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Effect of hydrothermal dewatering on the physico-chemical structure and surface properties of Shengli lignite

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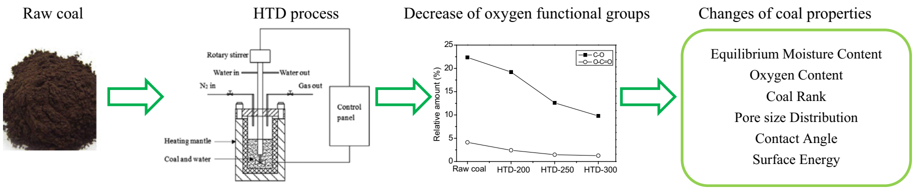
HIGHLIGHTS

- Variations and relationships of changes among coal properties during HTD process were analyzed.
- Surface energy of coal sample was test and related its hydrophilicity.
- Coal properties were mainly changed by the decomposition of oxygen functional groups.

GRAPHICAL ABSTRACT



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ABSTRACT

Shengli lignite from China was treated by hydrothermal dewatering (HTD) under 200–300 °C. The changes of physico-chemical structure and surface properties of Shengli lignite were tested and the relationship between these changes was analyzed. The equilibrium moisture content of Shengli lignite decreased from 29.75% in raw coal to 7.40% in HTD-300 (the sample treated by HTD under 300 °C) due to the decomposition of oxygen functional groups and the alternation of hydrophilic property of the coal sample. The coal upgrading by the HTD process was shown through the decrease in atomic ratios of oxygen to carbon (O/C) and hydrogen to carbon (H/C) due to the decomposition of functional groups and side-chains, which should be the important reason for the change of pore size distribution. The analysis of surface energy showed that the decrease of hydrophilicity was mainly caused by the reduction of acidic components, which provides another evidence for that the decomposition of carboxyl and hydroxyl resulted in the decrease of equilibrium moisture content.

1. Introduction

In China, the demand of energy is increasing continuously with the economic development. More than 60% of the energy was generated from coal in recent years. As the coal consumption increase, low rank coals, such as lignite, attract increasingly more attentions because of their low price and abundant reserve that is estimated be around 130.3 billion tons in China [1], primarily deposit in Inner Mongolia. However, the lignite in Inner Mongolia is characterized with low calorific value, high moisture content and high ash content, which significantly affect the utilization processes, such as combustion, gasification and liquefaction [2,3], and therefore may cause considerable waste of transportation capacity. Thus, dewatering and upgrading technologies are essential for large scale utilization of the lignite in Inner Mongolia.

Hydrothermal dewatering (HTD) is a process developed for efficient dewatering of low rank coals [4–8]. In the HTD process, the temperature is typically between 200 and 350 °C [4,5,9], and the vessel pressure is generated autogenously to stop water from evaporating [10]. After the HTD process, the physical–chemical properties of coal are significantly changed. Favas and Jackson [4]

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reported that the intra-particle porosity of HTD products was mainly affected by reaction temperatures. The volatile matter and oxygen contents decreased with the increase of temperature due to the decomposition of oxygen functional groups [5,11]. Yu et al. [9] found that the removal of oxygen functional groups, such as carboxyl and phenolic hydroxyl, significantly enhanced the slurry ability of lignite. The variation of contact angle was also thought to be a factor related to the change of slurry ability [9,11]. As a portion of the organic compounds decompose and soluble inorganic elements leach out to waste water, there has also been some research focusing on the gaseous and liquid products and waste water from HTD process [7,11–14]. The organic components in waste water could be used to produce combustible gas rich in CH_4 and H_2 by catalytic hydrothermal gasification [13,15]. The hydrothermal gasification process is found not only to be efficient for waste water treatment but also to be effective for energy recovery from wastewater. The organic and inorganic components in waste water could be absorbed by adsorbents as well. Butle et al. [16] reported that that lignite itself worked as a valid adsorbent for the partial or complete remediation of mechanical thermal expression waste water which is similar to the HTD waste water. The complicated and difficult treatment of waste water raises the operating cost for lignite hydrothermal dewatering. Though much research on HTD has been done, but there is still a lack of research that systemically studies of the changes of physical, chemical and surface properties of the coal related to the coal–water interactions during HTD process and the relationships between these changes.

In this study, Shengli lignite, from the eastern Inner Mongolia, was treated by the HTD process under 200–300 °C. Proximate and ultimate analyses and calorific value determination of raw coal and HTD products were carried out. Pore size distribution, functional groups on coal surface, contact angle and surface energy were tested. The relationships between the changes of these properties were studied as well.

2. Experimental

2.1. Coal sample description

The Shengli lignite used in this study was obtained from the east of Inner Mongolia, China. The properties of the raw coal obtained by proximate and ultimate analyses are listed in Table 1. The proximate analysis was carried out following the ISO 11722, ISO 1171 and ISO562 methods. Before the proximate analysis, all samples were stored under 25 °C and 65% humidity to reach equilibrium [9]. The ultimate analysis was carried out following the ISO 625, ISO 333 and ISO 334 methods. The calorific value determination was implemented according to the ISO 1928 method. All the data were determined from an average of 2 tests.

2.2. HTD procedure

The HTD process was performed on a 0.5 L cylindrical autoclave (PCF05-30, SLYQ, Yantai, China) (Fig. 1) equipped with an automatically controlled electrically heating mantle, a rotary stirrer and a controller, with a capacity of maximum pressure of 30 MPa and maximum temperature of 300 °C.

The lignite was prepared by crushing and sieving through a 1 mm hole sizer. Then, 100 g lignite and 250 g distilled water were mixed and added into the autoclave. Prior to heating, the autoclave was sealed and flushed with 2 MPa N_2 at room temperature to remove residual air and to inspect for leakage. The autoclave was heated at a heating rate of 10 °C/min with the content being stirred at 120 r/min. The temperature was maintained for 30 min after reaching the scheduled desired value. Then, the autoclave was cooled to room temperature by water. At last, the HTD product was separated from the solid–liquid mixture by filtration and collected for further tests. The experiments under each condition were implemented twice.

2.3. Pore size distribution and porosity determination

Pore size distribution was determined by Mercury Intrusion Porosimetry (MIP) and low temperature nitrogen adsorption method. In the MIP method, an AUTOPORE IV mercury porosimeter (micromeritics) capable of applying pressures between 3.4 kPa and 207 MPa, was used to analyze the distribution of macropores with diameters ranging between 0.05 and 60 μm [17,18]. The low temperature nitrogen adsorption method was used to analyze the distribution of mesopores and micropores with diameters ranging

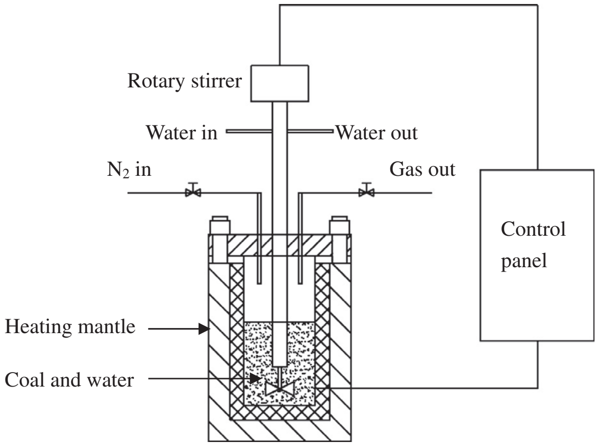

Fig. 1. Schematic diagram of hydrothermal dewatering rig.

Table 1
Proximate and ultimate analyses of raw coal and HTD treated coals.

Samples	Proximate analysis (%)				Ultimate analysis (%)					O/C	H/C	CV_{eq} (kJ/kg)	Porosity (cm^3/g)[b]	Contact angle (°)[c]
	M_{eq}	A_d	V_{daf}	FC^*_{daf}	C_{daf}	H_{daf}	N_{daf}	S_{daf}	O_{daf}[a]					
Raw coal	29.75	19.29	54.66	45.34	67.79	6.61	1.08	1.84	22.68	0.25	1.17	17,686	0.573	68.3
HTD-200	13.59	15.05	47.15	52.85	69.96	6.62	1.14	1.78	20.5	0.22	1.14	25,079	0.485	80.0
HTD-250	10.21	15.20	43.67	56.33	73.09	6.56	1.21	2.13	17.01	0.18	1.08	25,817	0.464	85.0
HTD-300	7.40	15.33	38.79	61.21	76.16	6.47	1.27	2.11	13.99	0.14	1.02	27,514	0.449	87.4

eq: Equilibrium moisture basis, d: dry basis, daf: dry ash free basis, M: moisture, A: ash, V: volatile matter, FC: fixed carbon, CV: calorific value, and HTD-200, HTD-250, HTD-300: samples treated by HTD process under 200 °C, 250 °C, 300 °C, respectively.

[a] By difference.

[b] Each entry is the average of 2 measurements with error of ±0.02 ml/g.

[c] Each entry is the average of 4 measurements with error of ±1.2°.