DESULFURIZATION OF PURE COAL MACERALS

Edwin J. Hippo* and John C. Crelling**

*Department of Mechanical Engineering and Energy Processes and
** Department of Geology, Southern Illinios University,
Carbondale, IL 62901

The objectives of this study were to modify the present density gradient centrifugation (DGC) techniques for coal macerals (1-6) to obtain 10-20 grams of target maceral concentrates and to determine the reactivity or ease of removing the organic sulfur in the various macerals with supercritical methanol extraction. Although the chemistry needed for this objective is not difficult, the accumulation of 10 to 20 gram quantities of "pure" petrographically verified single maceral concentrates has not been possible until now. The results of recent work (7) have demonstrated that the individual macerals can be separated and verified. The accumulation of much larger quantities than have previously been separated was a problem that has been overcome by pre-concentrating target macerals at their density cut points.

Supercritical fluid extraction of coals has previously been reported as a method in the production of liquid fuel products from coal under mild conditions and as a medium for selective desulfurization of coal (8-11). Alcohols are expected to exhibit greater solubility for polar organic molecules due to hydrogen bonding and dipole attractive forces, also providing the opportunity for chemical reactions during the extraction due to the nucleophilicity of the alcohol oxygen and the tendency to act as a hydrogen donor. In addition, enol rearrangements (12) may play a role in desulfurization.

As previously reported (8-9), different supercritical reaction conditions produced different extents of desulfurization of coals (33.9 - 65.7%). These variable desulfurizations are probably a result of differences in extents of conversion of the pyritic sulfur (to various alteration products, such as pyrrhotite), as well as organic sulfur functionalities (thiophenol, sulfide, and thiophenes) to light gases such as dimethylsulfide, hydrogen sulfide, and methylmercaptons.

EXPERIMENTAL

Maceral Separation

In this research, the DGC technique was modified and improved to obtain larger size samples. This was done in two ways. First, the coal was divided into its natural divisions, lithotypes, which are the easily identifiable natural associations of macerals that make up the coal seam. This can be done (and routinely is being done in the SIU-C Maceral Separation Laboratory) by careful hand-picking, or by centrifugation at a particle size (-100 to -200 mesh) that liberates the lithotypes

from each other. Even such similar macerals as pseudovitrinite and normal vitrinite are being successfully separated from each other now in this manner. Second, low frequency maceral phases (those occurring at less than 5% of the whole coal) can be pre-concentrated by centrifugation of bulk quantities (10 grams or more) at the density cut-off points for the target macerals. This procedure results in fractions which are enriched in the target maceral relative to the whole coal and allows relatively larger amounts of pure macerals to be obtained much more easily than starting with the raw coal. These pre-concentrated feedstocks are then subjected to the DGC technique.

Target macerals for this study include sporinite, vitrinite, pseudovitrinite, semifusinite and fusinite. These are the major maceral components which contain significant organic sulfur. Resinite and cutinite were not studied because the abundance of these macerals is low in Illinois coals and they contain relatively low concentrations of organic sulfur.

Desulfurization

The desulfurization of coal by supercritical methanol extraction was carried out in a microautoclave system (11) that consists of a 10cc stainless steel microautoclave linked to a metering valve and a quick disconnect fitting with high pressure tubing. The reactor system is attached to an automatic shaker, which is supported above a fluidized sand bath. The shaker allows the autoclave to be agitated during reaction to ensure uniformity of reaction. The fluidized sand bath is controlled using an Omega temperature controller to ensure temperature stability. The normal charge in the reactor consisted of 1 gram of coal and 2 grams of methanol. After reaction the solid residues were removed from the reactors and ground and then dried in a vacuum oven at 95 degrees Celsius for approximately 90 minutes. The total sulfur was then determined for all the solid residues.

Samples

The three coals used in this study were taken from the Illinois Basin. They include: 1) SIU 1386, from the Herrin No. 6 seam; 2) SIU 647J, from the Brazil Block seam; and 3) SIU 1749, a wash plant mixture of Illinois No. 5 and No. 6. All three coals are high-volatile bituminous in rank with standard vitrinite reflectances of 0.42, 0.49, and 0.79 % respectively. The maceral analysis reveals that coals #1 and #3 are typical midwestern coals composed mainly of vitrinite (82.7 and 85.4 %), while coal #2 has much higher liptinite (11.6 %) and inertinite (22.7%) contents.

RESULTS OF ANALYSIS

Effects of KOH

Prior to standardization the 5% KOH loading was tested against known KOH addition. At low-severity (350 degrees

Celsius, 60 minutes) the presence of KOH shows a slight positive effect on sulfur removal. Under slightly more severe conditions (450-500 degrees Celsius, 30 minutes) the difference between sulfur removal and tests with and without KOH addition increases. The sulfur removals under high-severity conditions (500 degrees Celsius, 60 minutes) shows either no effect or a negative effect of KOH addition. In many cases sulfur removals decrease as reaction times are increased from 30 to 60 minutes. These patterns are independent for the three coals studied and the preparation the coal receives. However, the extent of the reduction is coal dependent. Coal 1 and 2 show a slight reduction in sulfur removal, whereas, coal 3 gives large amounts of sulfur incorporation. This phenomena has been observed previously by Murdie (11). The incorporation is short-lived at moderate-severity and is difficult to pinpoint. At higher severity conditions the degree of incorporation may be permanent. The severe incorporation noted with coal 3 may be experimental coincidence in obtaining the maximum incorporation at the specified temperatures. However, coal 3 did show a consistent linear decrease in sulfur removal as a function of reaction time at 500 degrees Celsius. At 15 minutes reaction time 65% sulfur removal was obtained. At 60 minutes reaction time 6% sulfur removal was obtained. Although incorporation reactions complicate data interpretation, the increase sulfur removals in the presence of KOH were significant enough to standardize on this operation procedure. Thus, most of the data reported is for 5% KOH loadings.

Effects of Sample Preparation

Under mild-severity, micronized coal is less reactive than -60 mesh coal. At moderate-severity the micronized coal tends to be slightly more reactive than the -60 mesh size fraction of the same coal; and at high-severity the micronized coal is substantially more reactive than the -60 mesh size fraction of the same coal.

The data imply that slight oxidation in the fine coal particles retards desulfurization under mild conditions, but mass transport effects are more significant at high- severity. Retardation of sulfur removal under mild desulfurization conditions may be the result of surface oxidation of pyrite particles or oxidation of freshly exposed coal surfaces. The surface oxide on pyrite particles would be expected to be less susceptible to desulfurization at low temperatures. However, at higher temperatures the sulfates would be expected to decompose to SOx. Sulfur incorporation is more likely to occur at elevated temperatures. The micronized particles allow the product less time to react with components on the pore walls than -60 mesh particles. Thus, micronization reduces the chance of incorporation during the process of product diffusion to the bulk gas. Thus, higher sulfur removals can be observed in the micronized samples. On the other hand, when conditions in the bulk gas favor sulfur incorporation, the smaller particle size of the micronized coal will enhance sulfur incorporation.

Figure 1 demonstrates the effect of the trend in sulfur removal as a function of sample preparation. These results are typical of high-severity SME processing and reflect trends in maximum sulfur removal. The data are reported for samples prepared from coal 1, but the trend is also applicable for sulfur removals from coals 2 and 3. Less sulfur is removed from the -60 mesh size fraction than is removed from the micronized coal; less sulfur is removed from the micronized coal than is removed from the micronized/ demineralized coal; and less sulfur is removed from the micronized/demineralized coal than is removed from the micronized/demineralized/ cesium chloride-floated coal. These data reflect trends that are applicable for all process conditions studied at or above 450 degrees Celsius. The patterns are also independent of the sulfur incorporation phenomena. In other words, if sulfur incorporation is observed for a condition, the magnitude of the incorporation appears to be independent of the sample preparation.

Figure 2 shows sulfur removal under 500 degrees Celsius and 60 minutes reaction time for vitrinite and sporinite maceral concentrates of coal 2. Sulfur removal in the vitrinite and sporinite concentrates are substantially higher than sulfur removal in the micronized coal or the sample prepared by a 1.6g/ml floatation process. The vitrinite and sporinite concentrates contain 86% of the total organic sulfur in the coal. Assuming that none of the sulfur in the other macerals is removed, the results on the vitrinite and sporinite concentrates suggests that 65% of the organic sulfur should be removed in the micronized or floated samples. Since both the float and maceral concentrates contain about the same amount of cesium introduced during the preparation process, catalytic desulfurization effects can be eliminated as a cause for the high desulfurization rates in the maceral concentrates. Thus, the data suggests that other macerals inhibit sulfur removal or trap products of the desulfurization process.

Figure 3 depicts sulfur removal of maceral concentrates at milder experimental conditions. Similar trends are observed. Namely, vitrinite and sporinite concentrates evolve more sulfur than whole or floated coals. Thus, sulfur removals in the vitrinite and sporinite occur at a faster rate as well as reaching a higher maximum. Not enough tests have been conducted on the maceral concentrates to judge sulfur incorporation tendencies.

Figure 3 also contains data for one test conducted on the vitrinite concentrate of coal 1 at a high-severity condition. The sulfur removal in the vitrinite concentrate was found to be higher than the sample prepared by sequential micronization, demineralization, and floatation. The difference in sulfur removal between the maceral concentrate and the floated sample is not as great as the equivalent tests on samples prepared from coal 2. However, the vitrinite concentration in coal 1 is substantially higher than in coal 2. Therefore, the float sample from coal 1 would be expected to be similar to the vitrinite concentrate. The 5% lower sulfur removal in the float sample

indcates a large sensitivity in sulfur removal with variations in maceral concentration.

CONCLUSIONS

The modified DGC method employing a pre-concentration of macerals at specific density cut-points allows for accumulation of a sufficient quantity of pure maceral concentrates for testing the desulfurization properties of individual macerals. The concentration of 10gm aliquots of pure maceral concentrates represents a new advance in coal separation technology. This is the first time that such large quantities of pure macerals have been segregated by any technique.

The conditions under which samples are tested are extremely critical to the extent of sulfur removal. In general, increased temperature increases desulfurization. Also, sulfur removal increases with longer reaction times. The presence of KOH enhances the rate of sulfur removal. Sulfur can be reincorporated from sulfur-containing gaseous products, and KOH enhances the sulfur reincorporation. Some of the sulfur removal may be retarded by incorporation of products during diffusion of product gases through the pore system of the residual coal. Thus, very fine particle sizes are desirable for chemical desulfurization.

The type of sample preparation affects sulfur removal. In general, particle size reduction increases sulfur removal. Demineralization results in increased sulfur removal in subsequent processing. Variations in sulfur removal due to variations in coal properties are observed for the micronized and demineralized coals.

The demineralized coals contain pyrite. Pyrite is removed by floatation at a 1.6gm/ml solution. Floatation produces a very clean coal that is more reactive than the demineralized coal. For float samples, approximately the same maximum desulfurization level is obtained independent of desulfurization process and coal properties.

The float samples demonstrate that organic sulfur is more amenable to desulfurization than was previously thought.

Since high levels of sulfur removal are obtained during pyrolysis, the sulfur removals reported are not an artifact of sample dilution. Furthermore, either pyrite is less reactive than the organic sulfur or the pyrite (or derived products of pyrite) aid in sulfur incorporation reactions. The results suggest the thermal-chemical desulfurization should be preceded by a thorough physical cleaning that removes both pyrite and other coal minerals.

Finally, the main objective of this study was to investigate the desulfurization behavior of individual coal macerals. The sporinite and vitrinite concentrates are more reactive towards desulfurization processes than any of the other

materials that were studied. They also gave the highest desulfurization levels. Since they are more reactive than whole coals or floated samples, the other constituents in the coal matrix must reduce sulfur removals. This phenomena has not been reported previously. It implies that the inertinite macerals may behave in a manner similar to activated charcoal and chemically absorb copious amounts of sulfur during the desulfurization processes. The practical result of this phenomenon is that selection of coals on the basis of maceral composition could be necessary to optimize thermal-chemical desulfurization. Work in this area is continuing at Southern Illinois University at Carbondale.

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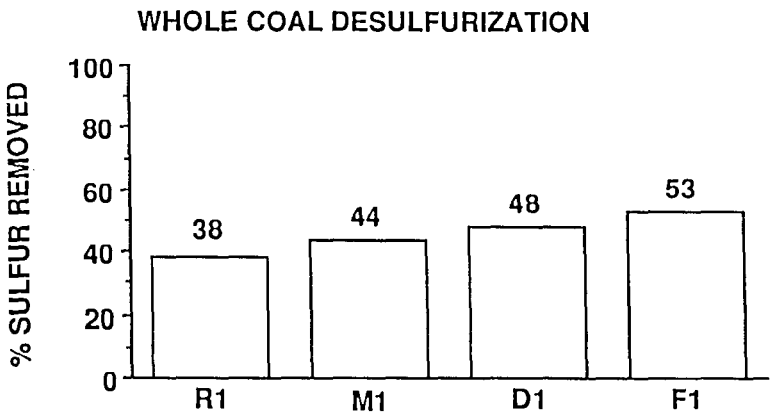

Figure 1. Typical results from a single coal sulfur removal with supercritical methanol extraction at 450 degrees C for 30 minutes showing the effects of pretreatment of the sample. (R = raw, M = micronized, D = micronized and demineralized, F = micronized, demineralized, and floated at 1.6 gm/ml.)

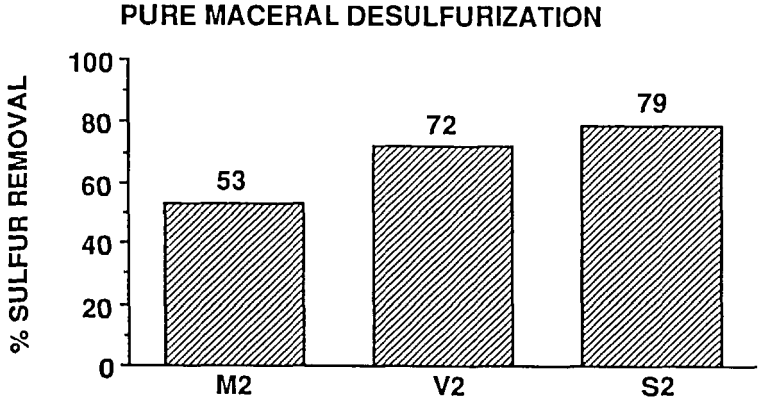

Table 2. Results of sulfur removal with supercritical methanol extraction (SME) on pure maceral fractions from the same coal sample at 500 degrees C for 60 minutes. (M = micronized coal, V = vitrinite, S = sporinite.) It should be noted that the high sulfur removals represent the removal of organic sulfur. Pyritic and sulfate sulfur have been removed earlier.

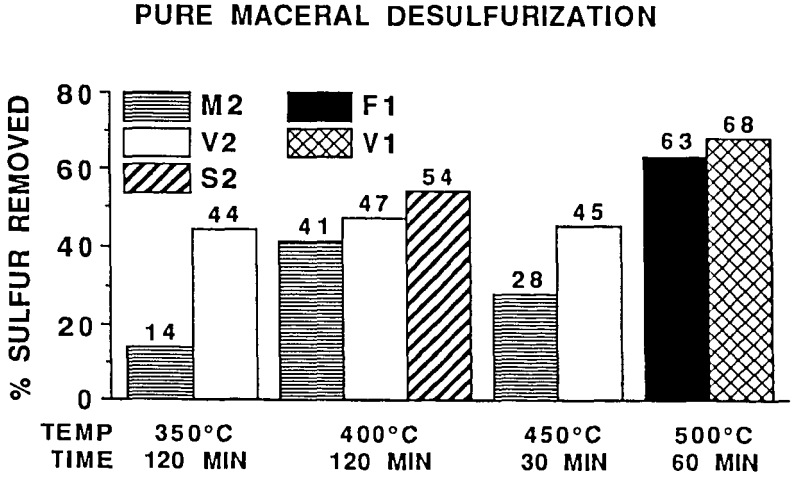

Table 3. Results of sulfur removal with supercritical methanol extraction on pure maceral concentrates. In all cases more sulfur is removed from the macerals than the micronized and/or floated coal. (M2 = micronized coal #2, V2 = vitrinite from coal #2, S2 = sporinite from coal #2, F1 = floated coal #1, and V1 = vitrinite from coal #1.)