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Research article

Effects of microwave/HAc–H_2O_2 desulfurization on properties of Gedui high-sulfur coal

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ABSTRACT

A high-sulfur coking coal obtained from Shanxi province in northern China was desulfurized by microwave/HAc–H_2O_2 treatment. The main properties of coal samples before and after desulfurization treatment, including the elemental composition, caking index, organic constituents and sulfur content were analyzed. Experimental results showed that microwaving treatment at 500 W for 40 s combined with HAc–H_2O_2 (1:5 v/v) resulted in a yield of 99.27% clean coal and a desulfurization rate of 22.62%. Proximate and ultimate analyses showed that the ash content in coal was decreased from 9.09% to 7.90%, while the volatile matter significantly increased by 0.75%, and that the oxygen concentration in the coal increased from 4.15% to 7.08% following treatment. After desulfurization, the decreases in the caking index (from 72.4 to 45.42) and the impairment of calorific value was also observed. The negative impacts on the technological properties of coking coal may be attributed to oxidization caused by a HAc–H_2O_2 addition with the acceleration of microwaving. Results from FT-IR and XPS analyses depicted a considerable increase in oxygen-bearing functional groups, in accordance with results obtained by an ion-exchange titration method. These findings confirmed that the oxidization plays an important role in the present desulfurization process, and takes a dominant responsible for the changes of various properties of coal.

1. Introduction

Coal is an economical source of energy in the world [1]. In China, consumption of standard coal reached 24.75 million tons in 2013, which accounted for 59.36% of primary energy resource utilization [2]. Coal is the main energy supply for China, and has played an important role in the explosive economic development over the past decades, and is expected to shape the energy landscape for many years to come [3–5]. One primary application of coal in industry is coke making. However, the quality of current coking coal in China is unable to satisfy the demand for producing high quality coke, as Chinese coking coal usually contains high concentrations of impurities, such as ash and sulfur, and also suffers from severely regional distribution issues [6,7]. It is well-known that the major parent coking coals and critical auxiliary coals are badly lacking in quality and supply, despite the presence of various coking coal reserves in China [6–8]. In addition, using poor-quality coal poses a major threat to environment because of the release of sulfur in the form of sulfur dioxide during combustion. As a result of sulfur coating the iron crystal surface, sulfur impurities also make steel more brittle and decrease its plasticity [9]. Consequently, efficient utilization of inferior coking coal, especially the removal of sulfur in high-sulfur coking coal, urgently requires a solution. Several desulfurization processes have been adopted in China, including physical coal preparation, biodesulfurization and chemical desulfurization [10–14]. However, problems with these existing technologies concerning cost, efficiency, applicability, and waste disposal have led to increased focus on advanced desulfurization processes [15].

Microwave technology can provide a number of advantages in industrial applications, such as rapid response, uniform energy distribution, selective heating and mild reaction conditions. Hence, it has been widely introduced into organic synthesis [16,17], wastewater treatment [18], environmental engineering [19], and mineral processing [20,21], and have also been used to the desulfurization of coal since the 1970s, with growing developments in recent decades [22–27].

There are different requirements regarding specific coal properties depending on application, necessitating a comprehensive understanding of coal demands across various processes. The caking propensity and coking property are the most critical natural properties to consider carefully in desulfurization processes [28,29]. The caking property is the precondition of the producing of coking property and makes the caking property become the predominant quality indicator of the coal used in coke making. Several previous studies have evaluated the effects of various process variables (such as microwaving time, microwave power, additive and granularity of coal) on desulfurization results and sulfur

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transformations which occur during microwaving processes [22,24,30–34]. However, there have been considerably less research concerning the mechanisms involved in comprehensive microwave desulfurization mechanism [33,35] and few reports regarding the influence on coal structure and the effect of microwave desulfurization on the properties of coking coal [15]. To investigate the effects of microwave desulfurization on the properties of coking coal, experiments were conducted to determine changes in coal qualities before and after microwave/HAc–H_2O_2 desulfurization. Experimental analyses completed as part of this study include proximate analysis, ultimate analysis, and determination of calorific value and caking index. The effects on the caking property of coking coal caused by the process, as well as the desulfurization mechanism by microwaving with HAc–H_2O_2, are discussed in detail.

2. Experimental

2.1. Coal sample characterization

Bulk coal samples were collected from the Gedui coal mine in Shanxi province in China. Sampling techniques similar to those of Jones riffles and conning and quartering methods were adopted [22,31]. Representative samples were dried in a vacuum drying oven and then ground to <0.50 mm in an N_2 atmosphere for further study. Table 1 presents sulfur contents in various coal samples, and results from proximate analysis and ultimate analysis of these coal samples have been summarized in Table 2.

For raw coal with an ash content of less than 10% and a volatile content of less than 20%, the sulfur content (dry ash-free basis) based on the ultimate analysis was 2.72%. The organic sulfur content of coal reached 2.00%, which accounted for 81.63% of the total sulfur in coal. Organic sulfur was found to be the most dominant form of sulfur in this type of coal and, dramatically, also the most difficult sulfur form to remove.

The influence of microwave desulfurization on the thermal properties of coking coal has been investigated by monitoring the evolution in calorific value during the coal desulfurization process. The low calorific value of coal sample determined on dry ash-free base ($Q_{net,v,daf}$) was used as an indicator of thermal properties of a coal. And the variation of the calorific value before and after microwaving process has been depicted in Table 2. The $Q_{net,v,daf}$ of raw Gedui coal was found to be 34,481.88 J/g, which is higher than 30,000.00 J/g, thus the Gedui raw coal can be classified as ultrahigh calorific value coal.

The caking index (G_{RI}) regarded as the indicator of caking property, in the present study, was based on the Roga index [36]. The caking index was measured before and after microwave treatment, following the methods in previous publication [37].

Oxygen makes up a substantial fraction of the organic component of coal, generally existing in functional groups such as hydroxyl group (–OH), carboxyl (–COOH), carbonyl (–CO) and ether (–O–). Previous experimental investigations and theoretical researches have devoted to elucidating the correlation between the oxygen in coal and the capability of coal to be the parent feed of coke producing [37,38]. In this study, the effects of microwave desulfurization process on the oxygen distribution were determined, qualitatively and quantitatively. The quantification of acidic oxygenic groups in coal, as well as the results of caking index test has been shown in Table 3. The ion-exchange method was applied to quantify the carboxyl and phenolic hydroxy groups, and corresponding main chemical reactions were listed as below [39]:

$$\mathrm{Ba(COO{-}Ar,R)_2 + 2H^+ \rightarrow 2Ar,R{-}COOH + Ba^{2+}}. \tag{1}$$

$$\mathrm{Ar,R{-}COOH/OH + Ba(OH)_2 \rightarrow (Ar,R{-}COO/O)Ba + H_2O}. \tag{2}$$

Table 1
Comparison in desulfurization performance between microwaving treatment and conventional heating.

Coal sample	Specification of sulfur species (wt.% ad)				Clean coal yield (wt.%)	Desulfurization rate (%)
	S_s	S_p	S_o	S_t		
Gedui raw coal	0.03	0.42	2.00	2.45	–	–
Before treatment	0.10	0.30	2.14	2.54	–	–
Microwaving	0.07	0.20	1.71	1.98	99.27	22.62
Conventional heating	0.07	0.23	1.97	2.27	99.39	11.18

2.2. Microwave/HAc–H_2O_2 desulfurization procedure

Desulfurization experiments were performed in a microwave reactor (MAS-II, equipped with infrared thermometer and air circulation system) purchased from Sineo Microwave Chemistry Technology Co. Ltd. (Shanghai, China). The operating frequency was maintained at 2.45 GHz, and the maximum power can be set to 1000 W. A brief experimental setup for microwave desulfurization is profiled in Fig. 1.

The desulfurization procedure is shown in Fig. 2. A sample of coal (5.0 g) was blended with reaction additives in a round-bottom Pyrex flask (250 mL). The flask was then placed in the microwave reaction chamber and experimental parameters were regulated using the operation panel. After the radiation program ceased, the microwaved coal samples were washed with hot deionized water in a filter. Then washed samples were recovered, dried to the air dried state for further analysis. Since minor particle of coal may contribute to the progress of desulfurization efficiency, raw coal was sieved to obtain a granularity of 0.074–0.125 mm prior to microwaving. A mixture of HAc–H_2O_2 solvent (1:5, v/v)- was chosen as the desulfurization additive, with a ratio of coal sample to additive of 1:3 (g/mL). And the ideal microwave irradiation parameters were set at 500 W and 40 s.

As shown in Fig. 1, in the glass condenser, cold water is injected through the bottom hole and flows out through the top hole. Based on this setup, the microwave additive is likely to only partially volatilize. The microwave reaction occurred in a mixed phrase of solids and liquids, allowing for a minimal destruction to the basic structure and properties of coal since the temperature of whole microwave system would retain relatively lower. During preliminary experiments to determine ideal desulfurization conditions, the liquid additive was volatilized when the condenser was not used. During the treatment, the temperature evolution was monitored via an infrared thermometer. This evolution cannot represent the temperature variation of the desulfurization mixture, but the surface temperature of the flask. Besides, the gasbags were used for collecting tail gas, and further analysis on the gaseous products would be presented in another publication.

In the present work, the desulfurization rate (Eq. (4)) was used as the main indicator for the desulfurization performance, as this rate accounts for the clean coal yield and the sulfur content of desulfurized coal simultaneously.

$$\text{Yield of clean }(\mathrm{Y}_j) = m_j/m_y{*}100,\% \tag{3}$$

$$\text{Desulfurization rate} = (100{*}\mathrm{S_y} - \mathrm{R}_j{*}\mathrm{S}_j)/\mathrm{S_y},\% \tag{4}$$

where S_y is the sulfur content of coal sample before desulfurization/%, S_j is the sulfur content of coal sample after desulfurization/%, Y_j is the yield of clean coal/%, m_y is the mass of original dry coal/g, and m_j is the mass of clean dry coal/g.

2.3. FT-IR analysis

Specimens for FT-IR were prepared using the potassium bromide (KBr) pellet technique. About 1.0 mg of ground sample was mixed