Notes

Analysis of Sulfur in Coal and Coal Desulfurization by Counterflow Oxidative Treatment

Keon Sang Ryoo,* Jong-Ha Choi, and Yong Pyo Hong

Department of Chemistry, Andong National University, Andong 760-749, Korea

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Coal has been used as a major fossil fuel source for generation of electrical energy for centuries. It is widely distributed in many countries around the world. The reserves of coal are estimated around $10{,}000 \times 10^9$ tons, which can, at current rate of consumption, supply the energy needs for several hundred years. It's preeminence as a fuel source has, however, been declined on account of an adverse impact on clean air. The main contributor to the air pollution is presence of sulfur in coal. It is said to be most significant impediment to the continuous use of coal in the future. The SO_2 emission in power plants has been identified as the largest source of acid rain which has been linked to damage to natural aquatic systems. It also harms forests and buildings, contributes to reduced visibility, and is suspected of causing ill health. Therefore, because of the growing public concern over health and ecological effects associated with coal use, legislations have been enacted the strict regulations and standards on the release of SO_2 into the atmosphere.

The sulfur content of coal varies considerably with the nature and origin of the fossil deposits. Sulfur in coal is present in two broad forms, inorganic and organic.[1] Nearly all forms of inorganic sulfur are iron pyrite (FeS_2). Typically, the pyritic form is estimated based on iron content, and is reduced significantly by size reduction followed by specific gravity separation or similar physical processes.[2,3] Sulfur in the organic form is chemically bound in the coal, and elemental sulfur (S_8) in coal is currently counted as organic sulfur according to the ASTM D-2492 guideline.[4,5] The removal of organic sulfur requires more complex and costly chemical processes. Such technologies includes coal gasification, or the conversion of coal to a synthetic oil or solid material.[6-11]

A coal desulfurization process was carefully explored with an experimental bench scale in our laboratory. The process is based on controlled mild temperature oxidation with a counterflow oxidative technique. The name of the technique is derived from its operative mechanism in which a flame is made to propagate in a direction counter to the flow of oxidant, thus creating a starved environment. The process has been used to bring about almost complete destruction of adsorbed chlorinated organics while preserving most of exhausted activated carbon without the use of an external energy source.[12] The successful results led us to explore a possibility for removal of sulfur from coal.

The project of the study is (a) to analyze sulfur in coal and (b) to evaluate and optimize a thermal oxidative process such that it yields high sulfur removal efficiency with the least processing costs.

Experimental Section

Analysis of Sulfur in Coal. Coal was obtained from a mine field at Kangwon Do, Korea. Coal sample was ground under either air or argon atmosphere and then fractionated with sieves. A mesh size (20-40) range was collected for further studies. The determination of total sulfur content in coal was performed using an elemental analyzer (Fisons Instrument EA 1108, Strada Rivoltana-20090 Rodano (Milan), Italy) installed with a reactor and a chromatographic column and a thermal conductivity detector (TCD) positioned in center of an oven. The combustion of coal sample in reactor was done at about 1,000 °C. The column made from stainless steel of 6 mm o.d., 4 mm i.d. was packed with Poropak QS (80-100 mesh) and operated isothermally at 70 °C.

To investigate the weight % of elemental sulfur (S_8) in coal sample, (elemental sulfur in coal is currently counted, according to the ASTM D-2492, as organic sulfur which is a significant source of error for the determination of sulfur forms in coal),[4] an integrated supercritical fluid extraction (SFE) system, as shown in Figure 1, was used. Prior to extraction of coal sample, elemental sulfur spiking experiments were carried out with soil to assess the recovery. The soil was collected locally and air dried at 250 °C, followed by sieved to the desired particles (20-40 mesh size). Approximately 50 g of sieved soil was extracted with 1 : 1 (v/v)

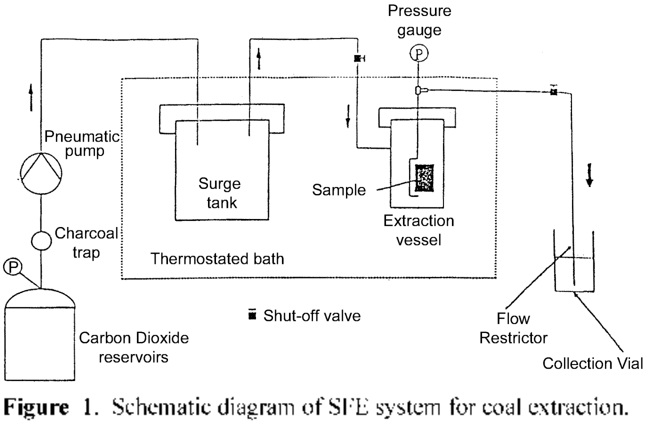

Figure 1. Schematic diagram of SFE system for coal extraction.

methylene chloride/acetone for 12 hours using a Soxhlet apparatus. The soil was then oven dried to remove the excess solvent, and tumbled so that it was throughly homogenized.

A 5 g of the soil was served as elemental sulfur spike recovery experiments for SFE. A portion of a solution of elemental sulfur in toluene was spiked on top of soil. The toluene solvent was then evaporated prior to the SFE extraction. The SFE extaction of soil sample was carried out with CO_2 at 300 atm and 313 K and CO_2/MeOH at same condition for 30-min in a static mode. The extracted elemental sulfur was collected into a vial containing 5 mL of toluene as collection solvent. A GC/MS (Shimadzu QP-5000, Shimadzu Corp., Kyoto, Japan) was used for the elemental sulfur analyses. Extract was analyzed using a SPB-1 FSOT column (a 30 m × 0.32 mm i.d., 5.0 μm film). Quantitative calibration standards were prepared with toluene solution (Aldrich, Milwaukee, WI, USA) containing elemental sulfur. By following the extraction of soil, weighed coal samples were SFE extracted for analysis of elemental sulfur.

Counterflow Oxidative Treatment for Coal Desulfurization. Coal desulfurization apparatus consists of an oxygen supply, a fixed bed reactor, and a series of impinger traps. The reactor was made of 1 cm i.d. × 45 cm long quartz tube with o-ring caps. The impinger traps were filled with 30% H_2O_2 solution. A 10 g of coal was packed into a reactor and then oxygen was introduced. The flow rates of oxygen were controlled using a needle valve on a pressure regulator and monitored with a calibrated rotameter. After a set purging interval (~5 minutes), coal was ignited at the bottom of the reactor until flame front was generated. The self-propagating flame was then moved counter to oxygen flow, burning a portion of the coal. The off-gas compositions exhausted from the reactor were analyzed with a GC/TCD, by measuring the response relative to standard gas mixtures (CO, CO_2, H_2, CH_4, and O_2, Scott Specialty Gases Inc., Durham, NC, USA). The gases were separated with carbosieve material (60-80 mesh) packed column at 80 °C oven temperature. The flame temperature was theoretically calculated from both the loss of coal and the relative ratio of CO and CO_2 in exhaust gas instead of temperature measurement appliance like a thermocouple during the process due to the transient nature of flame. The SO_2 emitted during the process was passed through a series of impinger traps. The SO_2 concentration was determined with an ion chromatograph (Dionex 14, Sunnyvale, California, USA) interfaced with a conductivity detector.

Results and Discussion

Determination of Total Sulfur Content. Figure 2 shows the chromatogram of each element obtained by an elemental analyzer. The peaks indicated were a carbon, a hydrogen, and a sulfur. The concentrations of each element were determined, by measuring the response relative to sulfanilamide ($C_6H_8N_2O_2S$) standard (Fison Instruments, S.P.A., Strada Rivoltana-20090 Rodano (Milan), Italy). It was found that total sulfur content in coal was around 1.8% by weight.

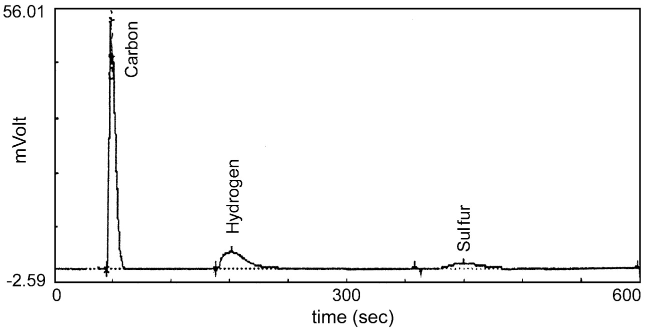

Figure 2. The analysis of carbon, hydrogen, and sulfur in coal by elemental analyzer.

Recovery Study of Elemental Sulfur from Soil. The quantitative reproducibility of elemental sulfur from soil was investigated by performing replicate SFE extractions. The SFE extraction of soil were accomplished with CO_2 at 300 atm and 60 °C and CO_2/5% MeOH at same pressure and temperature. Under these conditions, a minimum equilibration period of 30 min was required to reach steady state concentration. With CO_2 (300 atm and 60 °C) alone, the recovery of elemental sulfur was relatively low, falling in 78 = 5% range. According to the literature, it is generally accepted that polar matrixes such as soil and sediment are not readily amenable to extraction with CO_2 itself. To explore the possibility of better recovery, methanol was chosen as a polar modifier and directly introduced to the soil instead of mixing with a CO_2 in a cylinder. The extraction efficiency of elemental sulfur from soil with CO_2/5% MeOH at above-mentioned condition was enhanced, resulting in elemental sulfur recovery averaging 93 ± 5%. Results from the spiked soil extractions demonstrate that elemental sulfur can be quantitatively extracted in 30 min using SFE with CO_2/5% MeOH. Since the recovery of elemental sulfur was much higher using the methanol-modified CO_2, these fluids were used for coal extractions. The extract role of polar modifiers in SFE has not been elucidated so far, however, it is generally believed that polar modifiers improve recovery by increasing the solubility of analyte in the fluid and weakening the electrostatic interaction between analyte and sample matrix.

Analysis of Elemental Sulfur in Coal. The SFE extraction of coal was done with CO_2/5% MeOH (300 atm and 60 °C) for an equilibration period of 30 min in a static mode. During the initial 30 min of SFE extraction, elemental sulfur was not quantitatively detected unlike the recovery experiments of the spiked soil. Therefore, additional investigation was carried out to confirm that elemental sulfur could be extracted quantitatively from coal in its native form. It was considered that specific interactions between elemental sulfur and coal might be affected the rates of extraction during the SFE. To investigate this possibility, the SFE breakthrough studies of elemental sulfur from coal were performed. Plots of cumulative quantity of elemental sulfur from coal versus time with CO_2/5% MeOH are given in Figure 3. The results showed that extraction efficiency of elemental sulfur from coal was significantly increased after 60 min, and was kept constant thereafter. The percent ratio of elemental sulfur obtained by SFE was found approximately 35 = 7% of total

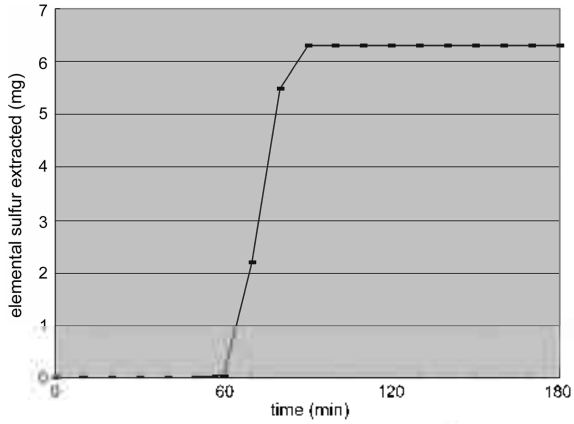

Figure 3. Breakthrough curve of elemental sulfur from coal by SFE with CO_2/5% MeOH at 300 atm and 60 °C.

sulfur in coal.

Counterflow Oxidative Treatment for Coal Desulfurization. The potential applicability of counterflow oxidative treatment for sulfur removal from coal was assessed through a limited bench scale experiment. Counterflow oxidative treatment process was based on controlled oxidation in oxygen depleted environment.[13] The process was conducted at oxygen flow rates of 60 mL, 120 mL, 350 mL, and 600 mL per minute and approximately 0.05-0.1% of the stoichiometric oxygen volume (oxygen flow rate × total burn time) was necessary to maintain a flame for combustion of coal. The flame temperature was estimated from both relative ratio of CO/CO_2 in exhaust gas and enthalpy of formation and heat capacity of CO and CO_2 and the loss of coal.[13] The temperature calculated varied from 1000 K~1,700 K at different oxygen flow rates. The percent sulfur removal efficiency was calculated by measuring the relative concentration of sulfur before and after counterflow oxidative treatment. The coal loss during counterflow oxidative treatment process was determined gravimetrically. Sulfur removal efficiencies and the loss of coal in accordance with the changes in oxygen flow rates are given in Figure 4 and 5. The results showed that the sulfur removal efficiency and coal loss were significantly affected by oxygen flow rate. The best sulfur removal efficiency and the least coal loss were obtained at low oxygen flow rate which was just enough to sustain a steady flame. Under this condition, it showed that approximately 70% of total sulfur was removed from coal while 13% of coal loss was consumed. As a matter of fact, this study has been tried to measure only the removal efficiency of organic sulfur from coal by counterflow oxidative treatment. But, it is thought that the removal efficiency of total sulfur should be counted including inorganic sulfur because sulfur from inorganic sulfur (FeS_2) existed in coal can be also released from coal due to above-mentioned high flame temperature. Even if the removal efficiency of sulfur were not high enough, counterflow oxidative treatment has shown considerable potential for removal of sulfur within coal because it runs in a single step and less energy intensive except for unevitable loss of coal spent during the process.

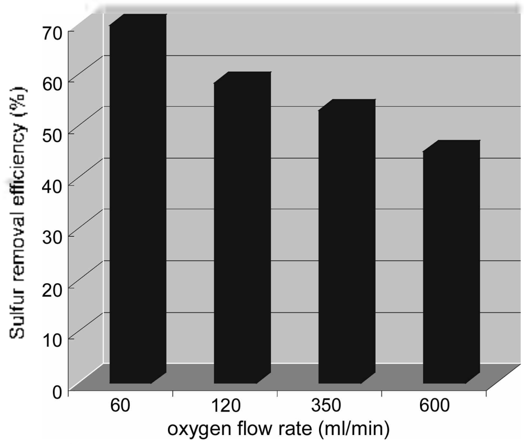

Figure 4. Effect of oxygen flow rate on sulfur removal.

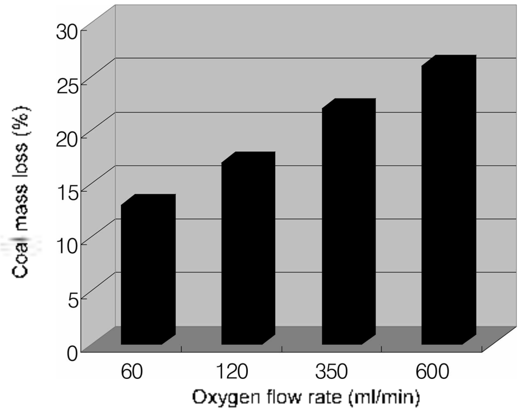

Figure 5. Effect of oxygen flow rate on coal mass loss.

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