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The Analysis of Sulfur Species from Coal by a Sonochemical Process

Il-kyu Kim*, Jang-Pyo Cheong and Seung-Hoon Lee*****

*School of Environmental System Engineering, Pukyung National University, Pusan, Korea
**Department of Civil and Environmental Engineering, Kyungsung University, Pusan, 608-736, Korea
***Environmental Science & Technology Research Center, Kyungsung University, Pusan, 608-736, Korea

The sonochemical process is evaluated as an effective and feasible method for the control of sulfur in coal. In the presence of a small amount of hydrogen peroxide, the sonochemecal process can significantly bring sulfur from the coal matrix into solution as sulfate ion. Results also indicate that hydrogen peroxide can significantly enhance the rate and the extent of sulfur oxidation. Room temperature appears to be the most optimal situation for sulfur oxidation. As temperature increases to 50°C, the effectiveness of the sonochemical process suffers due to the fast decomposition of hydrogen peroxide. Increasing energy density increases the rate and the extent of sulfur oxidation. Under the experimental conditions of this study, further increase in energy density yields no further increase in both the rate and the total oxidizable sulfate.

Key words : Sonochemical process, sulfur, coal, sulfate, hydrogen peroxide

1. Introduction

The presence of sulfur in coal is known to be a major cause of acid rain precursors.[1] Particula-rly, organic sulfur in coal is mostly insoluble and intractable aromatic cross-linked structure. White and Li identified some 78 compounds from ben-zene extracts of Homestead coal, of which at least 6 were organic sulfur compounds, all thiophenes, including phenanthro (4, 5-bcd) thiophene.[2] The total sulfur content in U.S. coals ranges from 0.2% to 10% by weight with majority in the range of 1.0 to 4.0%.[3] While the pyritic sulfur content covers a very wide range, the organic sulfur content is usually below 2%. The organic sulfide in bituminous coals constitutes from 5% to 30% of the total organic sulfur. Thiophenes including dibenzothiophene (DBT) range from 10% to 75%, being greater than 30% for most coals. For example, the dibenzothoiphenic and the single thiophenic sulfur content of Illinois #6 coal are 42.8% and 30.8%, respec-tively.[3] The corre-sponding sulfur content of Texas lignite are 16.3% and 57.1%, respectively.[3]

The inorganic sulfur such as pyrites can readily separated from coal by physical methods such as froth flotation, oil agglomeration, magnetic separa-tion, and dry separation.[3] While physical cleaning is able to remove inorganic sulfur species from coal, the removal of organic sulfur requires specific desulfurization strategies. Many chemical desulfurization approaches have been applied to coal with various levels of success.[4-5] But, none of these processes developed so far appears to be economically feasible under present economic conditions. Due to increasingly stringent air qua-lity control measures imposed by various govern-mental agencies and private environmental groups, the effective removal of sulfur, especially organic, from coals is of urgent importance.

This study presents the result of the desul-furization of coal using sonochemical process assis-ted by hydrogen peroxide. The effects of H_2O_2, pH, ultrasonic energy density, and tem-perature on the rate and the extend of sulfur oxidation were investigated. A preliminary reaction mechanism was proposed and discussed.

2. Experimental Section

2.1. Materials

Delmava Power Company (Wilmington, DE) supplied the coal sample used in this study. This coal was originally from Illinois (No. 6). Various researchers

have already reported the chemical characteristics of this coal sample.[6] This coal, typi-cally, has a 3.8% total sulfur content, 9.4% ash, 28.9 MJ/kg heat value, 0.71%sulfate, 0.4% pyrite, and 2.69% organic sulfur. The large coal crystal was ground to a coarse powder. A fine coal powder was then obtained by grinding the coarse particles in a mortar with a pestle under a nitrogen at-mosphere. The powder was sized with ASTM (American Standard Testing Material) sie-ves, to collect the size fraction less than mesh size No. 200. This size fraction has an average diameter of 63 um. The fine coal powder was stored in a vacuum dessi-cator until use. All water used in this study was ASTM type 1 reagent grade deionized-distilled water with 18 megohm-cm quality obtained from a Corning Mega-Pure Water Purification aystem, Model MP-290. Adjust-ments for pH were made with reagent grade sodium hydroxide (NaOH) from the Fisher Scientific Company and perchloric acid ($HClO_4$) from the Baker Chemical Company. All other chemicals used in this study were of ACS (American Chemical Society) cer-tified grade and were obtained from either the Fisher Scientific company or the Aldrich Chemical Company. All chemicals were used as received.

2.2. Apparatus

All experiments were conducted in a double-jack-eted reaction vessel (250 mL) sealed with a rubber lid. Openings were cut in the reactor lid to facilitate sam-ple extraction, pH measurement and acid and base addition. The reactor vessel was kept in a closed cab-inet to prevent the solution from being exposed to any light, as reported by Hsieh that light can induce a photo-oxidation reaction which might interfere with measurements.[7]

The pH of the solution was maintained and moni-tored by a New Brunswick Scientific pH Controller. The pH was adjusted with fresh so-lutions of NaOH (0.1M) and $HClO_4$ (0.1M). The temperature of the reacting solution was main-tained circulating water from a Braun Thermomix constant temperature bath, Model 1460, through the double-jacket A magnetic stirrer was used to provide continuous mixing at a constant rate.

2.3. Batch Sonochemical Oxidation Experiment

Each batch kinetic experiment was begun by filling the reaction vessel with 500 mL of sample and the desired concentration of sodium per-chlorate (0.1M $NaClO_4$). Once the pre-selected pH condition was attained, a given amount of coal powder was added to the reaction vessel. Generally the pH stayed constant upon the addition of coal particles, however, the pH was automatically adjusted with the pH controller. Once the desirable pH value was achieved, ultrasound and a given amount of H_2O_2 were applied simulta-neously to the solution as to begin the oxidation reac-tion. Each experiment was conducted for at least one-hour period. Samples were taken at 10, 20, 40, 60, 90, 120, 150, 180, 240, and 300 minutes. A 5-mL sample was with-drawn through a small hole in the lid and then immediately filtered through a 0.45 um Gelman mem-brane filter directly into plastic test tubes and sealed. Sulfate ion (SO_4^{2-}) was measured. Attempts were made to detect the other sulfur species including sulfite (SO_3^{2-}), thiosulfate ($S_2O_3^{2-}$), ele-mental sulfur (S^0), and sulfide (S^{2-}) species, but the concentrations of these sulfur species were non-detectable. Follow-ing the completion of each experiment, the reaction vessel and all glassware used were washed, and rinsed with Cole-Palmer Micro Liquid Laboratory Cleanser, thor-oughly flushed with tap water, and then rinsed all remaining sulfur species from the glassware sur-face prior to the next experiment.

3. Results and Discussion

The presence of H_2O_2 can greatly enhance both the rate and the extent of sulfur oxidation in coal. As shown in Fig. 1, the extent of sulfur oxidation increases with increasing H_2O_2. It appears that under the exper-imental conditions, the total sulfate concentration reaches a maximum level at an H_2O_2 concentration of 0.1M. Fig. 2 shows the effect of pH on the oxidation of sulfur in coal. Results indicate that at the extent of sul-fur oxidation increases with pH. Results in-dicate that the extent of sulfur oxidation in-creases with increas-ing energy density. While the extent of sulfur oxida-tion with energy density of 0.5W/ml reached the maximum value after 240min., the extent with higher energy density increases upon further increase in energy (Fig. 3). The rate of sulfur oxidation increases with temperature as expected. The extent of sulfur

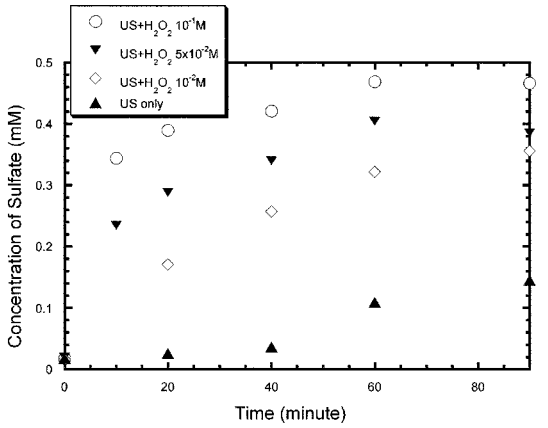

Fig. 1. Effect of H_2O_2 on Sulfur Oxidation from Coal (Experimental conditions : ultrasonic energy density =5Watt/mL, pH=7, initial concentration of coal sample=5g/L, ionic strength=0.1M $NaClO_4$, temperature=25°C.)

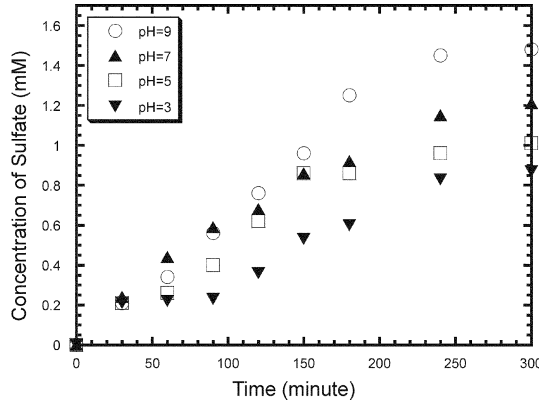

Fig. 2. Effect of pH on Sulfur Oxidation from Coal (Experimental conditions:$[H_2O_2]$=0.01 M, ultrasonic energy density=5 Watt/mL, initial concentration of coal sample=5 g/L, ionic strength =0.1M $NaClO_4$, temperature=25°C.)

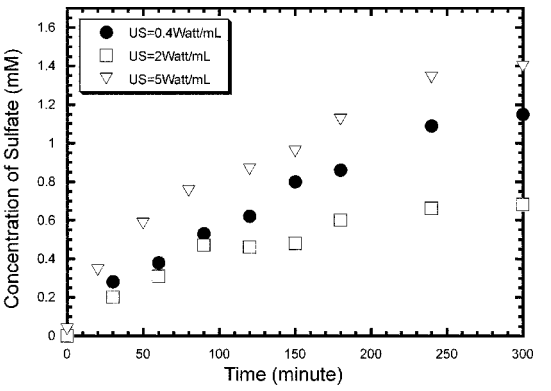

Fig. 3. Effect of ultrasonic energy density on Sulfur Oxidation from Coal (Experimental conditions:$[H_2O_2]$=0.01 M, pH=7, initial concentration of coal sample=5g/L, ionic strength=0.1M $NaClO_4$, temperature=25°C.)

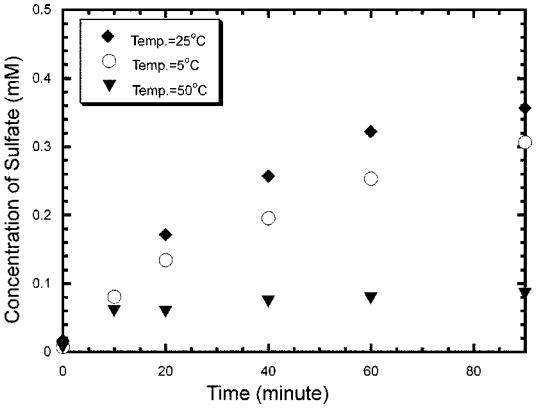

Fig. 4. Effect of Temperature on Sulfur Oxidation from Coal(Experimental conditions : ultrasonic energy density=5 Watt/mL, $[H_2O_2]$=0.01 M, pH=7, initial concentration of coal sample=5 g/L, ionic strength= 0.1M $NaClO_4$.)

oxidation, however, has an optimal temperature of ca. 25°C (Fig. 4). Apparently, as temperature in-creases to 50°C, H_2O_2 becomes vulnerable under such harsh environment; it readily eva-po-rates, thereby drastically decreases the H_2O_2 con-cen-tration in the system.

3.1. proposed reaction mechanism

In the absence of more experimental evidence, it is possible, based on literature information to propose a reaction mechanism for the oxidation of sulfur in coal. It is assumed that hydroxyl radical is the major initiator for the oxidation reaction. As mentioned, the reactions are initiated by the collapsing of cavitation bubbles in which water molecules can reach supercritical conditions and decompose, forming H• and OH•.

$$H_2O \rightarrow H\bullet + OH \quad (1)$$

$$C\text{-}S + OH\bullet \rightarrow C\text{-}SOH\bullet \quad (2)$$

$$C\text{-}SOH\bullet \rightarrow C\text{-} + SOH\bullet \quad (3)$$

$$SOH\bullet \rightarrow SO\bullet + H^+ \quad (4)$$

$$H_2O_2 + OH\bullet \rightarrow H_2O + HO_2 \quad (5)$$

$$HO_2\bullet \rightarrow H^+ + O_2\bullet^- \quad (6)$$

$$SO\bullet^- + O_2 \rightarrow SO_3^{2-} \quad (7)$$

$$SO_3^{2-} + H_2O_2 \rightarrow H_2O + SO_4^{2-} \quad (8)$$

$$OH\bullet \rightarrow O\bullet + H^{+} \quad (9)$$

$$2\ SO_3^{2-} + O_2 \rightarrow 2\ SO_4^{2-} \quad (10)$$

Upon the attack by the hydroxyl radical on a sulfur atom, C-S, on the coal surfaces, OH• Addition to the surface sulfur atom forms a surface C-SOH• complex which can undergo dissociation reaction to yield C- and SOH• Radical as shown in Eq. 2 and 3. (Note: Here C-represented the sulfur-free surface and C-S is the sulfur-laden coal surface.) The SOH• radical will undergo depro-tonation reaction to yield the SO• radical and proton (Eq. 4). Since H_2O_2 is rather abundant in the system, there will be reaction between H_2O_2 and OH• to yield $HO_2\bullet$. A weak acid, $HO_2\bullet$ will undergo a deprotonation reaction to form the su-peroxide radical, $O_2\bullet^-$ as shown Eq. (5) and (6).

Sulfite ions are formed when superoxide radicals react with $SO\bullet^-$ radicals (Eq. (7)).

Finally, sulfate ions appear when sulfite ion reacts with free oxygen molecules (Eq. (8)).

Based on the above mechanism, it is clear that the rate of the oxidation reaction is highly pH-dependent. According to reaction step (4) and (6), the formation of $SO\bullet^-$ and $O_2\bullet^-$ will decrease as pH decreases. A decrease in these species will certainly decrease the reaction rate. As pH goes up, OH radical will becomes deprotonated as shown in Eq. (9).

As a result, the oxidation rate will decrease due to decreasing supply of hydroxyl radical. Reaction between SO_3^{2-} and molecular oxygen, which is abundant in the system, can also lead to the formation of sulfate (Eq. (10)).

However, reaction between sulfite and free oxygen is rather slow. If Eq. (10) was responsible for the transformation of SO_3^{2-} to sulfate, then one will expect to detect the presence of sulfite. Since we never found sulfite in the solution, it is therefore believed that Eq. (8), not Eq. (10), is the final step for the generation of sulfate.

4. Conclusion

Results obtained from this research indicate that sulfur oxidation by the sonochemical process is an effective and feasible method for the control of sulfur in coal. In the presence of a small amount of H_2O_2, the sonochemecal process can signifi-cantly bring sulfur from the coal matrix into solu-tion as sulfate ion. Results also indicate that hy-drogen peroxide can significantly enhance the rate and the extent of sulfur oxidation. Room temperature appears to be the most optimal situation for sulfur oxidation. As temperature increases to 50°C, the effectiveness of the sonochemical pro-cess suffers due to the fast decom-position of hydrogen pe-roxide. Increasing energy density in-creases the rate and the extent of sulfur oxi-dation. Under the experimental conditions of this study, further in-crease in energy density yields no further increase in both the rate and the total oxidizable sulfate.

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