

PITCH RESIDUES FROM UPGRADING OF BITUMEN AND HEAVY OILS AS ADDITIVES IN COKE MAKING:
INFLUENCE OF PITCH PROPERTIES

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INTRODUCTION

Impending shortages of good coking coals throughout the world have prompted a series of investigations at CANMET (Canada Centre for Mineral and Energy Technology) into the utilization of western Canadian marginal coking coals in the production of metallurgical grade coke. One possible way to do this is to add residual pitch from thermal hydrocracking of bitumen and heavy oils to such coals (1). This pitch has been found to be an excellent additive for up-grading low fluid, low volatile, inert-maceral rich coals. The pitch acts as a fluidity-enhancing agent, and by interacting with the vitrinite of the coal, augments the supply of reactive carbon necessary for bonding together of inert macerals.

The purpose of this publication is to add further insight into the role of pitch in carbonization of coal/pitch blends. Pitches derived from thermal hydrocracking of bitumen at different degrees of severities were utilized for this purpose. This provided a means of assessing the properties of the pitches in the carbonization process without changing the basic chemical nature of the parent material.

EXPERIMENTAL

The properties of the pitches derived from thermal hydrocracking of Athabasca bitumen under various operating conditions are given in Table 1. These four pitches were produced under different degrees of severity during the process A being characteristic of pitch obtained under relatively mild conditions and D, of pitch obtained at high severities. A relation was found to exist between the degree of severity during hydrocracking and the various properties listed in Table 1 (e.g. CCR, aromaticity, softening point).

TABLE 1
Physical and Chemical Properties of Pitches

		Pitch			
		A	B	C	D
Volatile matter	%	73.1	64.8	53.5	44.6
Ash	%	1.8	2.3	3.2	5.8
Softening temperature	°C	50	95	105	135
Conradson carbon residue	%	34.7	42.2	50.7	64.6
Specific gravity		1.10	1.13	1.16	1.24
Benzene-insolubles*		2.6	4.2	11.6	20.6
Asphaltenes	%	37.2	44.6	48.1	55.2
H/C		1.32	1.19	1.09	0.94
Sulphur	%	5.58	5.63	6.33	4.85
Aromaticity**	%	38.2	49.4	56.3	69.8

* Ash-free basis, ** ¹³C NMR analysis

The coal used was a western Canadian, low fluid, high rank bituminous coal having a relatively high concentration of inert macerals. Proximate, ultimate and petrographic analyses of this coal are given in Table 2.

TABLE 2

Properties of the Coal

<u>Proximate Analysis</u>		(dry basis)
Ash	%	9.8
Volatile matter	%	21.2
Fixed Carbon	%	69.0
<u>Ultimate Analysis</u>		
Carbon	%	78.9
Hydrogen	%	4.3
Sulphur	%	0.8
Nitrogen	%	1.3
Oxygen (by diff.)	%	4.9
Ash	%	9.8
<u>Petrographic Analysis</u>		
Vitrinite	vol. %	51.8
Semi-fusinite	vol. %	34.2
Fusinite	vol. %	11.2
Micrinite	vol. %	2.6
Exinite	vol. %	0.2
Mean reflectance in oil, R_o		1.17

Coal/pitch blends with varying pitch concentrations were prepared and their fluidities determined by means of a Gieseler plastometer. The fluidities of the various blends are reported in Table 3. A value representing the concentration of pitch which can potentially interact with the coal during carbonization, C_p , is also given in Table 3. C_p was calculated on the following basis:

$$C_p = \left(\frac{\text{Concentration of pitch}}{\text{in the coal-pitch blend}} \right) \times \left(\frac{\text{wt. \% CCR in}}{\text{the pitch}} \right) \quad 1)$$

where CCR is the Conradson carbon residue (2) and approximates the contribution of carbonaceous material made by the pitch to the blend during carbonization.

The various coal/pitch blends were carbonized using a canister coking technique developed at CANMET (3). The blends were packed to a bulk density of 801 kg/m³ into perforated tin plate canisters 29.3 cm long and 7.6 cm in diameter. Twenty cans, each containing a different blend were side-charged into CANMET's 250-kg moveable wall coke oven.

The relative strengths of the cokes produced from the canister test were determined by a small sample tumbler test developed by Bituminous Coal Research (BCR) (4) and are reported in Table 3. These strength indices are a measure of size reduction in tumbled coke particles and therefore a large index corresponds to a weak coke.

Optical examinations of the various cokes were made with a Leitz reflected light microscope using an oil immersion lens. The micrographs were taken at 600X magnification using partially crossed nicols.

TABLE 3

Carbonization Data for Coal Pitch Blends

		Concentration of Pitch in Blend wt %					
		0	5	8	10	14	16
<u>Pitch A</u>							
Contribution of carbon from pitch, C_p	%	Nil	1.5	2.4	3.1	4.1	4.7
Fluidity of blend	dd/min	Nil	1.9	6.1	6.4	36	28
BCR* strength index		N/A**	49.0	36.4	38.2	37.4	38.1
<u>Pitch B</u>							
Contribution of carbon from pitch, C_p	%	Nil	2.1	3.3	4.1	5.7	6.6
Fluidity of blend	dd/min	Nil	1.5	5.7	7.1	120	530
BCR* strength index		N/A**	53.8	35.3	34.5	37.3	35.8
<u>Pitch C</u>							
Contribution of carbon from pitch, C_p	%	Nil	2.6	4.1	5.0	7.1	8.2
Fluidity of blend	dd/min	Nil	1.1	5.0	13.0	370	400
BCR* strength index		N/A**	52.7	36.7	36.9	39.0	40.3
<u>Pitch D</u>							
Contribution of carbon from pitch, C_p	%	Nil	3.3	5.2	6.5	9.1	10.4
Fluidity of blend	dd/min	Nil	1.0	4.0	6.8	260	1150
BCR* strength index		N/A**	57.8	43.1	35.1	41.3	45.1

* Bituminous Coal Research Inc., Pittsburgh, P.A.

** A non-agglomerated char was produced

RESULTS AND DISCUSSION

A photograph showing two representative cokes from the canister test is shown in Fig. 1. The coke shown at the top was produced from coal with no pitch additive and was poorly agglomerated. The coke at the bottom was agglomerated and hard and was typical of cokes produced from coal/pitch blends. The former coke could not be evaluated by the BCR tumbler test because of its non-agglomerated character. The strength indices of the cokes produced from coal/pitch blends are given in Table 3.

The strengths of the cokes produced from blends containing pitch A and pitch B were not found to vary significantly for pitch concentrations above 5%. On the other hand, additions of more than 10% pitch in coal/pitch C and coal/pitch D blends were found to be detrimental to coke strength. The influence of pitch concentration on coke strength was therefore more pronounced for pitch obtained from high severity thermal hydrocracking runs. It would be difficult to predict an exact optimum pitch concentration based solely on the results reported in Table 4 for coal/pitch D blends.

Coal/pitch blends having C_p values in excess of about 7% produced cokes of progressively weaker strengths. The Conradson carbon residue (CCR) contents of pitches A and B were sufficiently low to permit additions of up to 16% pitch to the coal without C_p values of the blend exceeding 7%. This would account for the lack of a minimum in BCR strength index for cokes produced from blends containing pitch

A and pitch B within the concentration range investigated.

Fluidity data for the various blends are summarized in Table 3. A marked increase in the fluidity of the blends was observed for pitch concentrations greater than 10%. The increase in fluidity was generally found to be more pronounced for pitch obtained from high severity thermal hydrocracking runs. This perhaps suggests that there is a better interaction between pitch and the vitrinite of the coal in cases where the pitch was treated under more severe conditions during thermal hydrocracking. It is evident from Table 1 that pitch aromaticity is directly related to the degree of severity during thermal hydrocracking. The interaction between the pitch and the vitrinite may therefore be related to the aromaticity of the pitch:

Based on some of the arguments presented above, the following relationship was found to be consistent with the data in Table 3:

$$\text{BCR strength index} = 26.47 + 1.75 C_p \exp \frac{0.97}{A^{3/2} F}; \quad 1.5 \leq C_p \leq 10.4 \quad 2)$$

Where C_p is defined according to Equation 1), A is the aromaticity of pitch determined by ^{13}C NMR and F is the fluidity of the coal/pitch blend. Equation 2) is plotted in Fig. 2 and was found to have a coefficient of correlation of 0.89.

According to Equation 2), the BCR strength index of a coke produced from a coal/pitch blend is not only dependent on the value of C_p , but also on the fluidity of the blend. Low values of C_p in the blend appear to be desirable in achieving good coke strength provided the fluidity of the blend is sufficiently high to make the exponential term in the equation approach unity. Once the exponential term has approached unity, additional increases in C_p may only contribute to a deterioration in coke strength. The inter-relationship between C_p and fluidity borne out by Equation 2) emphasizes the need for controlled fluidity in ensuring a uniform and efficient distribution of the binding material throughout the coal during carbonization. This is demonstrated, for instance, in the case of 5% addition of pitch D to the coal, Table 3. Although the C_p value was relatively high, low fluidity prevented proper distribution of the binding material in the coal during carbonization; consequently, a weak coke was produced.

In order to confirm this dependence on fluidity, a series of microscopic examinations was made on the cokes produced from the canister test. The coke produced from the coal with no pitch additive was found to be poorly bonded. Inert macerals were segregated within the coke structure with little or no binding material surrounding them (Fig. 3). Coal/pitch blends produced cokes of varying qualities depending on values of C_p and fluidity. Three specific cases were chosen to demonstrate this dependence: (i) coal + 5% pitch D, (ii) coal + 10% pitch D and (iii) coal + 16% pitch D.

In case (i), coal + 5% pitch D, some degree of bonding was observed between inert macerals, but the bonding was generally discontinuous and sporadic. This is exemplified for instance in Fig. 4. It is noteworthy that for blends having similar C_p values but higher fluidities, e.g. coal + 10% pitch A, bonding was found to be considerably more uniform than that shown in Fig. 4. The difference in bonding can therefore be attributed to the fluidity of the respective blends.

The coke produced from case (ii), coal + 10% pitch D, was found to exhibit excellent bonding. The binding material was uniformly and continuously distributed throughout the coke and the inert macerals were embedded within the coke matrix, Fig. 5. These observations were consistent with the relatively good BCR strength index obtained for this coke.

The deterioration in coke strength observed for case (iii), coal + 16% pitch D, was attributed to the development of micro-cracks within the coke structure, Fig. 6. The mechanism by which these cracks form is not well understood, but could perhaps result from an excess of binding material between the inert macerals of the coal, thereby weakening the overall structure.

From the three cases considered, it is evident that coke strength can be correlated to the micro-structure of the cokes. The coke quality appears to be a complex function of the amount of pitch added, the physico-chemical properties of the pitch and the fluidity of the coal/pitch blend.

It should be emphasized that the arguments presented in this paper apply specifically to inert-maceral rich, low fluid, high rank coals. Equation 2) has so far only been tested for this particular type of coal. It is possible that other coals may yield results that do not conform exactly to this equation. For instance, the coal used in this work had no inherent fluidity, and consequently a term for the fluidity of the coal itself does not appear in the equation. However Equation 2) does demonstrate the strong inter-relationship between the contribution of binding material made by the pitch and the fluidity of the blend.

CONCLUSIONS

High rank coals from western Canada which are rich in inert macerals, generally require a pitch additive to produce metallurgical grade coke. Pitch concentration in the coal/pitch blend dictates both the amount of binding material made available to the coal and the fluidity of the blend. Both these parameters depend on the physico-chemical properties of the pitch and on the extent of interaction between the pitch and the coal.

In order to produce good quality coke from a coal/pitch blend, the blend must possess sufficient fluidity to ensure a uniform and continuous distribution of binding material throughout the coal. Inert macerals of the coal must be adequately wetted and bonded together. Optimum coke strength is achieved when pitch is added in sufficient amount to generate a controlled fluidity with enough binding material to agglomerate the coke. If added in large amounts, the pitch can have deleterious effects on the resultant coke. The reason why too much pitch weakens the structure is not well understood, but appears to be related to the development of microcracks within the coke matrix.

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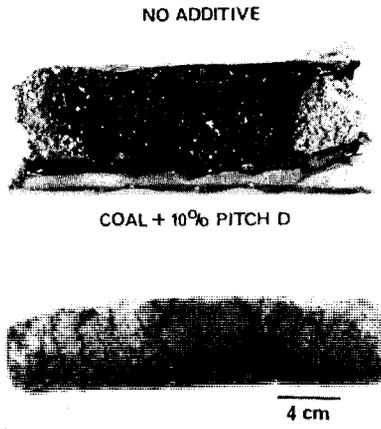


FIGURE 1: High Temperature Cokes Produced From Canister Tests

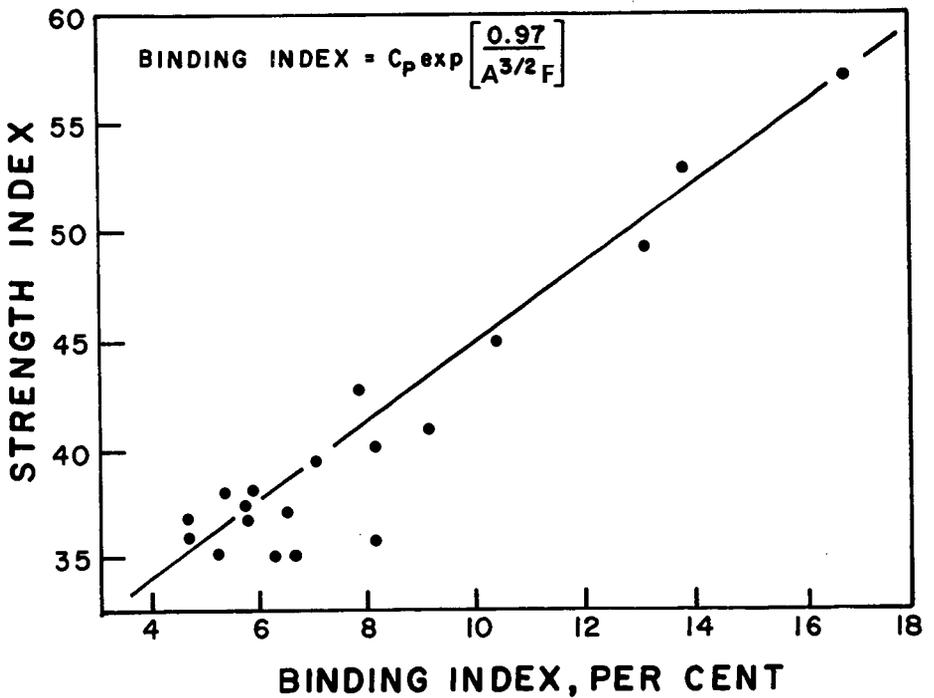


FIGURE 2: Relative Strength Indices for Various Coal/Pitch Blends

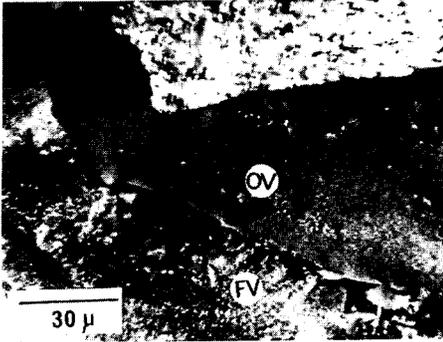


FIGURE 3: Optical Micrograph of Coke Produced from Coal With No Additive Showing Poor Bonding Between Fused Vitrinite (FV) and Oxidized Vitrinite (OV)

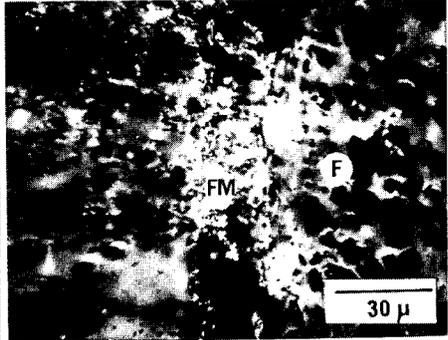


FIGURE 4: Optical Micrograph of Coke Produced from Coal + 5% Pitch D Showing Discontinuous Bonding of Fused Mass (FM) With Fusinitic Structure (F)

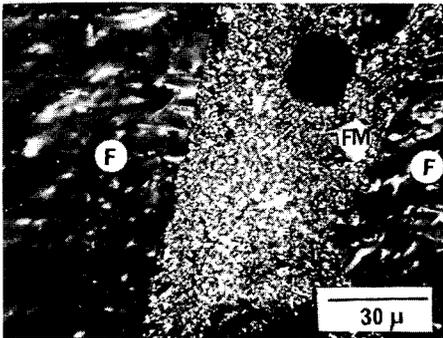


FIGURE 5: Optical Micrograph of Coke Produced from Coal + 10% Pitch D Showing Excellent Bonding of Fusinitic Structure (F) by Fused Mass (FM)

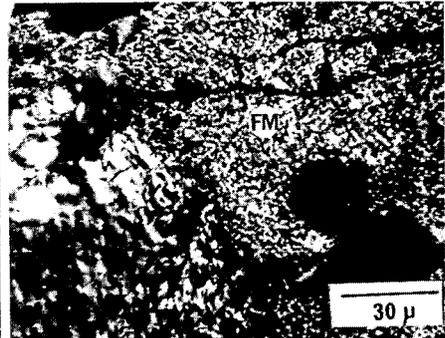


FIGURE 6: Optical Micrograph of Coke Produced From Coal + 16% Pitch D Showing Development of Microcracks Within Fused Mass (FM)

SYNTHETIC FUELS - PITFALLS AND PROMISE. Fred Schulman. Energy Systems Technology Corp., 927-15th St., N.W., Washington, D.C. 20005

Technical process improvements and policy restraints on OPEC's ability to increase oil prices at will are two essential components of a viable synthetic fuels industry. One without the other spells frustration and failure. The Arab oil embargo of 1973-74 and the subsequent five-fold increase in petroleum prices led to multibillion dollar programs to develop synthetic fuels. Expectations of a great new synthetic fuels industry were unfulfilled as prices and costs rose toward their equivalent-value-to-oil. Cost differentials in favor of imported oil continue to increase year by year despite many chemical and engineering innovations. For example, estimated costs of producing shale oil rose from \$7 per bbl in 1973 to \$30/bbl today. When the OPEC cartel raised oil prices another 54% last June, it became even more important to encourage domestic oil production and to develop energy alternatives. OPEC's new prices will force the base price of synthetic fuels to rise to \$46-50 by 1983. Rising feedstock costs imperil the domestic petrochemical industry and endanger chemical exports. This paper details some of these problems and suggests a number of energy policy actions aimed at establishment of the domestic fuels industry on a sound basis.

Development of a Simulated Catalyst Aging Technique

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INTRODUCTION

Under hydrocracking conditions, heavy oils produce deposits that accumulate on the catalyst surface. By poisoning and by hindering accessibility of the active sites, these deposits cause fouling of the catalyst. Material that is so deposited is either originally present in the feed, such as heavy metals and minerals, or is formed during hydrocracking, such as coke. Not all deposits deactivate the surface at the same rate. It was established by repeated regeneration that rapid fouling under typical bitumen hydrocracking conditions is caused primarily by coke formation (1). To obtain a longer-lasting formulation, catalyst development should therefore focus on types that resist coke formation. Such an effort would involve a systematic approach to catalyst production based on information obtained in aging tests.

To determine the true aging characteristics, actual processing conditions must be maintained because they affect product formation and thereby also the process of deactivation. However, a serious disadvantage of aging tests under actual processing conditions is that they are slow and thus consume a great deal of time and manpower. The time involved becomes critical if aging characteristics are required for a large number of catalysts. It is the purpose of this report to describe a technique that simulates catalyst aging and provides preliminary information in a much shorter time.

EXPERIMENTAL EQUIPMENT AND MATERIALS

A bench-scale fixed-bed reaction system was used, in which the bitumen mixed with hydrogen flowed up through the catalyst bed continuously. Liquid and vapour were separated in receiver vessels. The equipment was previously described in detail (2) but the following modifications were made to accommodate the particular requirements of the present study (3):

1. Bitumen was stored in a heated hopper from which it could be fed through taps into two 1000-mL burettes in a heated plastic cabinet. With a light positioned behind the cabinet and the inside of the cabinet heated to about 75°C, it was possible to monitor the feed level in the burettes. A Milton Roy "Constametric" pump, model number TCP 43-43 TJ, was used to feed the bitumen through heated lines into the reactor. A pressure gauge was placed at the pump outlet to monitor pressure at the pump head.
2. To reduce the reactor volume, a stainless steel insert was machined to fit it, reducing the inside diameter to 1.27 cm from 2.54 cm but maintaining length at 30.5 cm.

The catalyst selected for comparative runs was a commercial type Harshaw O603T with 3 wt % CoO and 12 wt % MoO₃ supported on alumina in the form of cylindrical 3.2-mm pellets. About 150 g of this catalyst represented a full reactor load but only about 30 g could be loaded with the insert. The rate of aging was evaluated using Athasbasca bitumen obtained from Great Canadian Oil Sands Limited at Fort McMurray, Alberta. Properties of the feedstock are listed in Table I.

TABLE I

Properties of Athasbasca Bitumen

Specific gravity	1.009 (15/15 ^o C)	Benzene insolubles	0.72 wt%
Sulphur	4.48 wt%	Carbon	86.36 wt%
Ash	0.59 wt%	Hydrogen	10.52 wt%
Conradson Carbon Residue	13.3 wt%	Nitrogen	0.45 wt%
Pentane insolubles	15.5 wt%	Pitch (525 ^o C+)	51.5 wt%

OPERATING CONDITIONS

The conditions that affect catalyst deactivation in a continuous flow system are temperature, hydrogen pressure, hydrogen flow rate and liquid space velocity. The hydrocracking process consists of a number of complex reaction steps, initially involving various constituents of bitumen. Catalytic processes on active surface sites participate in some of the reaction steps.

Although it would be difficult, because of complexity of the reactions, to predict accurately the impact of changes of any processing condition, some overall effects can be derived from the fundamentals of reaction kinetics. The rate of individual reaction steps varies with temperature and concentration of reactants. Cracking reactions are endothermic and accelerate with increasing temperature, whereas hydrogenation reactions accelerate with increasing hydrogen pressure. Coke formation depends on the rates of cracking and dehydrogenation, followed by polymerization. Therefore coke formation accelerates with increasing temperature and decreasing hydrogen pressure.

The conditions for "simulated aging" were chosen by performing a series of screening experiments to investigate the effect of variations in space velocity and temperature. The effect of hydrogen pressure on catalyst aging was studied previously using a different experimental system (4). In the present study, the hydrogen pressure was maintained constant at 13.9 MPa for all tests, which is within the practical range for hydrocracking. A satisfactory effect could not have been achieved by varying only space velocity; an increase in temperature was also necessary to reduce aging time sufficiently. After some preliminary experimentation, optimum deactivation conditions were found to prevail with a space velocity of 5 h⁻¹ and at a temperature of 495^oC.

The following series of tests under different operating conditions are documented in the present report:

Series 1

True or base deactivation rates were measured at 450^oC and at a liquid volumetric space velocity of 1 h⁻¹ based on the reactor volume packed with the catalyst pellets. The corresponding feed rate was 152 mL h⁻¹ as no insert was placed in the reactor. The hydrogen flow rate was maintained at 35.6 cm³ s⁻¹ at STP. This test is referred to as true aging and was run continuously for 56 hours, and then periodically in five - to eight-hour intervals, totalling about 200 hours in all. Analyses were performed on samples of the liquid product accumulated in two to five hours of operation.

Series 2

High space velocity tests were performed under the same conditions as for true aging - 13.9 MPa, 450°C, and without insert - except for a different arrangement of space velocities. Catalyst aging was carried out in two 12-hour periods during which space velocity was maintained at 5 h⁻¹, and the hydrogen flow at 95 cm³ s⁻¹ at STP. The level of activity, initially and after each 12-hour period was determined by changing the space velocity to 1 h⁻¹, the hydrogen flow to 35.6 cm³ s⁻¹ at STP for two hours and analyzing the liquid sample that accumulated during these two hours.

Series 3

Simulated deactivation rates were measured at high temperature and high space velocity. This test was run at 495°C and a liquid volumetric space velocity of 5 h⁻¹. The insert was placed in the reactor and the corresponding feed rate was 181 mL.h⁻¹. The hydrogen flow rate was maintained at about 70 cm³ s⁻¹ at STP. The series was referred to as simulated aging and was run continuously for 32 hours. The liquid product that accumulated during each hour of operation was withdrawn for analysis.

Series 4

A link between simulated aging and true aging was sought by additional tests in the following manner. The simulated aging conditions were applied for a period of time and were then changed to match the true aging conditions for approximately two hours during which two liquid samples were obtained. The run was then terminated, the reactor re-loaded with a fresh catalyst, and the test was repeated for a different time period under simulated aging conditions. Three different time periods - 2, 4 and 6 hours, respectively - under simulated aging conditions were examined. No insert was placed in the reactor and the simulated aging test was run at 495°C with the feed₃ rate of 760 mL.h⁻¹, space velocity of 5 h⁻¹, and the hydrogen flow rate at 70 cm³ s⁻¹ at STP.

Several processing conditions were applied differently in each series of tests. For instance, in Series 2, the space velocity was five times greater than in Series 1, whereas the gas flow rate was only about three times greater. In Series 1, the gas flow:feed ratio was lower than in Series 3, but higher than in the simulated aging in Series 4. In addition, the length:diameter ratio was increased in Series 3 by placing the insert in the reactor, thereby increasing the linear velocity:space velocity ratio through the catalyst bed. The use of the insert and varying flow regime resulted from experience with the experimental system and facilitated smooth operation. The changes made were necessary to prevent the reactor plugging and to maintain temperature profiles within the catalyst bed.

The impact of increasing temperature and space velocity is discussed in the next section of this report. Variations in hydrogen flow are not considered significant for the purpose of this investigation, because an excess of hydrogen was used in all experiments and because hydrogen flow seemed to exhibit only a small effect on product formation (5).

RESULTS AND DISCUSSION

True Aging

The deactivation pattern is shown in Fig.1 in terms of an increase in the specific gravity of the liquid product and an increase in its sulphur content. It can be predicted by extrapolation that further deactivation would

be recorded beyond 200 hours of operation. However, it can be seen that deactivation is more rapid in the early stages of the test than in the later stages. Since deactivation decelerates with time, the curves in Fig.3 may eventually level off, indicating a constant activity. The decelerating deactivation is in agreement with results of a previous study which also showed that this leveling-off is relatively more pronounced and takes place earlier with increasing hydrogen pressure (4). Whether a state of constant activity in fact exists is not known as the patterns in Fig.1 cannot be extrapolated with any precision. Furthermore, tests carried out continuously for longer than 200 hours of operation are necessary to determine deactivation patterns that are unaffected by start-up and shut-down procedures. These long-term tests are to be performed on a special testing system presently under construction.

High Space Velocity

The results of the high space velocity tests included analytical data on liquid product samples obtained for both high and base space velocities of this series. The results for the base space velocities served as a measure of deactivation after completing a period with high space velocity. The deactivation is indicated in the left-hand side of Fig.1,

A five-fold increase in feed rate had an insignificant effect on the rate of deactivation. One could rationalize this finding by assuming that lower conversions caused by reduced residence time would compensate for the greater feed rate in relation to coke formation. However, a more detailed analysis would reveal that the relationship between the space velocity and the rate of deactivation may be more complex, mainly because of the multicomponent structure of the reaction system. The concentration of reaction constituents depends on the rates of their formation and depletion. Thus the total yield of a component may not be a monotonic function of the residence time. If some coke precursors react faster than others, then their participation in total coke formation depends on the space velocity, a change in which may consequently be reflected in both the quantity and the quality of the coke deposits. In addition to chemical phenomena, mechanical regeneration may take place whereby particles of coke are detached from the surface by abrasion or by dissolution of the binding carbonaceous material. Should a similar process take place while bitumen is used, it would be enhanced by increasing the space velocity.

The high space velocity series indicated that the desired effect could not be established by changing the space velocity at base temperature. To accelerate aging substantially, the catalyst fouling was simulated at a higher reaction temperature. The term simulated aging is used to emphasize the severe consequences of the change in temperature.

Simulated Aging

The results of the simulated aging tests are shown in Fig.2. The activity dropped rapidly in the first period of the run, leveled off, and remained approximately constant beyond 15 hours of operation.

The performance under simulated aging reflected the effect of both high temperature and high space velocity. The performance seemed to be more sensitive to temperature, particularly with respect to the pitch fraction of the bitumen. The initial high pitch conversion observed could result from molecular weight reduction or growth. Molecular growth would result in precipitation of coke, most of which would be retained on the catalyst surface and reactor walls. The molecular weight reduction by cracking would generate compounds having a lower boiling point than those contained in the pitch. It

is apparent that, whereas both of the latter processes have taken place simultaneously, the growth rate was much smaller because the amount of coke formed accounts for only a fraction of the pitch converted. However, the high temperature of simulated aging compared with true aging shifted the balance towards coke formation as reflected in rapid catalyst deactivation.

Less extensive hydrogenation under simulated aging conditions, indicated by a low H:C ratio, was presumably due to a high aromatic carbon content. An analysis by Fourier Transform C-13 N.M.R. indicated that the unsaturated carbon represented about 30% of the total carbon in the initial product of simulated aging compared with about 20% of that of true aging. The following reasons may be considered to account for changes in the aromatic carbon content. More extensive splitting of side chains from aromatic rings caused by the higher temperature could have yielded more gas in the product. Apart from hydrocracking reactions, the higher temperature also shifts the naphthenes-aromatics equilibria towards formation of aromatics (6). In addition to the temperature effects, the high space velocity of simulated aging may have hindered the extent of hydrogenation because of the shorter contact time.

Link between Simulated and True Aging

Since the rate of deactivation under simulated aging conditions could not easily be related to the rate of deactivation under true aging conditions, a series of experiments was performed in which a link was sought between simulated and true aging. The purpose of these experiments was to measure the level of activity under true aging conditions after the catalyst had been subjected to simulated aging conditions for a certain period of time, and then to graphically estimate the time in which the catalyst would deteriorate enough to reach this level of activity while being subjected to true aging conditions.

The activity levels determined for three different time periods under simulated aging are marked on the right-hand side of the curves in Fig.1. By applying these results it was estimated that 2 hours of operation under simulated aging conditions would correspond to about 50-70 hours under true aging, and similarly, 4 hours to 100-150 hours, and 6 hours to 150-200 hours. Hence, assuming that simulated aging is approximately 30 times faster than true aging, one could extrapolate the pattern of true aging and speculate that it would level off in about 400 hours of operation.

Estimating the link between true and simulated aging in Fig.1 is an approximation only. However, it is apparent that by using simulated aging conditions, the deactivation was accelerated sufficiently to proceed substantially in a very short time. It is expected that by applying this method to a number of catalysts, preliminary information can be obtained by comparing their deactivation patterns such as the one shown in Fig.2. This information would then be available either in addition to the true aging data, or for use with catalysts on which true aging tests are not warranted.

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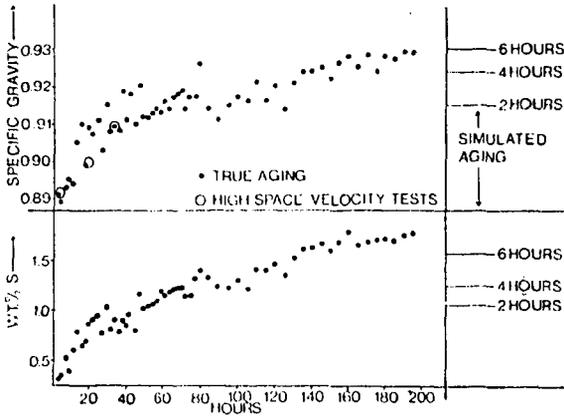


Fig.1 Specific gravity (15/15°C) and sulphur content (wt %) in the liquid product versus time on stream (h) during true aging. O indicates high space velocity experiments. Activity levels on right-hand side relate to different time periods under simulated aging.

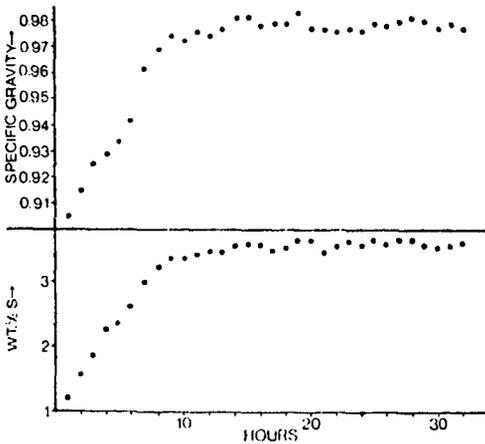


Fig.2 Specific gravity (15/15°C) and sulphur content (wt %) in the liquid product versus time on stream (h) during simulated aging.

REMOVAL OF ORGANIC SULFUR FROM COAL: THE USE OF LIQUID SULFUR DIOXIDE

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ABSTRACT

The utility of liquid SO₂ for the removal of organic sulfur from several Eastern bituminous coals has been explored. Reactions were carried out in sealed fritted glass tubes at elevated temperatures; after subsequent washing, the coal was analyzed for sulfur content. Approximately 40% of the organic sulfur could be removed in these simple exploratory experiments. In addition, comminution of most of the coals occurred and a portion of the coal was extracted. The extract from selected coals was characterized by thin-layer chromatography, by nmr (¹H and ¹³C) and infrared spectroscopy, and by field-ionization mass spectrometry. For comparison, extractions with phenol and *p*-cresol, under similar conditions, were also examined. The results of these preliminary investigations warrant further research to establish optimum conditions for the removal of sulfur compounds from coal by treatment with liquid SO₂ and to facilitate removal of residual SO₂ from the coal.

INTRODUCTION

Solvent extraction has been extensively used for compositional characterization of coals.^{1,2} Several existing coal refining processes³⁻⁵ use solvent treatment, along with pressurized hydrogen to facilitate some degree of desulfurization. Treatment with liquid SO₂ has been successfully used to remove organic sulfur compounds from petroleum on a commercial scale.⁶ The ability of liquid SO₂ to disintegrate various coals has been exploited to produce low-sulfur coal powders via release of pyrite.⁷ Utilization of liquid SO₂ treatment of coal for the removal of organic sulfur, however, has not been investigated. In this paper we report the results of a set of preliminary experiments in which the effectiveness of liquid SO₂ for removal of organic sulfur from bituminous coals PSOC 194, 267, 270, and 319 was investigated.

EXPERIMENTAL

Procedures for the manipulation and preparation of the sulfur dioxide (Matheson, anhydrous) have been described previously.^{8,9} Coal samples were obtained from the Coal Research Section, Pennsylvania State University. All other materials were of commercial origin and used as received.

Reactions were carried out in borosilicate glass tubes fitted with a medium-porosity fritted glass filter to provide two chambers of ca. 20 mL capacity each. The chambers were terminated with glass tubing of different sizes: one end permitted introduction of lump (ca. 1 cm) coal and the other end facilitated easy sealing under vacuum. For reactions at elevated temperatures, these tubes were placed in a Parr model 4641 autoclave reactor.

In a typical experiment, the reaction tube was charged with a coal sample (ca. 5 g) sealed on one end, and thoroughly evacuated. After distillation of sulfur dioxide (ca. 8 mL) into the tube at -78°C , the reaction tube was cooled to -196°C and sealed at the other end. Upon warming to room temperature, the tube, along with others, was placed in the autoclave and the autoclave was evacuated. The autoclave was then charged with ca. 100 mL of liquid SO_2 to provide backing pressure for the reaction tubes at elevated temperatures, closed, and heated at ca. $4^{\circ}\text{C}/\text{min}$ to the reaction temperature. After maintenance of the reaction temperature for 60 min, the autoclave was cooled, depressurized, and opened. Each reaction tube was then inverted in a cold bath at -78°C to separate the liquid SO_2 from the coal by filtration via the internal frit. The red to orange colored liquid SO_2 solution was frozen, the tube was opened, the coal was transferred to another container, and all volatile materials were allowed to evaporate over a two hour period. The viscous, oily extract remaining after evaporation of the liquid SO_2 was retained for subsequent analysis. The treated coal was washed for analytical purposes in a Buchner funnel with sequential aliquots of distilled water, acetone, water, 3.8 M nitric acid, water, and acetone until no yellow color was observed in each wash liquid. The coal was then dried at 110°C and analyzed for sulfur. In separate washing experiments with the raw coals, no yellow color was observed in the wash liquids; subsequent sulfur analyses of the coal indicated that only inorganic sulfur was removed from the raw coal by this wash procedure.

For comparison of the results of these coal/liquid SO_2 experiments, two other types of experiments were also run. Authentic samples of iron pyrite were treated with liquid SO_2 and liquid $\text{SO}_2/\text{H}_2\text{O}$ mixtures at 100°C using procedures analogous to those described above; no apparent reaction occurred. Samples (ca. 4 g) of PSOC 267 were treated with 10 mL of phenol and *p*-cresol in sealed tubes at 181° and 200°C , respectively. The coal was subsequently washed in a Buchner funnel with distilled water and acetone, dried at 110°C , and analyzed for sulfur.

All sulfur analyses, at least in triplicate, were accomplished with a Fisher model 470 sulfur analyser. Field-ionization mass spectra were obtained on a Varian model MAT CH5 spectrometer with sample temperatures from 120° – 280°C . The ^1H and ^{13}C nmr spectra were recorded on a JEOL FX90Q Fourier transform spectrometer fitted with a broadband probe and deuterium lock. Samples were in CDCl_3 solution with internal TMS reference. Infrared spectra of the extract (thin film on NaCl plates) were recorded on a Perkin Elmer model 621 spectrometer. Thin-layer chromatography of the extract was carried out with the nmr sample solutions using silica gel (Si-30) plates. Elution was accomplished with 10% acetone/hexane, 30% acetone/hexane, and absolute ethanol; either I_2 vapor or phosphomolybdic acid (5% w/v in ethanol) was used to develop the plates.

RESULTS AND DISCUSSION

Precombustion desulfurization of coal has been a topic of immense interest and importance^{10,11} since it offers an alternative to installation and operation of expensive post-combustion scrubbers for conventional combustion systems. Although a variety of processes are available for precombustion removal of inorganic sulfur compounds, practical procedures for removal of covalently bound organic sulfur are relatively uncommon. Thus, application of novel chemical approaches to the problem would appear to be appropriate. Early reports¹² of the ability of liquid SO₂ to disintegrate a variety of coals and to extract a portion of the coal along with our previous experience with this solvent suggested investigation of the utility of liquid SO₂ as a means of removing organic sulfur from coal. If successful, such a procedure would utilize a pollutant to remove the source of that pollutant.

Liquid sulfur dioxide is recognized as an excellent solvent for aromatic, heterocyclic, and alkyl sulfides⁸ which can be derived from coal.^{1,2,13} As a liquid, SO₂ is not easily oxidized or reduced and the adducts responsible for its solvent properties are both thermally and hydrolytically labile;⁸ thus any contamination of the coal by residual sulfur dioxide should be readily eliminated. Although other interactions and reactions will be considered in future reports, only reactions based on the mild Lewis acid characteristics of liquid SO₂ are of importance here. Thus, the reaction of significance is summarized by Eq.1:



Products from this reaction are usually highly colored and highly soluble in liquid SO₂.⁸ Physical disintegration of the coal by liquid SO₂, probably via similar donor-acceptor reactions with aromatic, amine, and oxygen containing functional groups, would serve to promote the reaction in Eq.1. It should be emphasized that frequently, the chemical properties of liquid SO₂ can be significantly altered by the presence of cosolvents;⁸ often, undesirable side reactions occur in such mixed media.

The characteristics of the bituminous coals utilized in these preliminary investigations are given in Table I; our sulfur analyses are given in parentheses. PSOC 267 and 270 were chosen since they contain significant amounts of organic sulfur but little pyritic sulfur which might confuse interpretation of preliminary results. Our analyses of PSOC 270 reveal that, although the lumps in our sample had the composition indicated in Table I, the fines in our sample had a sulfur content of ca. 6% with the additional sulfur being pyritic. All results reported here concern the lump coal of PSOC 270. For comparison, PSOC 194 which contains both pyritic and organic sulfur and PSOC 319 which contains only pyritic sulfur were also examined. Use of the fritted glass reaction tubes facilitated observation of reactions, isolation of the extracted material, and rapid examination of several coals and reaction conditions.

The results are summarized in Table II. At room temperature, liquid SO₂ readily wets each of the coals and begins to develop a yellow color upon contact. The yellow color becomes more intense upon standing and changes to intense orange or red-orange after heating. The color indicates the dissolution of donor-acceptor compounds formed between the solvent and coal constituents; the increasing intensity accompanies

an increasing concentration of these adducts. Disintegration of coal lumps was observed for PSOC 267, 270, and 319; the extent of disintegration increases progressively in the order listed. Although lumps of PSOC 194 were not disintegrated, close examination revealed appreciable swelling and expansion along fissures. It should be realized that the only mechanical agitation used during these experiments was a mild shaking of the tubes to initially mix the materials. At this stage, there does not appear to be an obvious pattern which links maceral content to degree of disintegration.

Inspection of Table II reveals that significant amounts of SO_2 are retained on the coal (Exp. 1). Effective removal of this residual SO_2 is essential. Mild heating (110°C) and washing with water or aqueous detergent solutions were less effective than the wash solution used in Exp. 2. When used alone, organic solvents are more effective than mineral acid or base (compare Exp. 2 and 3 with Exp. 4, 5, and 6). The utility of washing with the organic liquids for removal of the yellow SO_2 adducts increases in the order: hexane, benzene, CCl_4 , ethanol, and acetone. A sequence of washes using acetone, water, and HNO_3 (Exp. 7) effectively removes the residual SO_2 in most cases. Since the wash sequence was carried out during a filtration operation contact time with the HNO_3 was insufficient to appreciably modify the coal material itself; separate wash experiments using the acetone, water, HNO_3 sequence with the raw coal (PSOC 267 and 270) itself indicated that no appreciable mass change occurred and that no yellow materials were obtained under these wash conditions. Where pyrite is not present, the sulfur content of the coal after this wash sequence represents the organic sulfur remaining in the coal after the liquid SO_2 treatment. For PSOC 267 and 270, ca. 37% and 25%, respectively, of the organic sulfur can be removed by simple treatment of the lump coal with liquid SO_2 . Grinding the lump coal PSOC 270 (-60 mesh) improves the percentage organic sulfur removal to ca. 48%. Present results with coals containing pyrite are less easily interpreted since the wash sequence probably does not completely remove the pyrite. Furthermore, in separate experiments with authentic pyrite samples, it was demonstrated that neither liquid SO_2 nor liquid $\text{SO}_2/\text{H}_2\text{O}$ mixtures react with pyrite. For PSOC 319, where virtually all the sulfur is pyritic, the measured value of 1.6% sulfur after SO_2 treatment probably represents pyrite which is not removed in the wash sequence. For PSOC 194, the measured value of 2.1% sulfur after liquid SO_2 treatment more than likely represents both unreacted organic and pyritic sulfur. With PSOC 194, the failure of liquid SO_2 to disintegrate the coal probably limited extraction of the organic sulfur by the SO_2 .

Extraction of powdered PSOC 267 with phenol and *p*-cresol resulted in 52% and 66%, respectively, removal of organic sulfur compared to 37% by liquid SO_2 . The results of the extractions with phenol and *p*-cresol are similar to those reported elsewhere for other coals.

Although these results with liquid SO_2 are not as impressive as those with phenol and *p*-cresol, it has been demonstrated that organic sulfur can be removed by extraction with liquid SO_2 . It is also important to note that optimum conditions for liquid SO_2 extraction and for residual SO_2 removal have as yet to be established. Furthermore, these preliminary results when compared with other worker's results¹⁰ for a variety of organic solvents, are sufficiently encouraging to indicate that treatment with liquid SO_2 should be investigated further. Experiments to define conditions

more carefully and to investigate the use of appropriate reagents that will enhance the removal of sulfur compounds from coal by liquid SO₂ are underway.

The material obtained by evaporation of the SO₂ extraction liquid comprises 5-10% of the original coal. Most of this oily extract dissolves in chloroform, acetone, and concentrated HCl; this material is only partially soluble in benzene and is insoluble in hexane. Very finely divided particulate matter, observed to be in suspension in the chloroform and acetone solutions appears to resemble high molecular weight material obtained by Larsen and Choudhury¹³ during their investigation of the effectiveness of coal depolymerization reactions. Although it is likely that liquid SO₂ under these conditions merely extracts lower molecular weight material already in the coal, some small degree of depolymerization could also be occurring.

Thin-layer chromatography of the liquid SO₂ extract from PSOC 267 was carried out using a chloroform solution for deposition and eluted with progressively more polar solvents; long-wavelength UV illumination was used to observe fluorescence in the samples. Although no distinct bands were developed upon elution, three definite fractions that differ by polarity of constituents were apparent on the plates. Several conclusions can be drawn from these TLC experiments. The complete sample contains easily oxidizable functions. All alkyl functions are attached to aromatic residues. The less conjugated (blue fluorescent) fraction is less polar than the more conjugated (orange fluorescent) fraction. A very polar fraction, not transported by any eluent used, is even more highly conjugated (red fluorescent). These observations are consistent with the types of structures¹⁴ known to exist in coals as well as with the spectroscopic measurements to be described next.

The field ionization mass spectrum of the liquid SO₂ extract from PSOC 267 is illustrated in Fig. 1; the corresponding spectrum of the extract from PSOC 270 is similar in several features. The molecular weight distribution in these spectra are not as broad nor is the average molecular weight as high as might have been expected.¹⁴ The presence of very finely divided particulate matter, which presumably has higher molecular weight components that are not volatilized under the measurement conditions, could be responsible for such observations. The spectra contain striking patterns in which the mass difference among major components is 14 amu. These patterns suggest the presence of a variety of CH₂ containing structures. It is tempting to assign another pattern near m/e = 184 to dibenzothiophene since it strongly resembles that obtained with an authentic dibenzothiophene sample. The lack of high resolution mass spectral data, however, makes such an assignment pure speculation at this stage.

The infrared spectrum of the liquid SO₂ extract of PSOC 267 (neat, thin film) is shown in Fig. 2. It is apparent that the extract contains O-H, N-H, aromatic and aliphatic C-H groups, a variety of substituted aromatic structures, and probably ethers. There is no evidence of either residual SO₂ or of organic structures containing SO₂ substitution; no procedures other than evaporation of the liquid SO₂ under ambient conditions were used to process this extract.

Proton and ^{13}C (proton noise decoupled) nmr spectra of the liquid SO_2 extract of PSOC 267 are shown in Fig. 3. Qualitatively, the proton spectrum resembles that of CS_2 extracts of other bituminous coals as reported by Retcofsky and Friedel;¹⁵ our assignments follow those of these workers. The signals with $\delta < 1.8$ are assignable to alkyl type protons, those with $2.0 < \delta < 3.5$ are assignable to benzylic type protons and those with $6.9 < \delta < 8.8$ are assignable to aromatic type protons; the signal at $\delta \text{ ca. } 4.8$ is attributed to phenolic and alcoholic type protons. Integrated intensities provide the following distribution of protons: 20.9% aromatic, 1.9% -OH, 32.1% benzylic, and 45.1% other alkyl types. It would appear that the alkyl-H/aromatic-H ratio is higher for this extract than for CS_2 extracts of bituminous coals with similar carbon content (84.6% C in PSOC 267).

The ^{13}C nmr spectrum reveals further detail concerning the types of structures found in the liquid SO_2 extract of PSOC 267 since assignments are readily made by reference to the work of Fischer *et al.*¹⁶ Features in common with both SRC extracts and methylnaphthalene extracts of bituminous coal are found in the liquid SO_2 extract. The sharp signal at 14.1 ppm is assigned to terminal methyl groups on aliphatic side chains, that at 19.8 ppm to unhindered aryl methyl groups, and those at 22.7 and 31.9 ppm to α and β methylene carbons, respectively, on tetralin type structures. The sharp, dominant resonance at 29.7 ppm is readily assigned to methylene carbons in $\text{Ar-CH}_2\text{-CH}_2\text{-Ar}'$ groups whereas the weaker signals at 32.6, 37.4, and 39.2 ppm are characteristic of single methylene carbons bridging aromatic structures. The broad, low field band with a higher field asymmetry is typical of a composite of aromatic type carbons. Individual sharp signals within this band correspond to alternate polynuclear aromatics that are partially substituted.¹⁶ The apparent absence of signals at even lower fields from carbon atoms without proton substituents is attributed to lack of NOE enhancement for these nuclei.

Thus the liquid SO_2 extract of PSOC 267 has been shown to contain coal constituents similar to those obtained by extraction with common organic solvents. Although an abundance of alkyl groups (methyl and especially methylene) is found in the carbon structures as illustrated by the infrared, ^{13}C nmr, and mass spectra, it is not clear whether this is representative of PSOC 267 composition or is a consequence of the properties of liquid SO_2 . Less is known about the composition of heteroatom compounds in the extract: OH, NH and probably ether groups are apparent but available spectral data do not reveal other groups such as might be found in organic sulfur compounds. Unfortunately, the spectra obtained are not sensitive to divalent sulfur containing organic structures and reliable elemental analyses were precluded by lack of sufficient material. Since better characterization of this extract may eventually provide clues concerning the ability of liquid SO_2 to remove organic sulfur compounds, such efforts are to be made.

In summary, preliminary experiments have demonstrated that liquid SO_2 can be used to remove organic type sulfur compounds from bituminous coals and that the liquid SO_2 extract contains coal components similar to those found by extraction with organic solvents. The ability of liquid SO_2 to disintegrate some coals and to fracture others has been confirmed. Conditions to optimize the removal of sulfur compounds from coal and to facilitate removal of residual SO_2 from the coal are under investigation.

ACKNOWLEDGEMENTS

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TABLE 1. Characteristics of Bituminous Coals Treated with Liquid SO₂

	COAL (PSOC NO.)			
	194	267	270	319
Type	HVB	HVA	HVA	LV
Origin	OH	VA	AL	PA
Macerals (%/v)				
Vitrinite	73.3	60.9	68.1	85.5
P. Vitrinite	12.6	5.3	3.2	4.2
Micrinite	3.3	15.6	9.1	1.0
Fusinite	2.2	8.7	8.6	4.3
S. Fusinite	2.3	3.4	4.6	4.0
Resinite	3.6	1.5	0.8	0.0
Sporinite	1.8	3.2	5.0	0.5
Elemental Analysis (DAF)				
%C	78.23	84.63	83.34	86.49
%H	5.56	5.58	5.55	4.57
%N	1.72	2.53	1.74	1.61
%O(diff)	10.97	5.18	6.59	0.16
%S(total)	3.51	2.08 (1.967) ^a	2.77 (2.682) ^a	7.17
organic	1.26	2.01	2.70	0.10
pyritic	2.19	0.02	0.02	7.00
sulfatic	0.07	0.05	0.05	0.07

^aAnalyses done in this work.

TABLE 2. Experimental Results

Sample (PSOC No.)	Exp. No.	Solvent ^a	Reaction Temp. (°C)	Wash	%S	Organic Sulfur Removed
270						
lump	1	SO ₂	150	-	5.756	
lump	2	SO ₂	150	1.5M NaOH, H ₂ O	3.802	
lump	3	SO ₂	150	3M HCl, H ₂ O	3.522	
lump	4	SO ₂	150	H ₂ O, C ₆ H ₆	2.682	
lump	5	SO ₂	100	CCl ₄	2.602	
lump	6	SO ₂	100	acetone	2.316	
lump	7	SO ₂	150	multiple ^b	2.005	25%
lump	8	SO ₂ /C ₆ H ₆ ^c	100	-	3.089	
lump	9	SO ₂ /C ₆ H ₆ ^c	100	multiple ^b	1.992	25%
powder ^d	10	SO ₂	75	multiple ^b	1.397	48%
267						
lump	11	SO ₂	75	multiple ^b	1.241	37%
powder ^d	12	phenol	180	H ₂ O, acetone	0.9394	52%
powder ^d	13	p-cresol	200	H ₂ O, acetone	0.6580	66%
194						
lump	14	SO ₂	100	multiple ^b	2.134	
314						
lump	15	SO ₂	100	multiple ^b	1.584	

a. For liquid SO₂ reactions, 60 min reaction time was used and for organic solvent reactions, 5 hr was used.

b. The multiple wash consisted of the use of sequential aliquots of acetone, H₂O, 3.8 M HNO₃, H₂O, acetone (see text).

c. The SO₂/benzene solution was ca. 1:1 (vol).

d. Lump coal was crushed and ground to -60 mesh.

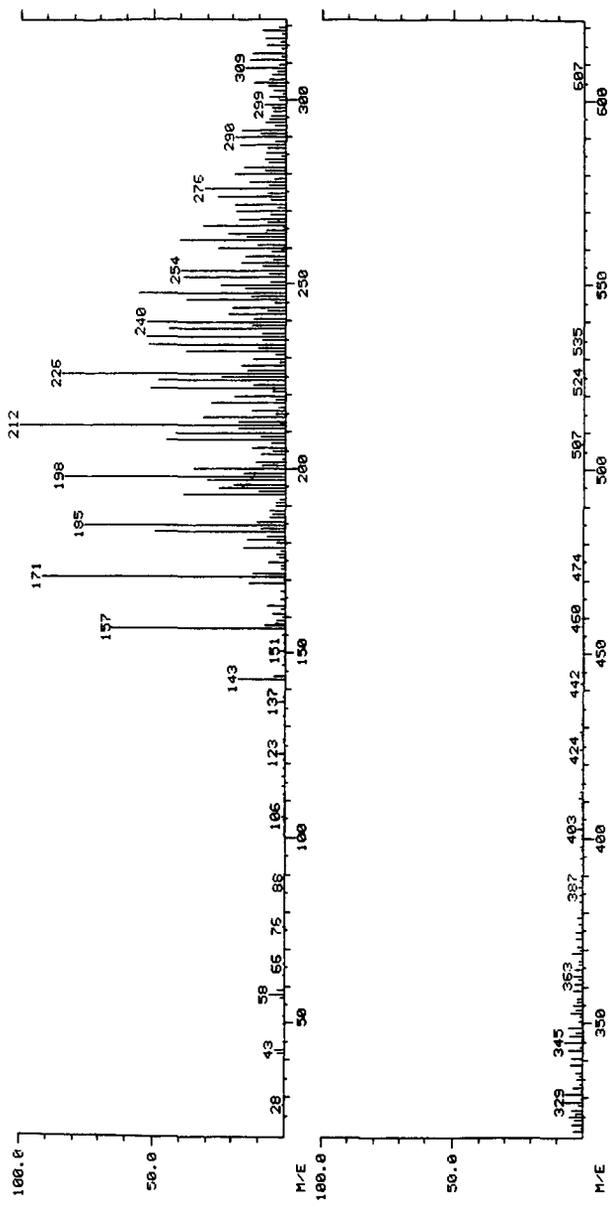


FIGURE 1. Field ionization mass spectrum of the liquid SO₂ extract of coal PSOC 267.

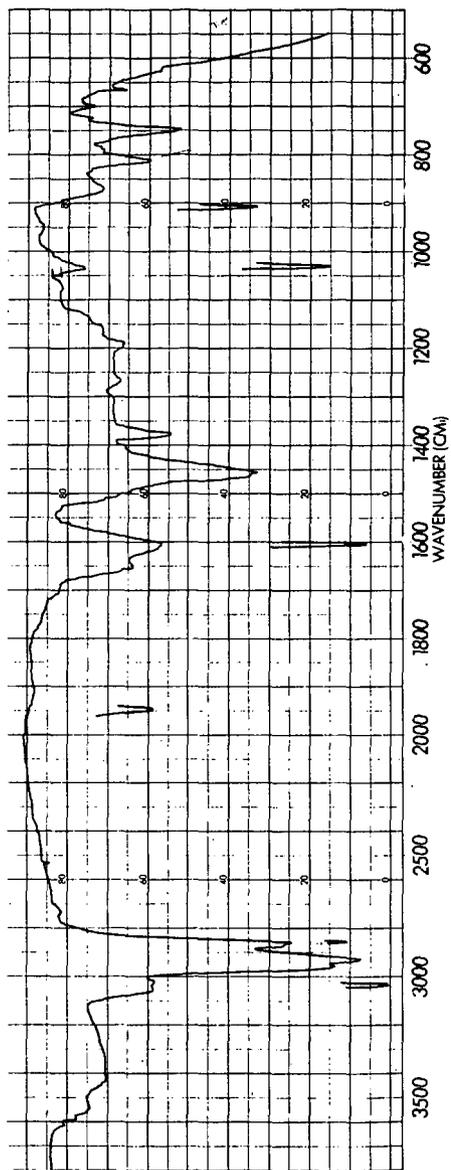


FIGURE 2. Infrared spectrum of the liquid SO₂ extract of coal PSOC 267.

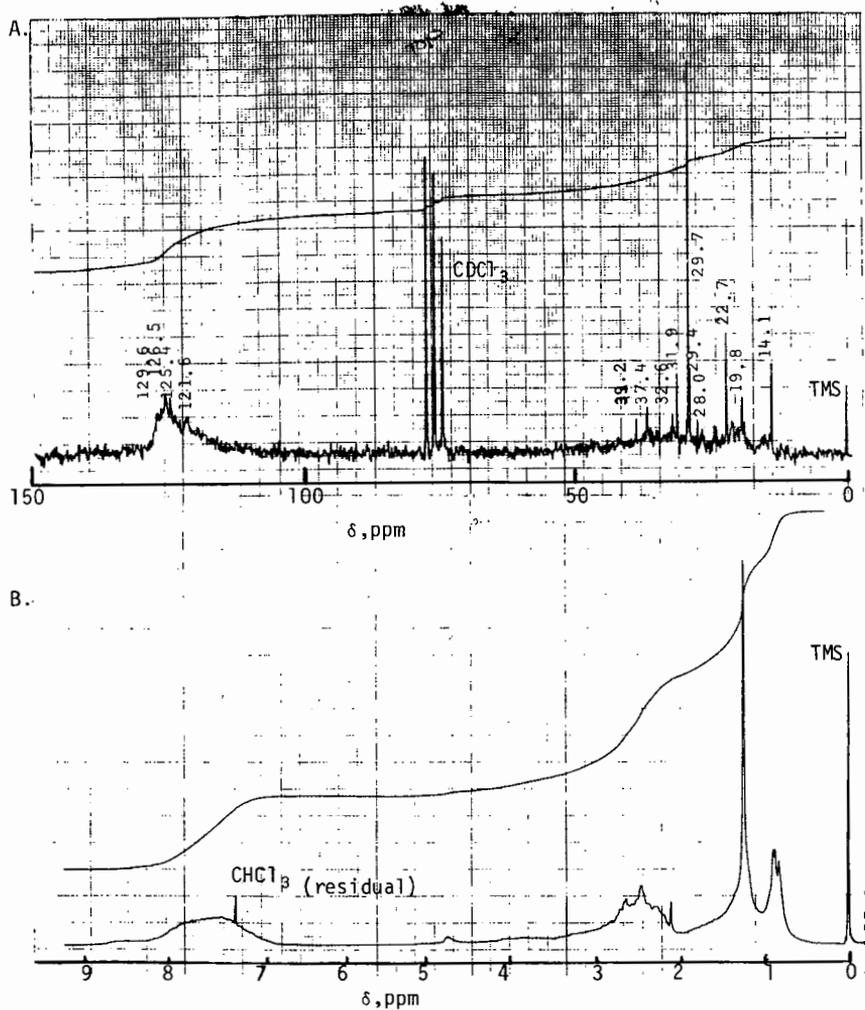


FIGURE 3. Nuclear magnetic resonance spectra of the liquid SO_2 extract of coal PSOC 267 (CDCl_3 solution, 5 mm tube). A. ^{13}C nmr spectrum, proton noise decoupled, 2000 pulses B. ^1H nmr spectrum, 10 pulses.

Evaluation of Oxydesulfurization Processes for Coal
I. The Effect of the Ames Process on Model Organosulfur Compounds

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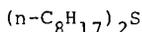
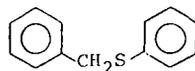
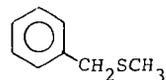
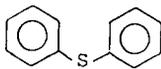
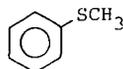
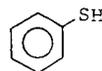
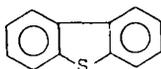
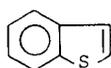
INTRODUCTION

One of the main obstacles to the use of coal as an alternate energy source is that it contains sulfur which contributes to air pollution when the coal is burned. It is estimated that only few percent of coals in the United States will be able to meet EPA SO₂ emission standards (1). Although some chemical procedures have been reported to be effective for desulfurization of coals, most, if not all, of the sulfur that is removed is inorganic. There is little information about what actually happens to the organic sulfur when coals are subjected to these process conditions. A major reason for this ignorance is the lack of information about the nature and distribution of the organosulfur functional groups in the coal.

Recently, several workers have reported that organic sulfur as well as inorganic sulfur can be removed by oxidative processes (2-6). Wheelock, *et. al.* (2) reported that under the following conditions: 150°C, 200 psig O₂, 0.2M aq. Na₂CO₃, 1 hour; up to 40% of the organic sulfur can be removed from coal without significantly reducing the recovery of combustible organic matter.

In this paper we wish to report our evaluation of the effectiveness of this Ames process in the desulfurization of coal. Instead of using coal, model organosulfur compounds were subjected to Ames process conditions. Our approach is based on the assumption that a definitive knowledge of the organosulfur functional groups and their distribution in coal is not a prerequisite for investigating the viability of desulfurization processes. Thus, it is sufficient to measure the propensity of a representative spectrum of organosulfur model materials toward desulfurization under process conditions.

In our study, the following organosulfur compounds have been subjected to Ames process conditions either by themselves or in the presence of coal. For comparison, some model sulfur compounds were also run under the same conditions except that nitrogen was used in place of oxygen. The results of our study are summarized in Tables I and II.



EXPERIMENTAL

Reactions in the Absence of Coal

The reactions were run either in an 1 liter or a 300 ml autoclave. In a typical run, approximately 5 g (for the 1 liter autoclave) or 1 gram (for the 300 ml autoclave) of organic sulfide was placed in a glass liner of an autoclave. After adding 300 ml (1 liter autoclave) or 50 ml (300 ml autoclave) of 0.2M aqueous sodium carbonate solution, the reactor was sealed, flushed with N_2 , and heated as rapidly as possible to 150°C. After the reactor had equilibrated at 150°C (10-15 minutes), the system was pressurized to 200 psig with oxygen and the reactor was flushed with a slow stream of oxygen for 3 minutes. A cold trap was connected to the vent tube of the autoclave to collect the starting sulfide (usually a small amount) which escaped from the reactor during the flushing process (the collected sulfide was combined with the reaction mixture in the autoclave after the reaction). The reactor was then sealed, and temperature (150°C), stirring (1500 rpm) and pressure (200 psig) were maintained for one hour. During the initial pressurization and the first 20-30 minutes of the reaction, cooling of the reactor with water was sometimes required.

After one hour, the heater was turned off; the reactor was cooled to room temperature and the contents were poured into a beaker. The reactor and the glass liner were washed with benzene and with water. The reaction mixture and these washings were combined and extracted with benzene, and the benzene extract was dried (Na_2SO_4) and filtered. To the reactions run in the 300 ml autoclave an internal standard was added directly to the dried benzene extract and the solution was analyzed by gas chromatography (GC) to determine the quantity of starting sulfide left and volatile compounds formed in the reaction. GC response factors for the sulfides, products and the standards were generated in the form of calibration table using standard solutions containing the sulfide, products and the standard. For the reactions run in the 1 liter autoclave, the volume of dried and filtered benzene extract was adjusted to 500 ml, and a 50 ml of aliquot of the benzene solution was withdrawn. An internal standard was added to the 50 ml solution; the solution was analyzed with GC.

The extracted aqueous layer of the benzyl phenyl sulfide or the benzyl methyl sulfide reaction mixture was acidified with concentrated hydrochloric acid, and washed with benzene. The benzene washings were dried (Na_2SO_4) and flash evaporated to afford a residue which NMR and IR analysis showed to be benzoic acid. The remaining aqueous layer was evaporated to dryness, and the residue was analyzed by NMR, IR, and UV spectroscopy.

Reaction in the Presence of Coal Under Oxygen or Under Nitrogen Atmosphere

The coal used was Iowa coal (Lovilia, 200 mesh) and was dried at 110°C overnight. The reactions in the presence of coal were run in a 300 ml autoclave. The reaction procedures were the same as those mentioned above except that ca 4.0 g of coal was added to the reaction mixture for each run. After the reaction, the reaction mixture and washings were combined and filtered, and the filtrate was extracted with benzene. The coal collected with filtration was washed with acetone, then benzene several times. The benzene and the acetone-benzene extracts were combined, dried (Na_2SO_4) and analyzed with GC using internal standards.

RESULTS AND DISCUSSION

Tables I and II demonstrate that among the model compounds that we studied, only thiophenol and compounds containing a benzylic sulfide linkage were oxidized to an appreciable extent. Thiophenol was converted to phenyl disulfide which was resistant to further oxidation. Benzyl phenyl sulfide was oxidized and cleaved to give benzaldehyde, benzoic acid and benzenesulfonic acid; benzyl methyl sulfide gave similar results. The other model compounds were unreactive under the Ames process conditions either by themselves or in the presence of coal. Even in the presence of coal, more than 70% of the starting sulfide was recovered. The reduced recoveries of starting

Table I. Reaction Results of Compounds Run Under the Ames Process Conditions in the Absence of Coal^a

<u>Compound</u>	<u>Recovered Yield (%) of Starting Sulfide</u>	<u>Product</u>
Benzothiophene	87	-----
Dibenzothiophene	96	-----
Thiophenol	0	Phenyl Disulfide
Phenyl sulfide	98	-----
Phenyl methyl sulfide	89	-----
Benzyl methyl sulfide	36	Benzoic acid Benzaldehyde Methanesulfonic acid
Benzyl phenyl sulfide	29	Benzoic acid Benzaldehyde Benzenesulfonic acid
N-Octyl sulfide	90	-----

^a Ames process conditions: 150°C, 200 psig O₂, 0.2M aqueous Na₂CO₃, 1 hour.

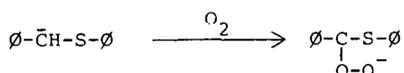
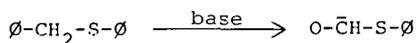
Table II. Reaction Results of Compounds Run Under the Ames Process^a Condition in the Presence of Coal^b

<u>Compound</u>	<u>Recovered Yield (%) of Starting Sulfide</u>	
	<u>N₂^c</u>	<u>O₂^d</u>
Dibenzothiophene	83	76
Phenyl sulfide	76	74
Benzyl methyl sulfide	75	13
N-octyl sulfide	--	82

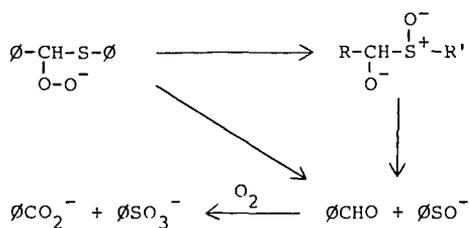
^a Ames process conditions: 150°C, 200 psig O₂, 0.2M aqueous Na₂CO₃, 1 hour. ^b Iowa Lovilia Coal. ^c Reaction run under nitrogen atmosphere. ^d Reaction run under oxygen atmosphere.

materials in the presence of coal (see Table II) can be attributed to absorption of the organosulfur compound by the microporous structure of coal and the mechanical loss associated with working up the reaction mixture. This hypothesis was confirmed by the correspondingly low recoveries of starting sulfides from reactions run in the presence of coal under nitrogen atmosphere--an inert atmosphere. Furthermore, no oxidation products were detected in the reaction mixtures. Clearly, of the compounds investigated thus far, only benzyl sulfides and thiophenol underwent any chemical reaction, and (the benzyl sulfides were the only compounds in which carbon sulfur bond cleavage occurred.

The base-catalyzed reaction of compounds containing a benzylic sulfide linkage with molecular oxygen has been studied under a variety of conditions. Wallace *et. al.* (7) reported that benzyl phenyl sulfide can be oxidized with molecular oxygen in 2M potassium *t*-butoxide-HMPA at 80°C to yield benzoic acid. The authors proposed that the reaction proceeded *via* the formation of an α -carbanion followed by reaction between the ion and oxygen.



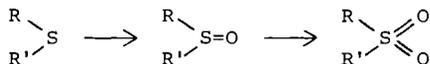
The resulting α -peroxide anion can then decompose in either a stepwise or concerted manner to form benzaldehyde and benzenesulfenate which are oxidized to the corresponding carboxylic and sulfonic acids. In the first step of this mechanism, the α -carbanion is stabilized by the d-orbital of the adjacent divalent sulfur atom.



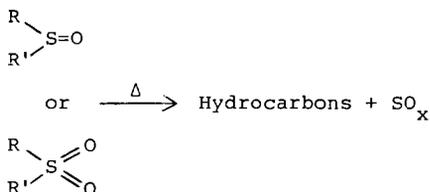
We believe that a similar mechanism is involved in the oxidation of benzyl phenyl sulfide under Ames process conditions.

Oxydesulfurization of the organic sulfides in coal has been formulated as a two-step process (8): 1. Selective oxidation of the sulfur to sulfoxides and sulfones with the latter as the favorable product; and 2. Thermal decomposition of the oxidation products, usually under basic conditions.

Step 1.



Step 2.



In this formulation, the reaction is initiated by oxidation of the sulfur and, in fact, is made possible by this oxidation which results in polarization and weakening of the carbon to sulfur bonds (8).

We find no evidence to support this hypothesis; oxidation of the sulfur was detected only in thiophenol and in the benzyl sulfides. In the first case, oxidation of mercaptans to disulfides is a facile reaction known to occur under conditions such as the Ames process. No further oxidation of the disulfide was detected. In the latter case, we submit that carbon-sulfur bond cleavage is initiated by oxidative attack at the benzyl position instead of at sulfur. This postulate is supported by our recent discovery that, under Ames process conditions, fluorene was oxidized rapidly and quantitatively to fluorenone while dibenzothiophene was removed unchanged from the same reaction mixture.

Oxidation of benzylic carbon hydrogen bonds in preference to sulfur would have a substantial impact on the development of processes for the oxydesulfurization of coal. We intend to investigate this phenomenon and explore methods for reducing or reversing the ratio of benzylic to sulfur oxidation.

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HIGH-PERFORMANCE LIQUID CHROMATOGRAPHY SEPARATION
OF OLEFIN, SATURATE, AND AROMATIC HYDROCARBONS IN HIGH-BOILING
DISTILLATES AND RESIDUES OF SHALE OIL

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ABSTRACT

A high-performance liquid chromatography (HPLC) method has been developed for the separation of olefin, saturate, and aromatic hydrocarbons found in high-boiling distillates and residues of shale oil and in whole shale oils. The dual-column chromatographic system uses silica gel in one column and silica gel coated with silver nitrate in a second column. Separated fractions are analyzed by infrared and carbon-13 nuclear magnetic resonance spectrometry to demonstrate the validity of the separation. The time required for a separation is about two hours. The separations are reproducible, and recovery of material after separation is generally better than 90 percent. The olefin, saturate, and aromatic fractions obtained from a separation are suitable for further analysis.

INTRODUCTION

As increased amounts of shale oil are processed together with petroleum, it becomes increasingly important to have methods available for the analyses of shale oil. A fundamental difference in the composition of shale oil and petroleum is that shale oil contains three major hydrocarbon compound types--olefins, saturates, and aromatics--while petroleum contains only saturates and aromatics. Olefins, because they are hydrogen deficient and unstable, cause problems in the processing of shale oil that are not encountered in the processing of petroleum. They are also of special interest because the amounts, and perhaps kinds, of olefins in shale oil are related to the retorting conditions that produce the shale oil. Techniques for the analysis of saturates and aromatics in petroleum are well known; however, methods for determining olefin, saturate, and aromatic hydrocarbons in the heavy distillate and residue portions of shale oil are needed.

Many techniques for the determination of olefins, saturates, and aromatics have been reported in the literature (1-11). The methods usually involve liquid chromatography with silica gel (3, 4, 10) or liquid chromatography combined with chemical reactions (1, 11, 12). The methods work well in the analytical applications for which they were designed--primarily the determination of hydrocarbon types in light distillates. Difficulties, such as incomplete separation of compound types, often arise when the methods are applied to the analyses of heavier hydrocarbon fractions. The purpose of the work discussed in this paper is to extend the analysis of olefin, saturate, and aromatic hydrocarbons to the high-boiling distillate and residue fractions of shale oil. Several requirements were established for a satisfactory analytical method: 1) the determination should be fast; 2) the results should be reproducible; 3) the samples should have minimum exposure to air, light, and heat; and 4) the separated hydrocarbon types should be chemically unaltered and therefore suitable for further analyses.

This paper describes a dual-column high-performance liquid chromatography (HPLC) method for the separation and determination of olefin, saturate, and aromatic hydrocarbons in high-boiling distillate and residue fractions of shale oil. The method can also be used to separate hydrocarbon types in whole shale oils. The dual-column technique uses silica gel to separate aromatic hydrocarbons from olefin and saturate hydrocarbons and silica gel coated with silver nitrate to separate olefin from satu-

rate hydrocarbons. Cyclohexane is used as solvent for the hydrocarbon samples. The time required for a separation is about two hours.

EXPERIMENTAL

Apparatus

Shale oil distillates and residues were obtained using an ASCO (Arthur F. Smith Co.) 2-in. Rota-Film (wiped-wall) still. Acids, bases, and neutral nitrogen compounds were removed from the samples using a gravity-flow glass column (2.5 cm x 90 cm) packed in three sections with anion resin, cation resin, and ferric chloride/Attapulugus clay. The column was wet-packed using cyclohexane.

Hydrocarbon separations were made using a dual-column system in a Waters Associates AGC/GPC-202 liquid chromatograph equipped with refractive index and ultraviolet detection units. The first column contained silica gel, and the second column contained silica gel coated with silver nitrate. Both columns were stainless steel (7.8 mm i.d. x 61 cm) and were supplied with 5-micron fritted end fittings. Infrared spectra were recorded on a Perkin-Elmer model 621 spectrophotometer, and carbon-13 NMR spectra were obtained using a Varian CFT-20 spectrometer.

Materials

Amberlyst IRA-904 anion-exchange resin (Rohm and Haas) was used for removal of acids, and Amberlyst A-15 cation-exchange resin (Rohm and Haas) was used for removal of bases. Attapulugus clay, 50/80 mesh (Engelhard Minerals and Chemical Corp.) coated with ferric chloride (Baker and Adamson) removed neutral nitrogen compounds from the samples. The preparation of resins and ferric chloride/Attapulugus clay has been described (13).

Silica gel 60G (E. Merck) for thin-layer chromatography was used as received to separate aromatics from saturates and olefins. The same silica gel coated with 20 percent silver nitrate (Baker and Adamson) separated saturates from olefins. The silver nitrate-coated gel was prepared by dissolving the silver nitrate in water, mixing the solution with silica gel, and removing the water on a rotary evaporator. The gel was activated at 110°C for 12 hours. Cyclohexane, benzene, and methanol were commercial HPLC-grade solvents from various suppliers and were used as received.

Shale Oil Samples

The shale oils used in this study were produced by in situ and aboveground retorting processes (14). The Site 9 oil was obtained from the Laramie Energy Technology Center (LETC) in situ experiment near Rock Springs, Wyo. The 150-ton retort oil is from the LETC simulated in situ 150-ton retort near Laramie, Wyo. Paraho and Superior oils are from aboveground retorts located at Anvil Points, Colo., Cleveland, Ohio, respectively.

Distillation of Shale Oils

Crude shale oils that had been centrifuged to remove particulate matter and water were distilled using a wiped-wall still. The still was operated at 20 torr to remove oil boiling below 210°C (corrected to atmospheric pressure). Distillate fractions boiling from corrected temperatures of 210 to 370°C and 370 to 535°C were obtained at lower pressures and increased temperatures. The residue was recovered material that did not distill at 250°C (corrected) and 0.2 torr. The residue was actually exposed to a temperature of 250°C for only a few seconds so that thermal degradation was minimal.

Preparation of Hydrocarbon Samples

A sample (1 g) of distillate, residue, or whole shale oil was dissolved in cyclohexane (100 ml) and passed through a gravity-flow glass column containing successive beds of anion (80 g) and cation (80 g) resins and ferric chloride/ Attapulugus clay (100 g). The column was washed with cyclohexane (500 ml) to recover the hydrocarbons. The cyclohexane was removed from the hydrocarbons using a rotary evaporator.

Preparation and Assembly of HPLC Columns

A reservoir column was attached to an empty HPLC column, and both columns were filled with dry silica gel or silver nitrate/silica gel (about 20 g). Cyclohexane was then pumped through the system to wet and compress the packing material into the HPLC column. The reservoir column was then detached. Columns packed using this technique contained 15 g of gel wetted with cyclohexane, and the gel was uniformly distributed in the column. After a separation, the silver nitrate/silica gel column could be reactivated by washing with cyclohexane (100 ml). The silica gel column was not reusable. Figure 1 shows the dual-column assembly, chromatograph, and detectors.

Column Calibration

During routine analyses, the cut point for the separation of saturates and olefins from aromatics on the silica column was made according to elution volume. The proper elution volume was established prior to the separations by passing samples through the silica gel column and monitoring the separation with ultraviolet and refractive index detectors. Once the proper elution volume had been established, the detectors were removed from the chromatographic system.

Separation Procedure

A routine separation was made in the following manner. A shale oil hydrocarbon sample (200 mg), dissolved in cyclohexane (1 ml), was placed on the silica gel column, and cyclohexane was pumped through the two columns for 40 minutes at a rate of 1 ml/min and a pressure of about 350 psig. Under these elution conditions aromatics are retained on column 1, while saturates and olefins pass through to column 2. Valves between the columns and a second solvent reservoir allowed continued pumping cyclohexane through the second column where olefins and saturates were separated. Saturates were eluted with cyclohexane from the silver nitrate column with continued pumping for 30 minutes at 1 ml/min. Olefins were then eluted from the silver nitrate column by pumping benzene/cyclohexane, 20/80 percent, through the column for 30 minutes at 1 ml/min. Simultaneously, benzene/methanol, 40/60 percent, was pumped through the first column for 60 minutes to elute aromatics. The total separation time was about 2 hours.

DISCUSSION

Identification of Hydrocarbon Types

Infrared and carbon-13 NMR spectrometry were used to analyze the hydrocarbon fractions prepared by the dual-column chromatographic system. The analyses demonstrate the validity of the separations. Both spectrometric techniques have special analytical advantages and limitations; when used together they permit a satisfactory analysis of the hydrocarbon fractions.

The fractions of saturates, olefins, and aromatics were first examined using infrared spectrometry. Two absorption bands were used to analyze the fractions: 1) the mono-olefin stretching band at 1630 cm^{-1} to identify olefins and 2) the aromatic ring carbon-carbon stretching band at 1600 cm^{-1} to identify aromatics. Saturates have no absorption bands in the infrared that distinguish them from other hydrocarbon types.

An example of the use of infrared spectrometry in analyzing hydrocarbon fractions presented in Figure 2, which shows the partial infrared spectrum of the total hydrocarbons from a 210-370°C distillate together with the partial infrared spectra of separated fractions. In Figure 2a, both mono-olefin and aromatic absorption may be seen in the spectrum of the total hydrocarbons. Figures 2b, 2c, and 2d show that a separation of aromatics, olefins, and saturates has been achieved. Only trace amounts of aromatics absorbing at 1600 cm^{-1} can be observed in the spectrum of the saturates (Fig. 2d) and olefins (Fig. 2c). Olefins are observed in only the olefin fraction (Fig. 2c).

In general, infrared spectrometry is a very useful method for analyzing the hydrocarbon fractions because it is fast and sensitive. It does, however, have limitations. First, in a mixture of hydrocarbon types, saturates cannot be distinguished from olefins or aromatics. Second, use of the 1630 cm^{-1} band does not allow the detection of conjugated di- and tri-olefins. Third, infrared analyses of complex mixtures of olefins cannot be quantitative because the molar absorptivities of individual olefinic compounds are quite variable. The correct value of molar absorptivity to use in an infrared calculation involving Beer's law is not known.

Carbon-13 NMR spectrometry was used to complement infrared spectrometry in the analyses of separated fractions. These data confirmed infrared data and provided additional information about the hydrocarbon types, especially the olefins.

Figure 3 shows carbon-13 NMR spectra of saturates (Fig. 3a), olefins (Fig. 3b), and aromatics (Fig. 3c) from a 370-535°C hydrocarbon concentrate. For quantitative determination of olefins, the spectral region of interest is between 110 and 140 ppm relative to tetramethylsilane (TMS). Saturates show no carbon-13 absorption in this region. Olefins show absorption bands between 114 and 138 ppm (15, 16); the position of absorption is dependent upon the type of olefin. Alpha olefin bands are observed at 114 and 138 ppm, while internal olefins have absorption bands between 114 and 138 ppm. Aromatic carbons are seen as a broad, symmetrical absorption envelope centered at about 128 ppm. Figure 3a shows that, in this particular separation run, the saturates contain 1 or 2 percent of another hydrocarbon type, probably aromatics. Olefins are observed only in the olefin fraction, not in the saturate or aromatic fractions. Trace amounts of aromatics appear to be in the olefin fraction, confirming the infrared data.

Carbon-13 NMR is useful not only because it aids in judging the quality of separation that has been achieved but also because it provides detailed information about molecular structure. For example, in an olefin mixture, the number of double bonds of an average olefin molecule can be calculated if the average molecular weight of the olefin mixture is known and if the ratio of aliphatic/olefinic carbons can be measured by carbon-13 NMR. However, carbon-13 NMR also has limitations. First, in a mixture of hydrocarbons, saturates cannot be distinguished from olefins and aromatics. Second, olefins may not be observable in a concentrate of saturates or aromatics if the amount of olefins is lower than about 3 or 4 percent. Third, with carbon-13 spectrometry alone, it may be difficult to distinguish between internal olefins and aromatics; in such a case ultraviolet analyses are useful.

Infrared and NMR analyses established that saturate, olefin, and aromatic compound classes were separated into three discrete fractions by the dual-column system. This allowed the quantitative determination of each class to be made gravimetrically.

Separation Results

a. Hydrocarbons in High-Boiling Distillates and Residues. - The dual-column method was used to separate hydrocarbons from three different boiling ranges of four shale oils. The results of the separations are shown in Table 1. All data were obtained gravimetrically. Duplicate determinations were made to show the reproducibility that

can be expected with the separation technique. In most cases the reproducibility is similar to that experienced in the silica gel separation of saturate and aromatic hydrocarbons in petroleum. The cause of the poor reproducibility experienced in some runs is not known. The recovery of separated hydrocarbon types was generally better than 90 percent.

From a characterization point of view, the data in Table 1 show some interesting trends. First, distillates and residues from the Site 9 in situ oil and the 150-ton retort oil contain smaller amounts of olefins and larger amounts of saturates than the other oils. Thus, it appears that the Site 9 and 150-ton retort oils were produced under milder retorting conditions than the Paraho and Superior oils. Second, the distributions of hydrocarbon compound types as related to distillation temperature can be seen. For example, in the Site 9 oil, the aromatics increase as the distillation temperature increases. The olefins are constant in the distillates and increase in the residue. These changes are at the expense of saturates which decrease as the distillation temperature increases.

b. Hydrocarbons from Whole Shale Oils. - The dual-column method permitted the fast determination of saturates, olefins, and aromatics in whole shale oils. The results of the separations are shown in Table 2. Both reproducibility and recovery values are similar to those seen in the separation of distillates and residues. Unknown amounts of light hydrocarbons from the whole shale oils were lost during the solvent-removal procedure.

SUMMARY AND CONCLUSIONS

An HPLC method has been developed for the separation of saturates, olefins, and aromatics in high-boiling distillates and residues of shale oil and in whole shale oils. The dual-column chromatographic system uses silica gel in one column and silica gel coated with 20 percent silver nitrate in a second column. The time required for a separation is about two hours. The separations are reproducible; recovery of material after separation is generally better than 90 percent. The saturate, olefin, and aromatic fractions obtained from a separation are suitable for further analyses.

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DISCLAIMER

Mention of specific models or brand names of equipment is made for information only and does not imply endorsement by the Department of Energy.

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TABLE 1. - Hydrocarbon separation results of distillates and residues

Sample	Wt. percent of total hydrocarbon fraction			Percent recovery
	Saturate	Olefin	Aromatic	
150-ton, 210-370°C dist.	64	5	19	88
"	63	7	20	90
370-535°C dist.	61	6	29	96
"	59	7	34	100
>535°C residue	45	11	43	99
"	45	11	38	94
Site 9, 210-370°C dist.	70	5	17	92
"	72	6	23	101
370-535°C dist.	64	6	24	94
"	59	5	29	93
>535°C residue	48	8	40	96
"	40	10	47	97
Paraho, 210-370°C dist.	25	27	30	82
"	36	23	26	85
370-535°C dist.	38	24	34	96
"	31	23	35	89
>535°C residue	19	10	48	77
"	23	13	44	80
Superior, 210-370°C dist.	25	29	30	84
"	27	36	28	91
370-535°C dist.	32	21	42	95
"	32	22	42	96
>535°C residue	27	22	47	96
"	31	19	48	98

TABLE 2. - Hydrocarbon separation results of whole shale oils

Shale oil sample	Wt. percent of hydrocarbons from total oil			Percent recovery
	Saturate	Olefin	Aromatic	
150-ton retort	53	17	22	92
"	40	21	22	83
Site 9 retort	46	18	18	82
"	55	15	20	90
Paraho retort	41	27	24	92
Superior retort	41	26	32	99
"	36	31	28	95

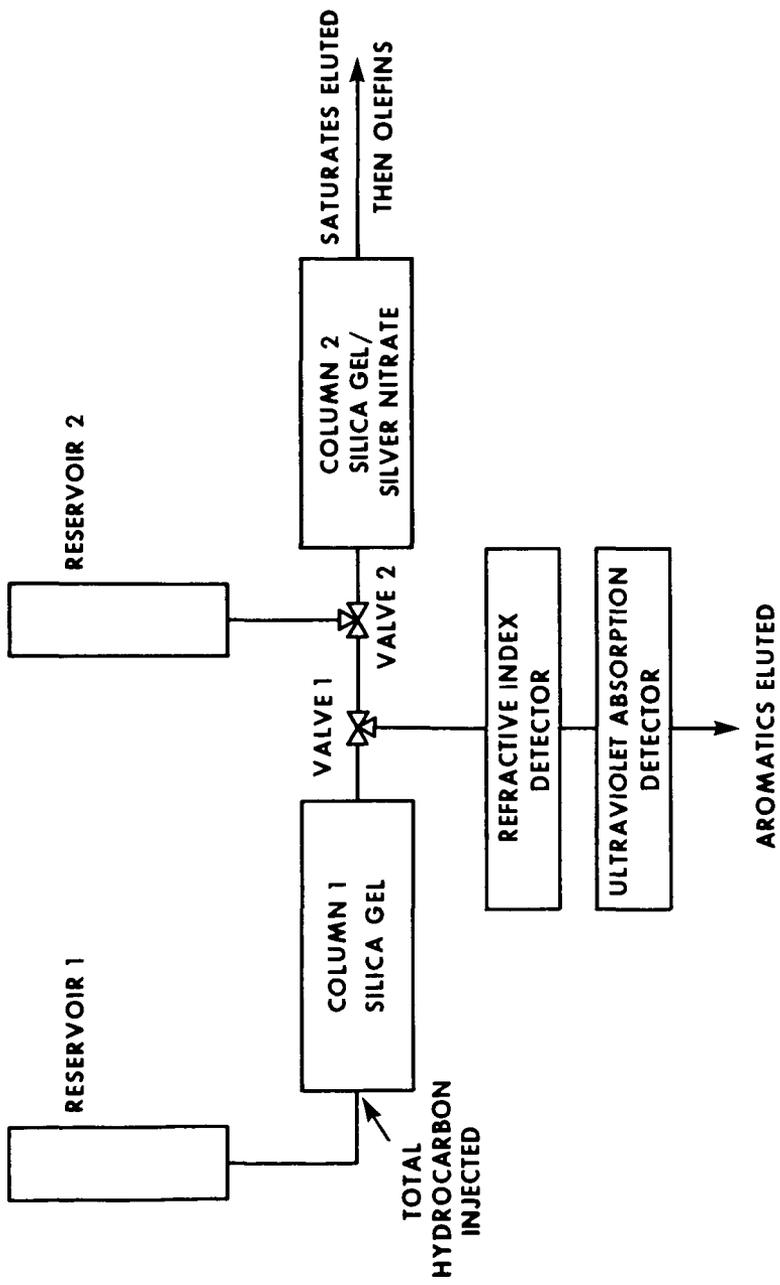


FIGURE 1. HPLC apparatus

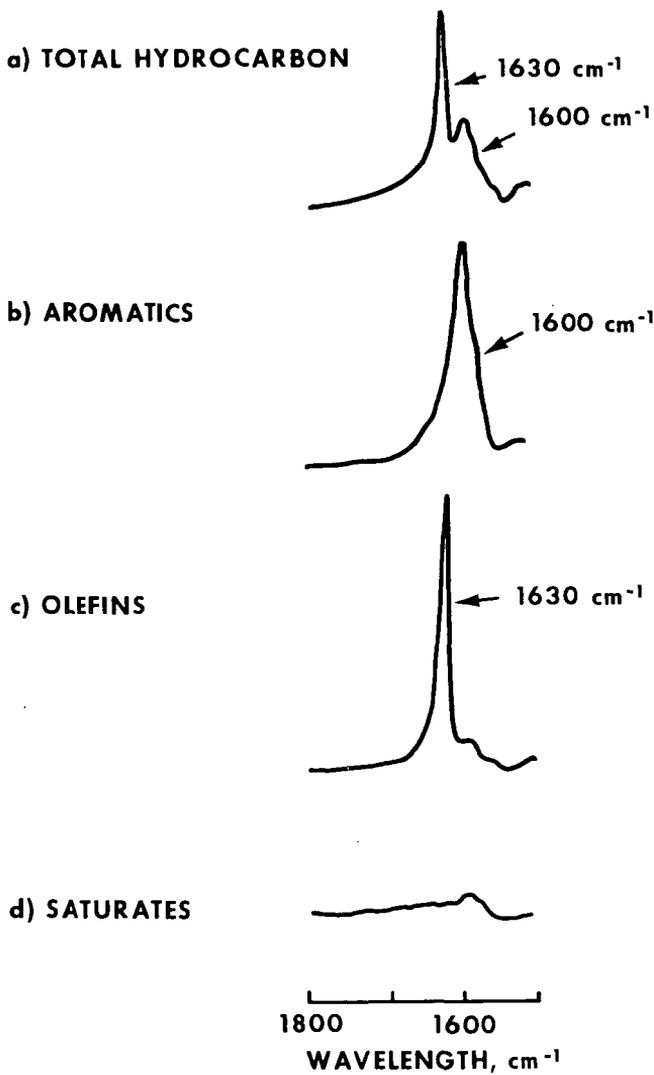


FIGURE 2. Partial infrared spectra of shale oil 210-370°C distillate total hydrocarbon and fractions

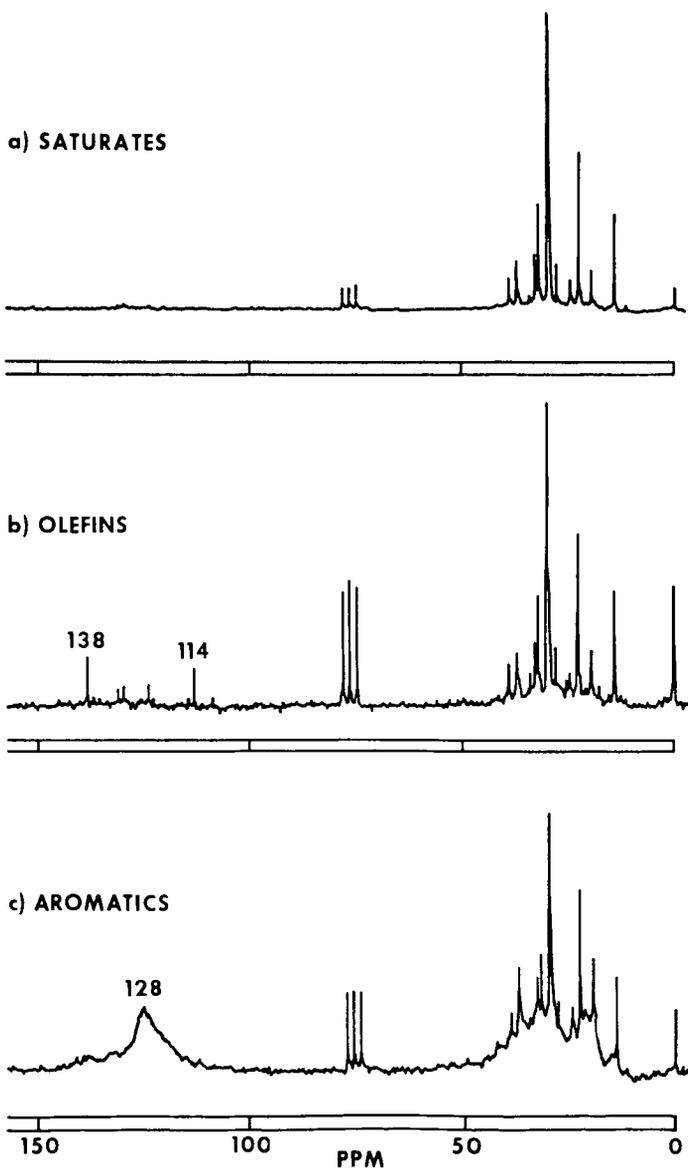


FIGURE 3. Carbon-13 NMR spectra of hydrocarbon fractions from Paraho 370-535°C distillate

LOW TEMPERATURE CLEAVAGE REACTIONS OF ILLINOIS NO. 6 COAL

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This paper presents a progress report on our efforts to determine the kinds and proportions of single bond in Illinois No. 6 coal that can be broken below 100°C. The principal obstacle to the use of present liquefaction processes is the high cost of plants that would employ the required high temperatures and pressures. Our work deals only with low-temperature processes near atmospheric pressure. It has focused on (1) the asphaltol fraction of Illinois No. 6 coal, which is the pyridine-soluble, toluene-insoluble fraction that comprises about two-thirds of the 15% of coal that can be extracted by pyridine, and (2) the pyridine-extracted coal, which is about 85% of the initial dry coal, and which represents the essence of the liquefaction problem.

Oxidations

Previous work by Huntington et al² described the effects on the same two substrates of (1) AIBN-initiated oxidations in pyridine solution at 50°C, and (2) refluxing with alcoholic KOH (78°) without oxygen. Either reagent would reduce the number-average molecular weight (\bar{M}_n , by vapor-phase osmometry) of the asphaltol by nearly 50% but sequential treatment with both reagents produced little additional effect, as if the two reagents were affecting similar bonds. Only about 10% of the extracted coal was made soluble in pyridine, but some substrate became soluble in alcoholic KOH.

NaOCl oxidation of very finely divided extracted coal in water suspension at 30° and pH 13 has been much more effective in dissolving this material.³ 76% of the carbon in the extracted coal has been converted to black acids (\bar{M}_n about 1000) soluble in aqueous base, and 7% to water-soluble acids; 4% of the initial carbon was undissolved; the remaining 12% is presumably in carbon oxides. Oxygen oxidation of extracted coal in water suspension at pH 13 and 50° is much slower but has led to 85% dissolution of the coal and recovery of 66% of the original coal in black acids. Oxidations of asphaltol, well dispersed in water at pH 13, gave better results: with NaOCl at 30°, 99% dissolution and 93% of the carbon in black acids; with oxygen at 50°, 98% dissolution and 80% of the carbon in black acids.

These oxidations in water suspension at pH 13 and oxidations with AIBN and oxygen in pyridine solution² at 50°C appear to proceed by different mechanisms. In radical-initiated oxidations of extracted coal, the H/C ratio decreases from .73 to .69, as if benzylic hydrogen were being removed preferentially. However, in both NaOCl and oxygen oxidations of both asphaltol and extracted coal in water, H/C increases somewhat, notwithstanding replacement of some H by O, suggesting preferential removal of aromatic groups. Possibly some hydroxylated aromatic rings are sites of attack. The principal products, black acids, from oxygen and NaOCl oxidations in water at pH 13 have similar compositions.

Cleavages of Asphaltols

Results of cleavages of asphaltols, probably at ether links, are summarized in Figures 1 and 2. Each half of each table starts from the center with asphaltol with slightly different \bar{M}_n . In general, reactions were run under nitrogen, and at room temperature except as noted. Products were sometimes separated by solubility but always washed free of reagents and solvents and dried in an Abderhalden drier at <0.001 torr, usually at 140°C in Figure 1, usually at 76°C in Figure 2. (The only need for 140° drying seems to be with samples that contain pyridine or amines and have not been acid-washed.) \bar{M}_n s were determined by VPO in pyridine, in which all products were soluble, at concentrations of 0.5 to 3g/L. Keys to abbreviations and

arrangement of data are given in Figure 2. Thus, molecular weights of products are in the middle of each second line of each block of data.

Experiments in the upper left quarter of Figure 1 show that eight extractions of asphaltol with 5% KOH at room temperature resulted in solution and recovery of 9% of soluble carbon. 23% of the original C was lost, at least partly as water-soluble and/or volatile products. Molecular weight reductions without heating parallel those at 78°.2

Reactions of asphaltol with benzylamine (lower left quarter in Figure 1), and then drowning the reaction in ether or methanol, resulted in part of the asphaltol becoming soluble in these solvents and a decrease in \bar{M}_n of about one-half. Treatment of the ether-insoluble product with alcoholic KOH resulted in fractionation of the product but not further degradation. The butylamine-methanol combination appears to behave similarly.

Pyridine hydroiodide in pyridine at room temperature decreases the \bar{M}_n of asphaltol to one-half to one-third of the original (upper right in Figure 1). This experiment was run on the premise that pyridine hydroiodide would be an acid in pyridine, which is an excellent solvent for asphaltol. However, methyl iodide was nearly as effective as HI. Asphaltol was treated with methyl iodide at room temperature in the hope of making sulfonium as well as pyridinium salts. The product was then heated to 140° at reduced pressure in the expectation of splitting out methyl iodide from pyridinium salts (without net coal bond cleavage) and conversion of the original sulfides to methyl sulfides and coal alkyl iodides, with net cleavage of sulfide bonds. However, the reduction in \bar{M}_n from 1250 to 660 is surprisingly high, since the 1.7% S content corresponds to only 0.66 S/asphaltol molecule, of which most is expected to be in heterocyclic aromatic rings. A somewhat greater reduction in \bar{M}_n is reported for a duplicate experiment in Figure 2. It is therefore possible that I⁻ alone may be able to cleave ether links, a conclusion to be supported in discussion of Figure 2. Thus, abilities of Me₃SiI⁴ and of hexamethyldisilazane plus ME₃SiCl (the latter intended for trimethylsilylation⁵) to cleave asphaltols may be due as much or more to halide ions generated as to the original reagent.

We tried sodium in liquid ammonia as an ether-cleaving reagent, but found that addition of sodium in liquid ammonia to a cold solution of asphaltol in butylamine gave better control, less reduction of the asphaltol, and a decrease in \bar{M}_n by nearly 50%. Treatment of this product with pyridine hydroiodide (right center of Figure 1) then gave further reduction in molecular weight. However, our data suggest that combination of the sodium and HI reactions gave no more cleavage than HI alone.

Figure 2 summarizes cleavage reactions of two other asphaltols with HI (check of Figure 1 experiment), HBr, toluene sulfonic acid, and some metal salts, all (except the MeI experiment) in pyridine solution. The other acids, even at 50°, are not as effective as HI at room temperature, but zinc bromide, and especially zinc chloride and LiI·H₂O,⁶ have given more molecular weight reduction than any of the acids. However, all of these reactions have apparently resulted in incorporation of pyridine in the products, as shown by the high recoveries and high nitrogen contents. Some products also lose weight slowly and persistently on heating at 140° in vacuo. A possible explanation is that cleavage of an aryl alkyl ether by metal halide gives metal phenolate and alkyl halide; some of the latter then reacts with pyridine solvent to give unstable quaternary pyridinium salts. However, the remarkable reactivity of these reagents at low temperatures may be associated with the use of pyridine as solvent.

Conclusions

This progress report shows that asphaltol from Illinois No. 6 coal can be extensively degraded at or near room temperature by several acidic and basic reagents and by some oxidizing and reducing agents, with good to excellent recovery of original

carbon. These agents appear to attack ether links, or maybe aromatic rings in oxidations at pH 13, but as yet we know of no precedent for reactions of aliphatic amines or alcoholic KOH with ethers at these temperatures. To determine the proportions of various kinds of breakable single bonds in Illinois No. 6 coal, we plan to carry out further degradations on asphaltol by combinations of reagents, and then extend the most promising of these reactions to extracted coal. We expect that this kind of information will provide the basis for new and economical approaches to coal liquefaction, which will employ much milder conditions and much less expensive processes and plants.

Acknowledgement

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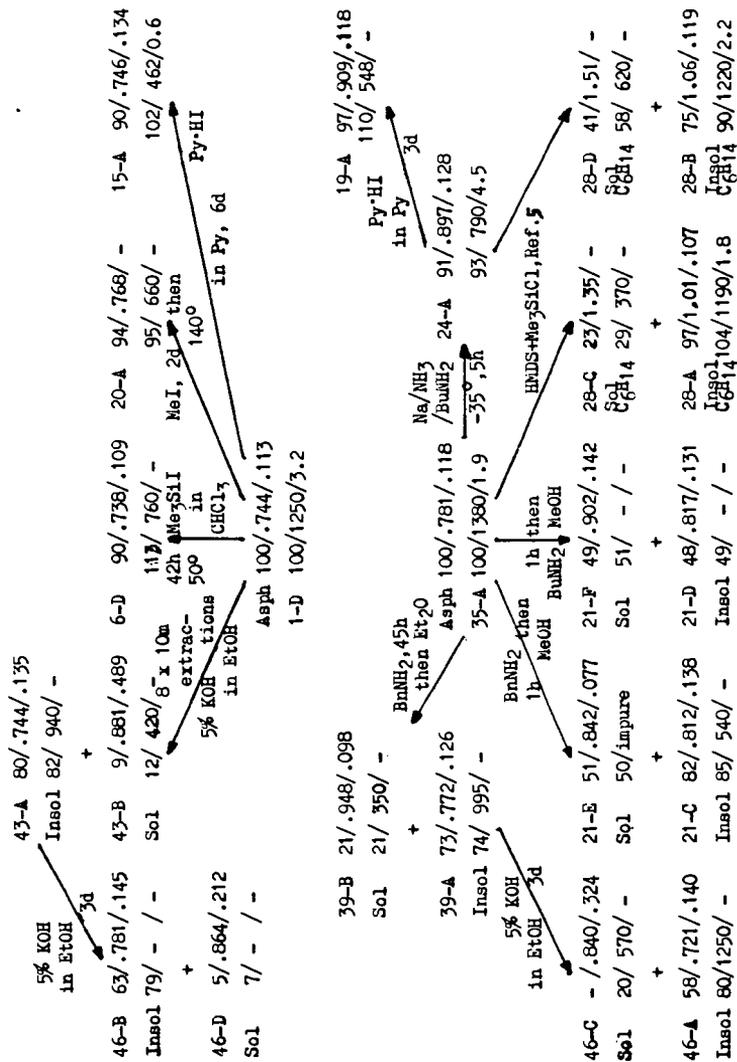
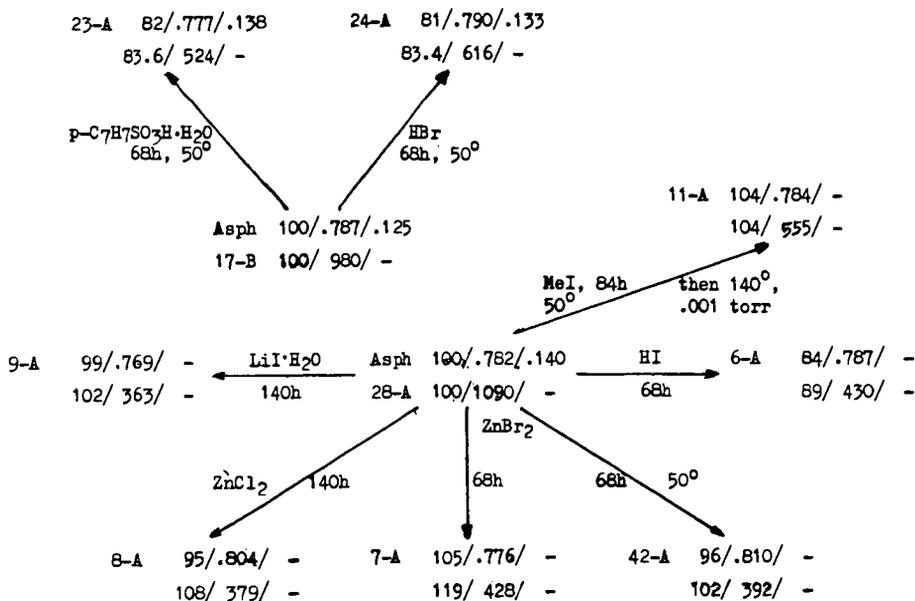


Figure 1. Cleavages of asphaltols, at room temperature, except as noted. Key and abbreviations are in Figure 2.



Key to arrangement of data:

Sample Atom % C/ H/C / O/C
 ↑
 Yield
 ↓
 No. Wt. % / \bar{M}_n /eq.OH/mole

Abbreviations:

As = asphaltol
 Bn = benzyl
 Bu, Et, Me = n-butyl, ethyl, methyl
 HMDS = hexmethyldisilazane
 d, h, m = days, hours, minutes

Figure 2. Cleavages of asphaltols in pyridine solution (except with MeI) and at room temperature (except as noted otherwise).

OXYDESULFURIZATION OF COAL TREATED WITH METHYL IODIDE --
IMPLICATIONS FOR REMOVAL OF ORGANIC SULFUR

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Introduction

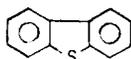
In the chemical desulfurization process being developed at the Ames Laboratory, coal is leached with a dilute solution of sodium carbonate containing dissolved oxygen under pressure and at elevated temperature. For many coals, most of the inorganic sulfur can be removed, and the organic sulfur content can be reduced by 25-40% (1,2). In some instances, as much as 70% of the organic sulfur has been removed. An essential piece of information in evaluating the effectiveness of a process for the removal of organic sulfur is the identity and reactivity of the various sulfur functions grouped under the term "organic sulfur."

Although much data is available on the content and distribution of the so-called pyritic, sulfatic, and organic sulfur in various coals, relatively little has been published on the nature and abundance of the organic sulfur groups in coal. Essentially no data are available on the reactivity of such functional groups under oxidizing conditions, such as those found during oxydesulfurization. In fact, no completely satisfactory method exists as yet for the direct determination of organic sulfur in coal, although a few methods are being developed. These methods are based either on microprobe analysis (3,4), or on low-temperature ashing of the organic components of coal (5), or on their thermokinetic reduction to hydrogen sulfide (6). As a routine, however, organic sulfur is still being determined as the difference between the total sulfur and the amount of the inorganic (i.e., pyritic plus sulfatic) sulfur, according to ASTM procedures.

Attempts to identify and quantitatively determine organic sulfur functions in coal have been few. On the basis of very sparse data, it is generally assumed that the organic sulfur in coal can be described almost completely by the following classes:

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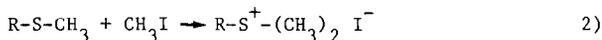
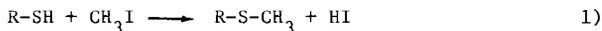
- Class 1. Aliphatic or aromatic thiols (mercaptans, thiophenols): R-SH, Ar-SH
- Class 2. Aliphatic, aromatic, or mixed sulfides (thioethers): R-S-R, Ar-S-Ar, R-S-Ar
- Class 3. Aliphatic, aromatic, or mixed disulfides (bisthioethers): R-SS-R, Ar-SS-Ar, R-SS-Ar
- Class 4. Heterocyclic compounds of the thiophene type: e.g., dibenzothiophene



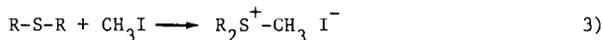
It is generally assumed that any chemical desulfurization process that can remove organic sulfur will do so because of the reactivity of compounds in Class 1, 2, and 3. Heterocyclic compounds in Class 4 are extremely stable to chemical attack and high temperature.

The fundamental approach in this study is based on the different reactivity of methyl iodide toward different organosulfur functions to produce sulfonium compounds. The general scheme of reactions for the various classes of sulfur groups can be summarized as follows (7):

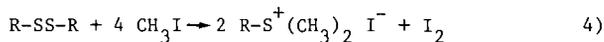
1. Mercaptans:



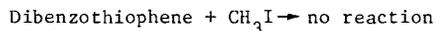
2. Sulfides:



3. Disulfides:



4. Heterocyclic compounds:



The reaction of coal with methyl iodide was used previously (8) to determine the thioether content of coal by measuring the uptake of iodine, presumably associated as iodide with the sulfonium compounds. But the iodine uptake is not a true measure of the thioether content because other compounds, notably heterocyclic nitrogen compounds, can also react resulting in uptake of iodine. To overcome this difficulty, the sulfonium compounds were washed out with a solvent like acetone, and the decrease in the sulfur content was then taken as the indicator of the thioether content (7). A similar procedure was adopted in this work.

Experimental

Materials

The coal used in this study was a high-volatile bituminous coal from the Star mine in Mahaska County, Iowa. The coal was pulverized, screened using U.S. Standard sieves, dried, and analyzed for ash, heating value, and sulfur distribution by ASTM procedures.

Fresh methyl iodide was used directly from the reagent bottle. In some experiments, the reagent was cleaned by shaking with mercury, but no significant difference was noticed in the results.

Methyl Iodide Reaction

A slurry of 20 g coal and 30 ml methyl iodide was placed in a large test tube, covered with foil, and allowed to stand for 3 days at room temperature. The slurry was then filtered and washed with about 2 l. acetone to remove reaction products and unreacted methyl iodide, until the test for iodide (silver nitrate) was negative. The treated coal was dried and analyzed again. Qualitative tests for residual iodide in the treated coal (hydrogen peroxide treatment followed by extraction of iodine into a benzene layer) showed only traces of iodide. The methyl iodide treatments were repeated on enough coal samples to provide a stock of treated coal to be used for the oxydesulfurization experiments.

Oxydesulfurization of Coal in Autoclave

The coal (40 g) was leached for 1 hr with 400 ml solution in a 1-liter autoclave described previously (1). The leaching was done at 150°C under 50 or 200 psia oxygen partial pressure. For non-oxidizing conditions, a partial pressure of 50 psia nitrogen was used. Water or 0.2 M sodium carbonate was used as the leaching solution. The residues from the alkaline leaching step were leached for a second time, also for 1 hr at 150°C, using water, 0.1 M sulfuric acid, 0.1 M phosphoric acid, or 0.2 M sodium carbonate in a nitrogen atmosphere.

Calculations

In order to account for the different levels of ash in the various coal residues, the sulfur content was converted from weight percent to pounds of sulfur per million Btu. This conversion, in effect, allowed the comparison of the organic sulfur content in the organic (i.e., combustible) portion of the coal.

In a few cases, the heating value was not actually determined but was calculated using a formula (1), based on the assumption that the ash-free heating value is relatively constant for the same coal, regardless of the treatment conditions.

Results and Discussion

Removal of Sulfur by the Methyl Iodide Treatment

The results of treating coal with methyl iodide are presented in Table 1. Based on the pounds of sulfur per million Btu, the methyl iodide treatment removed, on the average, 48.3% of the organic sulfur. This seems to indicate that at least one-half of the organic sulfur is in the class that is reactive toward methyl iodide. Since thiophenic compounds are unreactive and disulfide groups react too slowly at room temperature, the reactive portion of the organic sulfur is probably of the sulfide and mercaptan classes.

Further tests were run by treating mineral pyrite with methyl iodide under similar conditions and then washing with acetone. No reaction was observed; the sulfur content was unaffected. Also, simple washing of coal with 2 l. of acetone (without prior methyl iodide treatment) did not alter significantly the ash content, heating value, and sulfur distribution of the coal.

Another possible explanation for the reduction of the organic sulfur may be offered if methyl iodide simply methylates the coal, thus increasing its organic content and decreasing the sulfur content by "dilution." If this observation were a reflection of a methylating effect, then the heating value should have increased, the ash content should have decreased, and the "dilution" should apply to all types of sulfur in coal. Yet the changes in ash content, heating value, and weight recovery were insignificant; and the pyritic and sulfatic sulfur values were fairly constant. It seems, therefore, that organic sulfur was really removed by this procedure. It is not known, however, by what mechanism the sulfonium salts are washed away.

Removal of Sulfur by Oxidative Leaching

The results of leaching the methyl iodide-treated coal are presented in Table 2. The sulfur content should be compared not only to that of the initial coal but also to that of the methyl iodide-treated coal in Table 2. It can be seen that leaching with alkali only, (sample No. 016D), in the absence of oxygen, did not have any effect on the sulfur content. When leaching in the presence of oxygen, the total sulfur content decreased, largely because of a decrease in the inorganic sulfur content. The total sulfur content was lower when higher oxygen partial pressures were used or when the leaching solutions were alkaline. The organic sulfur content was relatively constant, although it appeared slightly higher under non-alkaline conditions when water only was used as the leachant.

In Table 3 results are presented for desulfurization experiments in which a second leaching step was added after the first leaching step with an alkaline solution. The additional leaching was done in a non-oxidizing nitrogen atmosphere, using water, sulfuric acid, phosphoric acid, or sodium carbonate solutions. Aside from one run which appears to be anomalous, the total sulfur content did not seem to be reduced by the second leaching step.

The organic sulfur content, however, appears to be slightly higher than that obtained after one leaching step, under alkaline conditions and in the presence of oxygen. It may be possible that under the nitrogen atmosphere of the second step, some of the pyrite may be converted to elemental sulfur. Such a conversion would be characterized by a decrease in the pyritic sulfur, an increase in the organic sulfur, but no change in the total sulfur. Such a conversion would also be favored by acidic conditions.

Methyl Iodide Treatment of Oxydesulfurized Coal

The results in Table 4 show the effect of methyl iodide treatment on Star coal that had been precleaned by a float-sink technique and subsequently leached for 1 hr with 0.2 M sodium carbonate at 150°C under 50 or 200 psia partial pressure of oxygen. By comparison with the sulfur values in Table 1, the cleaning and leaching apparently removed only the inorganic sulfur, leaving the organic sulfur content largely unaffected. Leaching at higher oxygen partial pressure seemed to remove more total sulfur.

Curiously, subsequent treatment of the leached coal with methyl iodide did not seem to remove any organic sulfur as it did when applied to the raw, unleached coal (see Table 1). This lack of reactivity may be due to physical changes in the coal caused by the high temperature (150°C) of the leaching. Alternatively, the chemical leaching may have caused a conversion of reactive organosulfur groups into unreactive groups. Perhaps also the difference in the particle size (-200 mesh in this set of experiments compared to -150/+200 mesh in previous experiments) can be a contributing factor.

Conclusions

Treatment of coal with methyl iodide followed by extensive washing with a solvent to remove the reaction products has been used to remove approximately one-half of the organic sulfur content in an Iowa high volatile bituminous coal. The pyritic and sulfatic sulfur content was not affected by the methyl iodide treatment. Washing the coal with solvent only did not produce any effect either. On the basis of chemical reactions reported in the literature, it is assumed that the reactive sulfur groups that were removed by this treatment may be organic sulfides or mercaptans.

Subsequent leachings of the methyl iodide-treated coal under various conditions of oxydesulfurization did not reduce further the organic sulfur content. The inorganic sulfur content, however, was reduced by the oxydesulfurization steps. It can be assumed that all the reactive and accessible organic sulfur was removed by the methyl iodide treatment, and further chemical desulfurization was directed only against the inorganic sulfur.

When the coal was first precleaned by a float-sink technique and then leached by the oxydesulfurization procedure, the organic sulfur content was not affected by subsequent treatment with methyl iodide. This lack of reactivity of the organic sulfur toward methyl iodide may be caused by physical or chemical changes in the coal brought about by the high temperature or chemical nature of the oxydesulfurization process.

Acknowledgment

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Table 1. Effect of methyl iodide (MeI) treatment and acetone (Me₂CO) washing on sulfur content of coal.^a

No. ^b	Treatment	H.V., Btu./lb.	Ash, %	S Content, lb./10 ⁶ Btu.				S Redn., %	
				Tot.	Pyr.	Sulf.	Org.	Org.	Tot.
001D	None	12579	8.34	2.02	0.98	0.15	0.89	--	--
029D	Me ₂ CO	12495	8.95	2.06	1.08	0.20	0.78	--	--
003	MeI + Me ₂ CO	12552	8.29	1.68	1.08	0.17	0.43	50.6	16.8
004	MeI + Me ₂ CO	12490	8.46	1.62	1.18	0.14	0.30	66.3	19.8
005	MeI + Me ₂ CO	12506	8.57	1.78	1.04	0.10	0.64	28.1	11.9
Ave (of 003, 004, 005)		12516	8.44	1.70	1.10	0.14	0.46	48.3	15.8

^aStar coal (-150/+200 mesh).

^b"D" denotes average of duplicate analysis.

Table 2. One-step oxydesulfurization of MeI - treated coal.^a

Sample No. ^b	Leach soln.	O ₂ psia	H.V., Btu./lb.	Ash, %	S Content, lb./10 ⁶ Btu.				
					Tot.	Pyr.	Sulf.	Org.	Org.
001D	-- None	--	12579	8.34	2.02	0.98	0.15	0.89	
Ave. of 003, 004, 005	-- MeI	--	12516	8.44	1.70	1.10	0.14	0.46	
013	H ₂ O	50	12046	6.75	1.28	0.44	0.17	0.67	
006	Na ₂ CO ₃	50	10220	12.90	1.21	0.52	0.16	0.53	
014D	H ₂ O	200	11818	6.68	1.06	0.20	0.12	0.75	
012	Na ₂ CO ₃	200	11787	13.02	0.91	0.39	0.08	0.44	
016D	Na ₂ CO ₃	0 ^c	12245	7.41	1.63	0.95	0.11	0.57	

^aStar coal (-150/+200 mesh), treated with MeI and then leached 1 hr at 150°C with H₂O or 0.2 M Na₂CO₃ under 50 or 200 psia O₂.

^b"D" denotes average of duplicate analysis.

^cNon-oxidizing atmosphere of 50 psia N₂ partial pressure.

Table 3. Two-step desulfurization of MeI - treated coal.^a

Sample No. ^b	2nd step Leach	H.V., Btu./lb.	Ash, %	S Content, lb./10 ⁶ Btu.			
				Tot.	Pyr.	Sulf.	Org.
1st Leach Step with 0.2 M Na ₂ CO ₃ under 50 psia O ₂							
018D	H ₂ O	11119	14.28	1.30	0.67	0.03	0.60
020D	0.1 M H ₂ SO ₄	11529	6.72	1.24	0.46	0.05	0.73
023	0.1 M H ₃ PO ₄	11479	12.26	1.31	0.53	0.03	0.63
024D	0.2 M Na ₂ CO ₃	9042	13.33	1.20	0.52	0.07	0.61
1st Leach Step with 0.2 M Na ₂ CO ₃ under 200 psia O ₂							
027D	H ₂ O	11763 ^c	9.32	0.86	0.21	0.05	0.60
035D	0.1 M H ₂ SO ₄	11614 ^c	6.03	1.03	0.30	0.08	0.65
031D	0.1 M H ₃ PO ₄	11478 ^c	12.27	1.16	0.52	0.05	0.59
033D	0.2 M Na ₂ CO ₃	9831	19.65	1.20	0.65	0.08	0.47

^aStar coal (-150/+200 mesh), treated with MeI and then leached 1 hr at 150°C with 0.2 M Na₂CO₃ under 50 or 200 psia O₂. For 2nd step, leached 1 additional hr at 150°C under 50 psia N₂ with indicated leach solution.

^b"D" denotes average of duplicate analysis

^cH.V. calculated.

Table 4. Methyl iodide (MeI) treatment of leached coal.^a

Sample No. ^b	Treatment	H.V., Btu./lb.	Ash, %	S Content, lb./10 ⁶ Btu.			
				Tot.	Pyr.	Sulf.	Org.
060D	Leached under 50 psia O ₂	9162	9.53	1.29	0.24	0.05	1.00
062D	MeI treatment of Sample 060D	11370	10.63	1.26	0.24	0.01	1.01
064	Leached under 200 psia O ₂	10810	11.71	1.04	0.11	0.02	0.91
065D	MeI treatment of Sample 064	11534	10.56	0.96	0.10	0.01	0.85

^aStar coal (-200 mesh) precleaned and leached 1 hr at 150°C with 0.2 M Na₂CO₃ under 50 or 200 psia O₂.

^b"D" denotes average of duplicate analysis.

MOLECULAR COMPONENTS OF COAL AND COAL STRUCTURE. D. Bodzek and A. Marzec. Department of petroleum and Coal Chemistry. Polish Academy of Sciences. 44-100 Gliwice, 1 Maja 62 St. Poland.

High volatile bituminous coal was extracted at room temperature by means of 18 solvents having their electron-donor /DN/ and -acceptor /AN/ properties quantitatively determined. Extracts were analysed by field ionization and high resolution mass spectrometry. Extractable compounds having molecular masses in 200-600 a.m.u. range constitute 30% wt. of coal organic material. Hydrocarbons / $C_n H_{2n-6}$ up to $C_n H_{2n-34}$ /, nitrogen compounds /CHN, CHN_2 , CHN_3 /, oxygen compounds /CHO, CHO_2 / and nitrogen-oxygen compounds /CHNO, CHN_2O , $CHNO_2$, CHN_2O_2 , CHN_3O / were identified in the extracts. On the basis of extraction data /extract yields, solvent DN and AN numbers/ and MS analysis the conclusion has been drawn that extractable compounds are bonded to coal macromolecular network by electron-donor-acceptor bonds. These bonds are destroyed during extraction by substitution activity of solvents. Solvent substitution capabilities depend on their donor and acceptor numbers.