

ADVANCES IN COAL CHARACTERIZATION BY PROGRAMMED-TEMPERATURE OXIDATION

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ABSTRACT

This paper describes the current status for the characterization of coal by controlled-atmosphere programmed-temperature oxidation (CAPTO). Distinctive gas evolution patterns are observed among coals of different rank and between raw and treated coals. In addition to two resolved SO₂ peaks, assignable to the oxidation of pyrite and the decomposition of sulfate, two others, assignable to organic structures in the coals, are observed.

INTRODUCTION

Interest continues to be strong in methods to reduce the levels of SO₂ and NO_x in the atmosphere as a control strategy for acid deposition. Retrofit technologies (pre- and post-combustion and combustion modification) used singularly or in combination offer the coal-fired utilities a potential route to meet state and federal regulations while limiting capital expenditures in comparison to repowering technologies. Conventional physical cleaning methods result in some inorganic sulfur (pyritic and sulfatic) reductions from coal while the advanced physical coal cleaning procedures under development offer the potential for significant pyrite reduction. Physical cleaning along with coal switching and post-combustion scrubbing techniques are the primary routes currently in use by the utilities in an attempt to meet air emission regulations.

Numerous precombustion chemical beneficiation procedures were developed in the 1970's that removed most of the inorganic sulfur (pyritic and sulfatic) and some of the organic sulfur from coal. Morrison¹ provides an excellent review of these technologies. Bioprocessing as a route for sulfur removal from coal is now under intensive study². Continued development of advanced coal cleaning technologies generates a need for suitable analytical techniques to monitor progress of the work.

The ASTM organic sulfur determination for coal is based upon the difference between the total sulfur analysis and the sulfatic and pyritic sulfur analyses of coal (Method D2492). The method works well for most untreated coals. However, the presence or formation of certain inorganic sulfur species in coals, particularly treated coals, that are partially insoluble in hydrochloric or nitric acid, results in a higher reported value for organic sulfur. This limitation presents a serious problem to all laboratories involved in coal desulfurization and other clean coal research. A number of routes to characterize the sulfur distribution in coals have been, and continue to be, studied. Friedman³ recently presented a critical review of sulfur analyses of coal and Stock et al.⁴ reviewed methods to determine sulfur distribution in American bituminous coals. A generally accepted, routine method to distinguish between the organic-sulfur functional groups or to classify the organic sulfur present in treated and untreated coals is vital to those involved in clean coal research.

Reductive and oxidative techniques have been developed as potential routes to classify the sulfur types present in raw and treated coals. Yergy et al.,

using a reductive approach, monitored the hydrogen sulfide evolved from a linear increase in temperature and noted five different types of hydrogen-induced sulfur release. Additionally, Attar⁸ described a non-isothermal kinetic method for estimation of the organic sulfur functional groups in coal. Majchrowicz et al.⁹ recently described an automated approach to the temperature programmed reduction route. However, these reductive approaches do not respond to much of the organic sulfur in coal and cannot be utilized to give any reliable quantitative information for the inorganic, organic, and total sulfur in coal.

Numerous groups have also investigated oxidation as a route to identify sulfur species. Chantret¹⁰, monitored airflow through a differential thermal analysis chamber for SO₂ and CO₂. Temperature rise in an absorbent, lead dioxide for SO₂ and Ascarite for CO₂, was used to detect the presence of the gases. LaCount et al.¹¹ using a thermal oxidative technique coupled with evolved gas analysis, described a route to qualitatively and quantitatively^{12,13} characterize the sulfur, carbon, and hydrogen in coals and treated coals. A coal sample thoroughly dispersed in an inert diluent used to control the exothermic oxidation reactions was exposed simultaneously to a linear increase in temperature and an oxygen/argon flow. Continuous measurement of the concentration of gases evolved from the sample provided a concentration/time or temperature profile for each evolved gas. By use of model compounds and polymeric substances, each SO₂ evolution maxima produced from coal was eventually related to the probable structural type causing the maxima. Integration of the profiles provided an estimate of the sulfur forms and the total sulfur in the coal sample. Total sulfur values were in good agreement with those obtained from ASTM analyses. However, significant overlap of the SO₂ evolution maxima resulting from pyrite and organic sulfur prohibited quantitative estimation of the sulfur forms in raw coals.

Boudou et al.¹⁴ briefly reviewed work in programmed pyrolysis, reduction, and oxidation. Using procedures similar to Chantret's and several other methods, they studied the sulfur species in several high organic sulfur coals.

Calkins¹⁵ described pyrolysis experiments directed toward the determination of organic-sulfur-containing structures in coal and briefly reviewed work in this area. Fixari et al.¹⁶ studied oxidative pyroanalysis as a route to the elemental analysis for the volatile and nonvolatile fractions of coals.

Other routes for a direct determination of organic sulfur in coal have been investigated. Some of these involve the electron microprobe^{17,18}, the scanning electron microscope¹⁹, or the transmission electron microscope²⁰. The equipment involved is costly and variations in the organic sulfur content in coal requires averaging over a number of sites in each sample. Huffman et al.²¹ investigated the molecular structure of organic sulfur in coal macerals by X-ray absorption fine structure (XAFS) spectroscopy. However, additional work is required on model systems to clarify ambiguities in the interpretation of the XAFS data.

A step-wise procedure using perchloric acid for determination of sulfate, sulfide, pyrite, and organic sulfur in a single coal sample has been reported²². However, the procedure is tedious and probably not suitable for routine analyses.

DISCUSSION

This paper describes recent improvements in oxidation conditions and in the detection system of the controlled-atmosphere, programmed-temperature oxidation (CAPTO) apparatus previously described¹⁵. The effort is directed toward development of methodology to obtain well resolved evolution profiles that will enhance our understanding of the nature of sulfur present in coal. This knowledge is basic to the development of improved technology for sulfur removal from coals and for selecting those coals which have the greatest

beneficiation potential. The unit also offers potential as a one-step direct analysis route for the inorganic, organic, and total sulfur present in untreated and treated coals.

Several current applications utilizing a partially modified instrument are discussed. A complete description of the totally redesigned CAPTO instrument/method (patent pending) will be presented elsewhere.

INSTRUMENT MODIFICATIONS AND METHOD

Portions of the system shown in *Figure 1* have been previously described¹³. An FTIR spectrometer is used as a detector for analysis of the SO₂, CO₂, H₂O, and NO₂ formed instead of the nondispersive infrared analyzers formerly used.

The CAPTO technique is used to analyze coals, treated coals and other high molecular weight substances reduced to a particle top size of -60 mesh, or smaller. The sample is thoroughly dispersed in a diluent (to reduce exotherms that occur during oxidation) and exposed simultaneously to a linear increase in temperature and to an oxygen/argon flow. The oxidized gases are monitored continuously and intermittent evolution maxima are observed for SO₂, CO₂, H₂O, and NO₂ as the oxidation proceeds. If the SO₂ evolution maxima are well resolved, a quantitative estimation of the sulfur types present in the sample can be obtained. However, the oxidation conditions used in previous work (diluent, 10% O₂ in argon, and a temperature ramp of 2 - 5°C/min.) resulted in overlap between the evolution maxima detected from pyritic sulfur and that from the second major occurrence of organic sulfur in coal.

In order to improve the oxidative technique, experiments were completed with the reaction parameters (temperature ramp, oxidant flow, and oxygen concentration) varied systematically. Optimum temperature ramp and flow were established. Using these conditions the programmed temperature oxidation of coal samples was studied as a function of oxygen concentration.

A series of CAPTO experiments were performed with ROM Illinois No. 6 coal. A different oxygen concentration was used in each experiment. The oxygen concentration in argon was varied from 4% to 16% in 2% increments. No improvement in resolution of the SO₂ evolution profile was noted. In fact, the pyritic and second organic SO₂ evolution maxima showed a decrease in resolution with increasing oxygen concentration. Careful measurement of the pyritic SO₂ evolution maxima revealed a slight shift to higher temperatures with increasing oxygen concentration (e.g. 4% - 430°C; 10% - 435°C). A CAPTO experiment using 20% oxygen resulted in one SO₂ evolution maxima at 445°C for the pyritic and aromatic sulfur.

Although loss of oxidative selectivity between the two major occurrences of CO₂ and SO₂ derived from organic structures in the coal was a concern, CAPTO experiments were completed using pure oxygen. The results (*Figure 2*) show that the oxidative selectivity between the first (290°C) and second (420°C) major evolutions of SO₂ from organic structures is retained and, importantly, the pyritic sulfur is oxidized at a higher temperature (478°C) than the organic sulfur. *Figure 2* also shows SO₂ evolution due to decomposition of iron sulfate at 585°C.

Previously, ¹³C CP-MAS n.m.r. work¹³ was completed on coal samples both before and after a CAPTO experiment that was terminated at 400°C. The n.m.r. spectrum prior to the experiment clearly indicated the presence of aromatic structures and nonaromatic structures ($f_a = 0.69$). After the sample was exposed to CAPTO conditions up to 400°C, the spectrum revealed an essentially unchanged aromatic region; however, the nonaromatic region had been almost totally eliminated ($f_a = 0.87$). Thus, the lower temperature CO₂ and SO₂ evolutions resulting from organic structures were attributed to carbon and sulfur lost primarily from oxidation of nonaromatic coal structures, and the CO₂ and SO₂

evolutions from organic structures above 400°C were attributed primarily to carbon and sulfur lost during oxidation of the aromatic coal matrix. We still believe this to be a generally valid premise. However, as noted in our earlier work¹³, stable aryl sulfides and sulfones oxidize above 400°C and would be included in addition to thiophenic structures in what we term "aromatic".

APPLICATION OF CAPTO TO MICROBIAL TREATED COAL

An example in which both CO₂ and SO₂ evolution profiles are important in characterizing a coal/treated coal is shown below. A -200 mesh Illinois No. 6 ROM coal was treated with a mixed consortium of *Thiobacillus ferrooxidans* for 15 days at 30 - 35°C (CO₂ purge). The CAPTO results from the untreated and treated coal are shown in Figures 3 and 4. The SO₂ evolution profile for the untreated coal shows the presence of temperature maxima for nonaromatic sulfur (290°C), aromatic sulfur (410°C), pyritic sulfur (478°C), and sulfate (590°C). This sulfur profile is consistent with other Illinois No. 6 raw coal samples tested in our laboratory. The SO₂ evolution profile from the treated coal shows that (1) the nonaromatic SO₂ evolution temperature is unchanged and (2) the pyritic sulfur and sulfate have been removed. However, a portion of the aromatic sulfur has been oxidized at 385°C, 25°C below the oxidation temperature of aromatic sulfur in the untreated coal.

The CO₂ evolution profile for the untreated coal (Figure 4) shows temperature maxima for nonaromatic carbon oxidation at 290°C and aromatic carbon oxidation at 420°C. The CO₂ evolution profile for the treated coal shows the oxidation temperature of the nonaromatic carbon to be unchanged, but a portion of the aromatic carbon is oxidized at 390°C, 30°C below that of the untreated coal.

The CAPTO technique is sensitive to changes in coal structure and sulfur content resulting from the bioprocessing of coal.

APPLICATION OF CAPTO TO MOLTEN CAUSTIC LEACHING

A Pittsburgh Seam (ROM) coal (Ohio No. 8) from Belmont County, Ohio was thoroughly mixed with an inorganic diluent, and simultaneously subjected to an oxygen flow and a programmed linear increase in temperature. Pyrite oxidation occurs after the organic sulfur has been oxidized as shown in Figure 5. This sample of Pittsburgh Seam coal was taken from a feed coal used in a molten caustic leaching treatment. The CO₂ and H₂O evolutions are also shown in Figure 5.

The products resulting from two different molten caustic treatments were also examined oxidatively under the same CAPTO conditions as the feed coal. The results are shown in Figures 6 and 7. The molten caustic leached product used to produce the CAPTO results of Figure 6 had been treated with 1:1 KOH/NaOH, 2:1 caustic/coal at approximately 438°C (kiln outside wall temperature). Essentially all of the pyrite and iron sulfate have been removed by the caustic treatment. A small broad SO₂ evolution peak centered at 330°C is present indicating that the nonaromatic/aromatic sulfur content has been significantly reduced compared to that of the feed coal shown in Figure 5.

The molten caustic leached product used to obtain the CAPTO results shown in Figure 7 had been treated with NaOH at a caustic to coal ratio of 2:1 at approximately 415°C (kiln outside wall temperature). Sulfur dioxide from pyrite and iron sulfate do not appear in the profile. The aromatic sulfur has been markedly reduced in this sample; however, a small residual aromatic sulfur evolution centered at 415°C is noted. The nonaromatic sulfur has been removed to a lesser degree and a small SO₂ evolution peak centered at 290°C is noted. These results confirm our earlier findings¹³ that the molten caustic treatment in this temperature range removes more aromatic sulfur than nonaromatic sulfur.

The CO₂ and H₂O evolution profiles have also been recorded and plotted in *Figures 6 and 7*. This information is routinely obtained from the oxidative degradations and provides a route to continuously measure the C/H ratio as oxidation proceeds. Thus, it is of value beyond the C/H ratio obtained simply from total carbon and hydrogen analyses. Note the differences between the CO₂ evolution profiles in *Figures 6 and 7*. A shoulder denoting oxidation of nonaromatic carbon at 310°C is present in *Figure 7*. *Figure 6* (results of treatment at 438°C) shows less nonaromatic carbon compared to the coal treated at 415°C (*Figure 7*). *Figure 7* also shows considerably more water resulting from oxidation of nonaromatic hydrogen than *Figure 6*. The molten caustic product (*Figure 6*) formed at 438°C appears to be much more "charlike" than the product (*Figure 7*) formed at 415°C. One would expect the product formed at 415°C to have better combustion properties than the product formed at 438°C.

Measurement of CO₂ evolved as the oxidative degradation proceeds also helps to better define the point at which the SO₂ produced must be derived from a noncarbon source. The CAPTO technique is sensitive to changes in coal structure and sulfur content resulting from changes in molten caustic leaching conditions.

CAPTO MODEL SYSTEMS

The redesigned CAPTO apparatus utilizes a high oxygen concentration flow. A change in concentration from 10% oxygen in argon to 100% oxygen is associated with an increase in the pyrite oxidation temperature from 430°C to 478°C. While the oxidative selectivity between the two major occurrences of CO₂ and SO₂ from organic carbon and sulfur has been retained, the oxidation temperatures have decreased. Additionally, one must expect that the oxidation temperatures of standards and model systems originally used to establish a correlation between their oxidation temperatures and the oxidation profile of coals will change. Accordingly, the key standards and model systems are being oxidized under the new conditions. The oxidation results obtained to date are compared in *Table 1*. The SO₂ evolution temperatures of the model systems under the new conditions are consistent with the coal assignments.

CONCLUSIONS

Using high oxygen concentrations, the CAPTO SO₂ evolution peaks due to the oxidation of the aromatic and pyritic sulfur are sufficiently resolved so that small differences in the amounts of nonaromatic, aromatic, and inorganic sulfur may be detected. This is important for use of CAPTO in selecting those coals which have the greatest upgrade potential when subjected to new or existing sulfur removal technologies.

The improved resolution may also be sufficient for CAPTO to be used as a one step direct determination of organic, inorganic and total sulfur. We are presently completing extensive quantitative studies to assess the feasibility of this determination.

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Table 1
SULFUR DIOXIDE EVOLUTION TEMPERATURES
OF COALS AND MODEL SYSTEMS

COAL/MODEL SYSTEM	TEMPERATURE, DEGREE C AIR 2	TEMPERATURE, DEGREE C AIR 2
Illinois No. 6 (ROM)	330	295
Nonaromatic	470	420
Aromatic	470	470
Pyritic	430	485
Sulfate	-	585
Pittsburgh Seam (Ohio No. 8, ROM)	300	300
Nonaromatic	475	420
Aromatic	435	482
Pyritic	430	552
Sulfate	-	592
Pyrite (Water Table concentrate)	620	485
Pyritic	620	580, 595
Sulfate	620	595
Perrone sulfate	620	595
Ferric sulfate	620	595
Polydibenzothophene	540	450
Polythiophene-tetrahydrothophene)	300	290
Nonaromatic	300	475
Aromatic	475	410

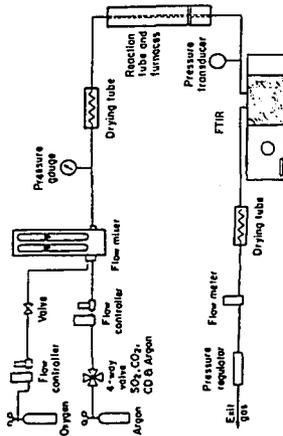


Figure 1. Controlled-atmosphere, programmed-temperature (CAPTD) instrument flow system.

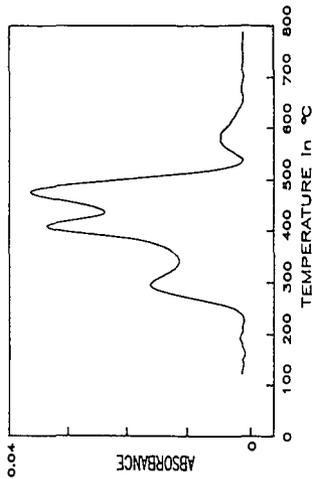


Figure 2. CAPTD evolution profile for sulfur dioxide from Illinois No. 6 ROM coal.

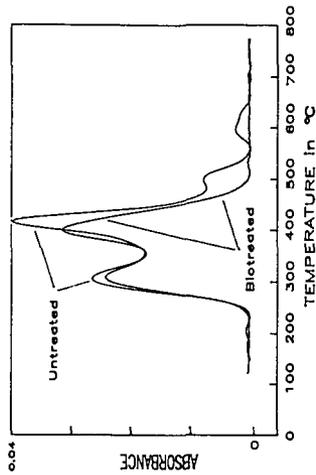


Figure 3. CAPTD evolution profiles for sulfur dioxide from 80 mg of Illinois No. 6 ROM coal (blotreated and untreated).

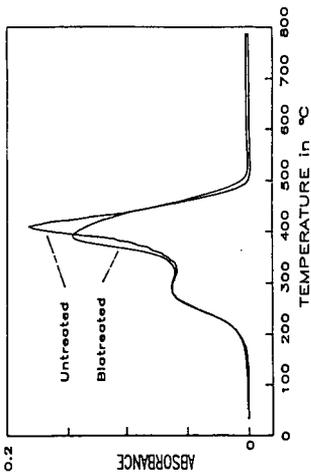


Figure 4. CAPTO evolution profiles for carbon dioxide from 80 mg of Illinois No. 6 ROM coal (biotreated and untreated).

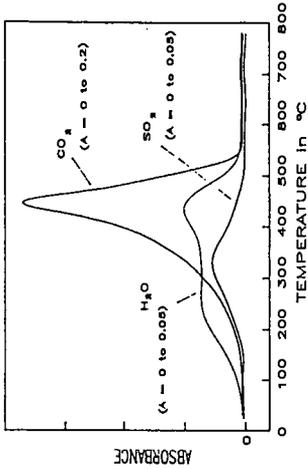


Figure 6. CAPTO evolution profiles from molten caustic treated (436°C) Pittsburgh No. 8 coal.

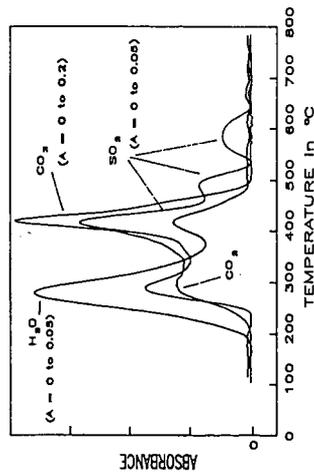


Figure 5. CAPTO evolution profiles from Pittsburgh No. 8 ROM coal (Belmont County, Ohio).

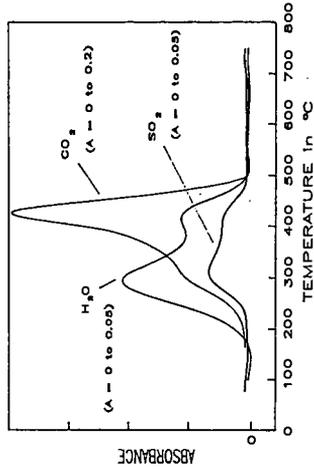


Figure 7. CAPTO evolution profiles from molten caustic treated (415°C) Pittsburgh No. 8 coal.