothermal modification on (i) the nitrogen and sulphur conformation and (ii) their conversion has not been found in the published works. Accordingly, the present work reports the hydrothermal modification effect on the conformation of nitrogen and sulphur of three Chinese lignite samples. The acquired results are to facilitate the large-scale utilization and upgrading of Chinese lignite in future.

2. Methodology

2.1. Coal sample preparation

The coal samples used here were three typical Chinese low-rank coals: Zhundong (ZD) coal from the Xinjiang province, Yimin (YM) lignite from Inner Mongolia, and Zhaotong (ZT) lignite produced in the Yunnan province. Zhundong sub-bituminous coal has a high alkali metal content. Zhaotong coal is a high moisture content young lignite. Yimin coal belongs to late Jurassic lignite. The properties of the three coal samples are listed in Table 1. ZD is a kind of low-ash coal, with an only 3.71% ash content. YM has a lowest sulphur content, which is 0.11%. The content of nitrogen in ZT is 1.21%, which is almost 3 times than that of ZD coal.

Each of three coal samples were ground and sieved with 8 mesh screen, prior to use in the hydrothermal upgrading experiment.

2.2. Hydrothermal modification method

A diagram of the hydrothermal upgrading system is shown in Fig. 1. The hydrothermal reaction vessel used in this paper is a high-temperature and high-pressure reaction chamber. For each coal type, 200 g raw coal sample and 500 ml of deionized water were placed in the hydrothermal reaction vessel, and stirred with a glass rod until blended. The reaction vessel was sealed and secured then pressurized with N_2 to 4 MPa. Hydrothermal upgrading was performed at three temperatures, i.e., 200 °C, 250 °C, and 300 °C, respectively. A heating rate of 3 °C/min was used in each situation. Once the target temperature was reached, the samples were kept for 1 h at the elevated temperature while being stirred at 100 r/min. The vessel was then allowed to cool to ambient temperature. The mixture in the vessel was filtered to separate the upgraded coal sample from the process water. The solid sample was dried and then ground and sieved with a 200 mesh screen. The proximate and ultimate analyses of coal samples after the hydrothermal modification are also listed in Table 1.

2.3. X-ray photoelectron spectroscopy (XPS) method

XPS was used to determine the conformation of nitrogen and sulphur in coal samples before and after the hydrothermal modification. In the XPS process, the sample is irradiated with X-rays, which excite inner electrons or valence electrons at the atomic or molecular level. The electron which is excited by the X-ray relaxes in a process that releases a photoelectron. If the binding energy is set as abscissa and intensity as ordinate, energy spectrum figures of the photoelectron can be obtained. These energy spectra include information on the various configurations of compounds in the sample. The XPS measurements in this study were carried out on a Kratos Axis Ultra DLD multifunctional electron spectrometer. The energy resolution was 0.68 eV/(C 1s) and the spatial resolution was less than 3 μm. Samples weighing 0.1 g of the raw coal and hydrothermally upgraded samples were analyzed. The step size was set as 0.1 eV, the internal standard calibration was set as 284.6 eV. The spectral features of the nitrogen 1s peak and sulphur 2p peak were used for analysis.

3. Results and discussion

3.1. Effect of hydrothermal modification on coal composition

Most notable in Table 1 is the effectiveness of the hydrothermal upgrading process in dehydrating the coal samples. Hydrothermal treatment at 300 °C decreases the originally high moisture of 15.38%, 15.99%, and 33.45% to clearly lower levels of 10.24%, 6.92%, and 6.59% for the ZD, YM, and ZT coal samples. In the temperature range from 200 to 300 °C, the amount of moisture lost through the hydrothermal process increased with the process temperature. During this process, water is removed from the coal irreversibly. As the micropores collapse, it is removed by expansion

Table 1
Proximate and ultimate analysis of coal samples.

Coal		Proximate analysis (wt%)				$Q_{net,ad}$	Ultimate analysis (wt%)				
		M_{ad}	A_d	V_d	FC_d	(J/g)	C_d	H_d	N_d	$S_{t,d}$	O_d
ZD	Raw coal	15.38	4.38	30.75	64.87	22,330	75.12	2.68	0.57	0.38	16.86
	200 °C	11.71	3.90	30.48	65.62	23,347	76.77	3.19	0.57	0.35	15.22
	250 °C	11.28	4.25	29.38	66.37	23,233	76.92	3.12	0.53	0.37	14.81
	300 °C	10.24	4.51	27.90	67.59	24,126	77.96	3.12	0.56	0.52	13.32
YM	Raw coal	15.99	14.03	34.33	51.63	19,597	64.89	3.57	0.81	0.13	16.57
	200 °C	10.17	14.67	33.30	52.03	20,354	64.61	3.53	0.85	0.14	16.20
	250 °C	9.30	14.58	32.24	53.19	21,503	66.12	3.58	0.77	0.13	14.82
	300 °C	6.92	15.20	30.11	54.68	22,717	67.14	3.59	0.73	0.13	13.21
ZT	Raw coal	33.45	25.85	47.15	27.00	9861	40.08	3.43	1.82	0.57	28.26
	200 °C	11.48	27.37	41.29	31.34	15,298	46.33	3.64	1.91	0.50	20.26
	250 °C	9.01	28.59	38.75	32.66	17,826	51.32	3.54	1.97	0.51	14.08
	300 °C	6.59	30.59	37.92	31.50	16,670	46.96	3.78	1.92	0.49	16.26

Note: M, moisture content; V, volatile matters; A, ash; FC, fixed carbon; Q_{net}, lower heating value; ad, on air-dried basis; d, on dry basis; S_t, total sulphur.