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Full Length Article

Impacts of sonication and post-desulfurization on organic sulfur species by reductive pyrolysis

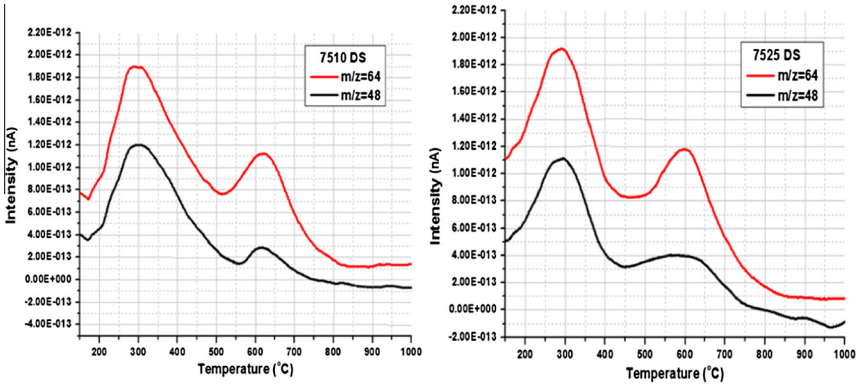
Sh. Mesroghli [a], J. Yperman [b,*], G. Reggers [b], E. Jorjani [a], R. Carleer [b]

[a] Department of Mining Engineering, Science and Research Branch, Islamic Azad University, Tehran, Iran
[b] Research Group of Applied and Analytical Chemistry, CMK, Hasselt University, Agoralaan – gebouw D, B-3590 Diepenbeek, Belgium

HIGHLIGHTS

- Desulphurized sonicated coal using PAA result in complex sulfur form changes.
- Role of AOP on coal oxidation as a function of different sonication times was investigated.
- High amounts of oxidized sulfur compounds are present in desulphurised sonicated coal.
- Quantitative organic sulfur form changes were determined.
- Sonication for 20 min resulted in the highest organic sulfur reduction.

GRAPHICAL ABSTRACT



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ABSTRACT

A comparative research on the effect of the ultrasound irradiation and peroxyacetic acid (PAA) desulfurization on sulfur forms in high sulfur coal samples (gathered from Tabas mine in Iran) was studied by reductive pyrolysis method. The total sulfur reduction after chemical desulfurization by PAA for sonicated samples is achieved in a range of 49–58%. Moreover, the studied sonicated-desulfurized samples showed that the pyritic and sulfate sulfur were mainly attacked by PAA. The maximum organic sulfur reduction was obtained for longer sonication treatment times (15 and 20 min) being around 42–44%. For the first time the role of advanced oxidation process (AOP) in the sonication treatment of coal samples has been considered. The profiles of m/z 48 (SO^+) and 64 (SO_2^+) obtained by Atmospheric Pressure-Temperature Program Reduction on-line coupled with MS (AP-TPR/MS) experiments for sonicated and sonicated-desulfurized samples exhibited identical trends over the whole temperature range. This achievement demonstrated the presence of high amounts of oxidized sulfur functionalities as a function of sonication treatment and post-chemical PAA desulfurization. Furthermore, AP-TPR "off-line" coupled with TD-GC/MS showed quantitative changes in the refractory sulfur forms as a result of sonication settings before and after desulfurization.

1. Introduction

Sonication is a process in which sound waves are used to agitate particles in solution. Ultrasound is a cyclic sound pressure with a frequency greater than the upper limit of human level of hearing starting from the frequency of 20 kHz. Ultrasound behaves

* Corresponding author.
E-mail address: jan.yperman@uhasselt.be (J. Yperman).

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differently in liquid and liquid–solid media compared to gas medium [1].

Ultrasound in aqueous medium produces highly reactive species such as OH radicals, H_2O_2 and ozone that are also strong oxidizing agents. These radicals are capable of initiating and enhancing oxidation and reduction reactions. By using ultrasound in aqueous medium, an oxidation phenomenon called: "advanced oxidation process" (AOP), occurred. Sonication enhances mass transfer and chemical reactions and is expected to reduce or eliminate the use of chemicals, resulting in minimum disposal problems [1].

Several methods have been considered for removal of total sulfur and different forms of sulfur from coal prior to combustion. These approaches can be subdivided into physical and chemical methods. Many chemical desulfurization methods have been accomplished in recent years [2–22].

Some researchers have focused on ultrasonic coal desulfurization; existing literature fails to explain the mechanisms involved in the ultrasonic-assisted coal desulfurization and conclusions drawn by these researchers are very general in nature. The ultrasonic desulfurization methods studied are either aqueous or chemical based. The main advantage of ultrasonic method is the simultaneously removal of ash and sulfur.

Zaidi [23] investigated ultrasound-promoted desulfurization of low rank coals with diluted solutions of sodium hydroxide (0.025–0.2 M) at 30 and 70 °C. The range of sulfur removal was higher for samples sonicated at a lower temperature. However, the mechanism involved in the interaction between sonication and dilute sodium hydroxide is not explained. Ze et al. [24] investigated the enhancement of desulfurization and de-ashing of coal using sonication and then flotation. Zibo coal and a water mixture were sonicated for 10 min using 20 kHz frequency and 200 W power. Results revealed that ultrasonic conditioning can drive physical separation of pyrite and thus enhance the performance of coal flotation methods used for desulfurization.

The hydrogenation of cyclohexene, biphenyl and quinoline, as the hydro-desulfurization of benzothiophene in the presence of formic acid (a hydrogen precursor) and a Pd/C catalyst by ultrasound irradiation was studied and found to be effective at ambient temperature and pressure [25]. Several carbon-based sorbents assisted by ultrasound for desulfurization of a model jet fuel were used by Wang et al. [26]. The results showed that the selective adsorption ability of $PdCl_2$ was higher than those of Cu(I)Cl and metallic Pd. The oxidative process for sulfur removal from petroleum products feedstock has been investigated by Mello et al. [27]. Dibenzothiophene is used as a model sulfur compound. The effect of sonication time, volume of oxidizing reagents, kind of solvent for the extraction step and kind of organic acid as hydrogen precursor were investigated. Higher efficiency of sulfur removal was achieved using sonication in comparison to experiments performed without its application under the same reaction conditions.

Recently, a study combining microwave irradiation and sonication as a pre-treatment method to produce ultra clean coal in a leaching process using HF followed by HNO_3 shows that the sulfur content (1.89 wt%) of non-pretreated sample decreased down to 1.26 wt%, whereas this reduction for microwave-ultrasonic pretreated sample was more noticeable and decreased down to 0.8 wt% [28].

In the present research, the impact of pre-sonication at different times of irradiation on high sulfur Tabas coal sample followed by an optimized chemical desulfurization using peroxyacetic acid (PAA) has been studied. The main purpose is to define the differences in the effects of different sonication time settings on the organic sulfur forms and especially in the production of oxidized organic sulfur compounds. The same investigation is done for the desulfurized sonicated samples. To analyze the mentioned changes, an analytical method called "AP-TPR/MS" and "AP-TPR TD-GC/MS" is used.

2. Experimental

2.1. Coal sample characteristics

A 40 kg coal sample from active stopes in C_1 seam of Tabas coal mine with high sulfur content was collected. Sampling techniques similar to those of Jones riffles, conning and quartering methods were adapted and representative samples were prepared for further studies. High sulfur Tabas coal is subjected to a sonication process and to a post chemical treatment by PAA. The results of proximate and ultimate analysis have been illustrated for all sonicated and sonicated-desulfurized coal samples in Tables 1 and 2 respectively.

The ultrasound treated samples are labeled in the following way, for example: "7510" is related to the sample fraction size under 75 μm and sonicated for 10 min.

2.2. Sonication process

Ultrasound as a sonication pretreatment is used in desulfurization process. Ultrasonic is a series of vertical waves that are alternating unevenly. There are two effects of cavitations formed by ultrasound near the extended liquid-solid interfaces in the liquid-solid systems: micro jet impact and shock wave damage [29]. Each cavitated bubble reaches a temperature of nearly 5000 K and a pressure of more than 50 MPa [30]. The temperature at the interface between the water and the bubble can be as high as 2000 K. The rate of heating and cooling can be faster than 10^9 K/s. As a result, ultrasonic treatment can change the pulp nature [31].

In this study, a Q280 multifunction ultrasonic transmitter has been used for coal sample pretreatment. The frequency of its ultrasonic head was 43 kHz and the power of its ultrasonic transmitter was 225 W. Around 10 g of coal (less than 75 μm) was mixed with 150 ml of distilled water into a beaker. The prepared pulp with the beaker as its container was fixed and soaked into the water media in the ultrasound transmitter to start sonication process. The sonicated samples were filtered and subsequently dried in an oven at 100 ± 5 °C for 1 h. To evaluate the effects of irradiation time on sulfur functionalities, the coal samples were irradiated for 10, 15, 20 and 25 min. The dried sonicated samples were cooled in a desiccator, weighed and its sulfur forms were determined.

2.3. Chemical desulfurization

After sonication at different times, the samples were chemically desulfurized with PAA. The procedure involved dispersing 8 g of sonicated coal in 240 ml of glacial acetic acid and warming up to the desired temperature of 55 °C and then adding 80 ml of H_2O_2 solution (30% v/v) holding temperature at 55 °C [32]. The experiments were performed in a 500 ml Pyrex reactor isolated with glass wool equipped with a thermometric probe and stirrer. Based on a previous study [19], identical optimized parameters for desulfurization of Tabas coal by PAA were applied: desulfurization time of 90 min and temperature adjusted to 55 °C. After 90 min of reaction, the reactor was cooled down and the residual solution was filtered. The desulfurized coal was washed with hot distilled water and dried in an oven at 100 °C for 1 h and analyzed for sulfate, pyritic and total sulfur content. All chemical reagents were obtained from Merck manufacturer. The results of sulfur content before