

NOVEL APPROACHES FOR DETERMINATION OF DEGREE OF
ASSOCIATION OF COAL-DERIVED PRODUCTS BY VAPOR PRESSURE OSMOMETRY

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INTRODUCTION

Vapor Pressure Osmometry (VPO) molecular weights of coal-derived asphaltenes obtained from coal liquids produced in five major coal liquefaction demonstration processes have been determined as a function of concentration in the solvents tetrahydrofuran (THF) and benzene (1). It was shown that association of coal-derived asphaltenes takes place in both solvents over the concentration range of 4-36g/l. In this study, the VPO molecular weights of the same asphaltenes have been obtained over a wider concentration range of 4-60g/l and a self-association model of asphaltenes in solution has been derived and the dissociation constants, one for the dissociation of dimeric complexes and one for the dissociation of higher order complexes, have been calculated with the aid of a modern computer.

This is the first time that VPO has been used to quantitatively correlate the degree of association of coal-derived asphaltenes in solution, although a number of other techniques have been used in the past (2-8, 13, 14).

THEORETICAL

In order to investigate the self-association of phenol in carbon tetrachloride solution, Coggeshall and Saier (2) carried out an IR study of the hydroxyl stretching region of phenol and obtained very good agreement between theory and experiment by using two equilibrium constants. They derived the following two expressions:

$$\alpha_n = n\alpha \frac{K}{K_1} \left[\frac{\alpha C}{K} \right]^{n-1} \quad 1)$$

$$K = \frac{C\alpha}{2(K_1 - \bar{K})} \left[2K_1 - \frac{\bar{K}}{2} + \sqrt{2K_1 \bar{K} + \frac{\bar{K}^2}{4}} \right] \quad 2)$$

where

- n = integer
- α_n = fraction of monomer bound in nth polymer
- α = fraction of monomer unassociated
- C = concentration in moles per liter
- K_1 = dissociation constant of dimer
- K = dissociation constant of all other polymers = $K_2=K_3\dots$
- \bar{K} = $2\alpha^2 C / (1 - \alpha)$

If C is the initial concentration of monomer before any association, at equilibrium the concentrations of monomer, dimer, trimer, etc., are C,

$$\frac{\alpha_2 C}{2}, \frac{\alpha_3 C}{3}, \dots, \frac{\alpha_n C}{n} \text{ and the molecular weights are } M_0, 2M_0, 3M_0, \dots \text{ and } nM_0.$$

Since the molecular weight measured in VPO is the number average molecular weight, it is given that

$$MW_{obs} = \frac{Mo \alpha C + 2Mo \cdot \frac{\alpha_2 C}{2} + 3Mo \cdot \frac{\alpha_3 C}{3} + \dots + nMo \frac{\alpha_n C}{n}}{C \cdot \left[\alpha + \frac{\alpha_2}{2} + \frac{\alpha_3}{3} + \dots + \frac{\alpha_n}{n} \right]} \quad 3)$$

where MW_{obs} is the number average molecular weight from VPO.

With the use of the relationship $\sum \alpha_n = 1$, $\frac{1}{1-x} = 1 + x + x^2 + \dots$, and

Equation 1, one may simplify Equation 3 and get

$$MW_{obs} = \frac{Mo}{\alpha \left[1 + \frac{K}{K_1} \frac{1}{\alpha C} - 1 \right]} \quad 4)$$

In theory, the equilibrium constants K and K_1 can be obtained by solving Equations 2 and 4 simultaneously at two different concentrations. The approach will be discussed in the next section.

EXPERIMENTAL

Coal-derived asphaltenes were separated by solvent fractionation (9, 10) from coal liquids produced in five major demonstration liquefaction processes: Synthoil, HRI H-Coal, FMC-COED, Catalytic Inc. SRC, and PAMCO SRC.

A Mechrolab Model 301A Vapor Pressure Osmometer was used to determine molecular weights with benzil employed as a standard. Both the non-aqueous probe and the thermostat were designed for 37°C. In normal runs, 6-8 molecular weights over the range 4-60 g/l were measured in the solvents benzene or THF.

A modern computer was used to solve the calculation problem according to the following steps:

- (a) Assume values of K and K_1 .
- (b) Calculate for α and β at two concentrations, C_1 and C_2 , from Equation 4 where MW_{obs} is the molecular weight from VPO. When the concentration is C_1 , the fraction of monomer unassociated at equilibrium is α , and when the concentration is C_2 , it is β .
- (c) Substituting C_1 , C_2 , α and β into Equation 2 and get

$$K = \frac{C_1 \alpha}{2(K_1 - \bar{K}_1)} \left[2K_1 - \frac{\bar{K}_1}{2} + \sqrt{2K_1 \bar{K}_1 + \frac{\bar{K}_1^2}{4}} \right] \quad 5)$$

$$K = \frac{C_2 \beta}{2(K_1 - \bar{K}_2)} \left[2K_1 - \frac{\bar{K}_2}{2} + \sqrt{2K_1 \bar{K}_2 + \frac{\bar{K}_2^2}{4}} \right] \quad 6)$$

where $\bar{K}_1 = 2 \alpha^2 C_1 / (1 - \alpha)$

$\bar{K}_2 = 2 \beta^2 C_2 / (1 - \beta)$

Since K is independent of concentration, by combining Equations 5 and 6, it is given that

$$\frac{\alpha C_1}{2(K_1 - \bar{K}_1)} \left[2K_1 - \frac{\bar{K}_1}{2} + \sqrt{2K_1\bar{K}_1 + \frac{\bar{K}_1^2}{4}} \right]$$

$$= \frac{C_2\beta}{2(K_1 - \bar{K}_2)} \left[2K_1 - \frac{\bar{K}_2}{2} + \sqrt{2K_1\bar{K}_2 + \frac{\bar{K}_2^2}{4}} \right] \quad (7)$$

- (d) Solve Equation 7 for K_1 by the Newton-Raphson method.
- (e) Calculate K from Equation 5 or 6.
- (f) Repeat the same procedures until the calculated values of K and K_1 are close enough to the assumed values.
- (g) Using the equilibrium constants obtained above the molecular weights over the concentration range of 4-65 g/l can be calculated based on this model. The fraction of monomer unassociated at each concentration is obtained by solving Equation 2 and the fraction of monomer bound in any degree of polymer can be also obtained from Equation 1.

A number of different equilibrium constant pairs, K and K_1 , have been tried for five asphaltenes in benzene. The ones which afford the minimum standard deviations between the experimental and calculated molecular weights have been chosen.

RESULTS AND DISCUSSION

The VPO molecular weights for all five coal-derived asphaltenes, in benzene are shown in Figs. 1 to 5. The results indicate that association of coal-derived asphaltenes takes place in both solvents over the concentration range of 4-60 g/l. The calculated equilibrium constants, together with the standard deviations are summarized in Table I where the % Dev. is defined as:

$$\frac{\text{Standard Deviation of MW}}{\text{MW of Monomer}} \times 100\%$$

All % Dev. values are less than 5.5%. This suggests that this two parameter model is efficient in describing the self-association of asphaltenes from five different processes in benzene and THF. The calculated molecular weights, fraction of monomer and monomer bound in dimer and trimer are also plotted in Figs. 1 to 5 for the five asphaltenes.

It is interesting to note from Equation 4 that $MW_{obs} \approx Mo/\alpha$ as $C \rightarrow 0$ and $Mo/\alpha \approx Mo$ since $\alpha \rightarrow 1$ as $C \rightarrow 0$. This agrees with the experimental results obtained from VPO and reported in Reference (1) that molecular weight values found in different solvents, by extrapolating the plots to infinite dilution are in accordance. These infinite dilution molecular weight values approximate the true monomer molecular weights and were used as Mo throughout this study.

The association of petroleum asphaltenes has been studied by a variety of techniques (3-8) and the mechanism of self-association has been described largely in terms of electronic association. The mechanism of bonding in coal-

derived asphaltenes is important and is under study (11). The association of these species has been reported in terms of hydrogen bonded complexes which can be separated into acidic and basic components (12). The hydrogen bonding of these two components and some model complexes has been further studied by NMR (13,14). Unfortunately, all of the reports on coal-derived asphaltenes contain only qualitative results. However, these studies tend to support the self-association model derived here, since it is very likely that in solution dimer could be formed through the bondings between the acidic proton and basic nitrogen or oxygen of two molecules or trimer could be formed through the bondings between those of three molecules. The association of monomer into dimer, trimer in solution depends on the solvent used. It is more significant in the less polar solvent benzene than THF, so the variation of molecular weights vs. concentration in benzene is greater.

This study is significant because, based on this model, the heat of formation of the polymers can be calculated from equilibrium constants at various temperatures and the mechanism of the bonding can be studied. This is the first time that VPO has been used to quantitatively correlate the degree of association of coal-derived asphaltenes in solution.

Comparing the equilibrium constants K_1 and K of these five different asphaltenes in benzene, it is found that Synthoil and PAMCO SRC asphaltenes have stronger association between molecules while FMC-COED and Cat. Inc. SRC asphaltenes have less. The equilibrium constants in THF are generally larger than in benzene, since THF is more polar solvent and tends to dissociate the asphaltene molecules as they are dissolved. But this dissociation tends to go to completion in either solvent at infinite dilution.

The curves labeled 1,2,3 in Figs. 1 to 5 show the distribution of asphaltene between monomer, dimer and trimer as a function of total asphaltene concentration. For example, if 20 gm of Cat. Inc. SRC asphaltene is dissolved in 1 l benzene at 37°C, the fractions of monomer, dimer and trimer are 0.70, 0.18, 0.07 (from Fig. 1), while the remaining 0.05 is contained as polymers higher than trimer. The concentrations of monomer, dimer and trimer can be calculated and are:

$$\text{concentration of monomer (moles/l)} = \frac{20}{483} \times 0.7 = 2.9 \times 10^{-2} \text{M}$$

$$\text{concentration of dimer (moles/l)} = \frac{20}{483} \times 0.18 \times \frac{1}{2} = 3.7 \times 10^{-3} \text{M}$$

$$\text{concentration of trimer (moles/l)} = \frac{20}{483} \times 0.07 \times \frac{1}{3} = 9.7 \times 10^{-4} \text{M}$$

If the rest is assumed tetramer then concentration of tetramer (moles/l) = $\frac{20}{483} \times 0.05 \times \frac{1}{4} = 5.2 \times 10^{-4} \text{M}$ where the number 483 is the molecular weight of monomer.

In benzene solution, as the concentration increases, the fraction of asphaltene existing as the dimer reaches a maximum, and then decreases, and higher multimers become increasingly important. In highly concentrated solutions these larger multimers start to precipitate. Evidence for association of monomeric asphaltenes into 4-6 average layers in the solid state has been found by x-ray diffraction spectroscopy (15).

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Table 1. Calculated Equilibrium Constants and Standard Deviations of Coal-Derived Asphaltenes in Benzene

Process	Monomer MW **	K_1	K_2	Standard Deviation	% Dev.
Synthetic Asphaltene	560	0.0762	0.0671	13.7	2.4
IRI Asphaltene	492	0.118	0.0866	9.0	1.8
FMC-COED Asphaltene	375	0.210	0.0813	20.7	5.5
Cat. Inc. SRC * Asphaltene	483	0.225	0.109	12.2	2.5
PANCO SRC * Asphaltene	532	0.0610	0.0971	18.6	3.5

*Isolated from vacuum distilled bottom product.

** From Ref. (1).

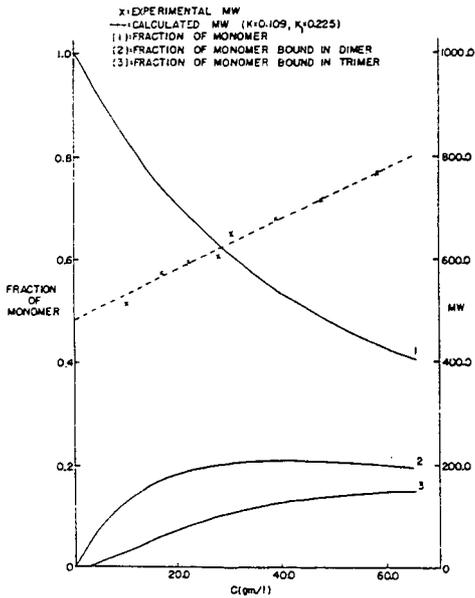


FIG. 1 FRACTIONS OF MONOMER AND VPO MW VS CONCENTRATION CAT. INC. ASPHALTENE IN BENZENE

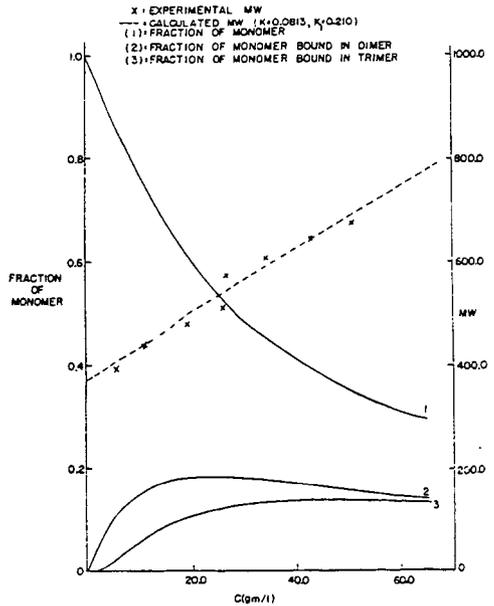


FIG. 2 FRACTIONS OF MONOMER AND VPO MW VS CONCENTRATION FMC-COED ASPHALTENE IN BENZENE

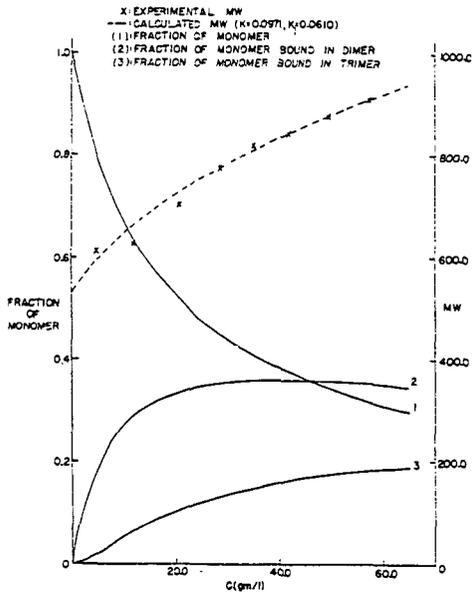


FIG. 3 FRACTIONS OF MONOMER AND VPC MW VS CONCENTRATION PAMCO ASPHALTENE IN BENZENE

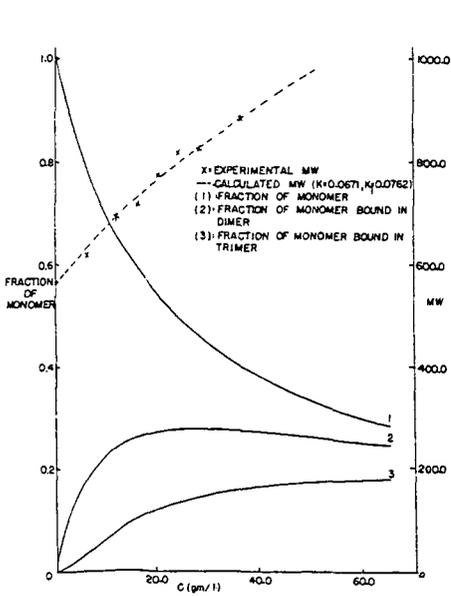


FIG. 4 FRACTIONS OF MONOMER AND VPO MW VS CONCENTRATION SYNTHOL ASPHALTENE IN BENZENE

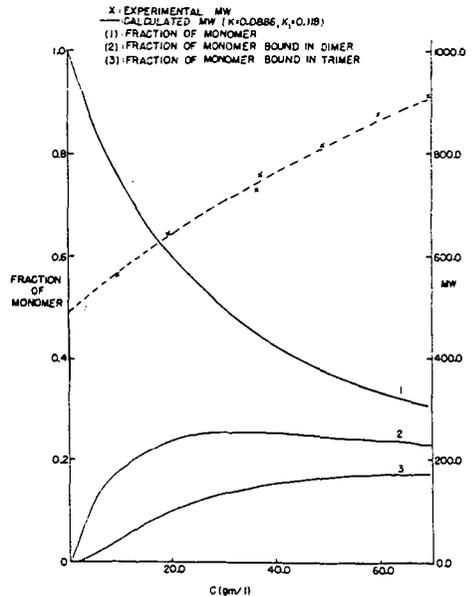


FIG. 5 FRACTIONS OF MONOMER AND VPO MW VS CONCENTRATION HRI ASPHALTENE IN BENZENE

On the Distribution of Organic Sulfur Functional Groups in Coal.

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1. SULFUR IN COAL

Traditionally, the sulfur in coal has been considered in two classes: 1) inorganic sulfur and 2) organic sulfur. In the class of inorganic sulfur, two types of compounds were considered: the disulfides and the sulfates. The organic sulfur is all the sulfur which is connected to the hydrocarbon matrix. Standard analytical techniques (1)(2)(3) are used to estimate the concentration of each class of sulfur in coal samples.

The inorganic sulfur, which is mainly iron pyrite, FeS_2 , is present in the form of isolated crystals. Part of the FeS_2 particles are usually separated from the coal by simple physical separation. However, the organic sulfur can be removed from coal only if the chemical bond between carbon and sulfur is broken. The chemistry, the thermodynamics and the kinetics of the reactions of sulfur in coal have been reviewed recently (4)(5)(6) and the reader is referred to these manuscripts for details.

The chemistry of the reactions of FeS_2 and their rate are obviously different from that of the organic sulfur. Moreover, since the organic sulfur is present in the form of different functional groups, each functional group reacts at a different rate (6)(7).

2. ORGANIC SULFUR FUNCTIONAL GROUPS IN COAL

Very little data on the functional groups in which the organic sulfur appear and on their distribution has been derived by direct observation on coal. However, it is plausible to assume that the organic sulfur is present in coal in the same types of sulfur functional groups that can be found in oils and in other organic sulfur containing molecules. Moreover, if a general rule that applies throughout organic chemistry is applied to the sulfur in coal, we can say that the organic sulfur groups in coal react in the same way as their low molecular weight homologs and produce the same types of reaction products. For example, organic thiols, RSH, can be reduced by hydrogen to hydrogen sulfide, H_2S :



Thus, all the thiols, irrespective of the size and the shape of the radicals, R, can be reduced by H_2 to RH and H_2S . Variations in the rate of the reduction may, however, exist for different R's.

The most important sulfur functional groups in coal are believed to be:

1. derivatives of thiophenes and alkyl thiophenes

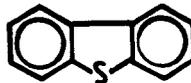
The most important parent structures are:



Thiophene



Thianaphene



Dibenzothiophene

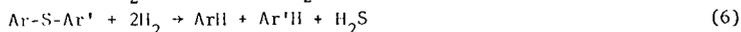
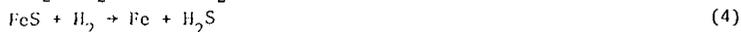
2. aryl sulfides: $\text{Ar-S-Ar}'$
3. aliphatic sulfides: R-S-R
4. cyclo sulfides, e.g.,
5. thiaphenoles

The presence of disulfides, sulfoxides, and sulfones were never demonstrated. It is believed that disulfides and sulfoxides are too unstable to survive the coalification process. Most of the organic sulfur is present in the forms of thiophenes and alkyl, aryl, and cyclic sulfides (4)(5)(6)(7). Most of the information was obtained from examination of the smaller molecular products

which were obtained by breaking the organic coal matrix (depolymerization). Obviously, the technique which is used to depolymerize the coal would have a deterministic effect on the results, since drastic depolymerization techniques may change the structures of the sulfur constituents as well as that of the hydrocarbon parts. Several reviews of the chemistry of sulfur in coal can be found in the older literature (8) (9) (10) (11) (12). Some aspects of the organic sulfur groups have recently been discussed by Attar and Corcoran (7).

3. THE PRINCIPLE OF THE PROPOSED METHOD OF ANALYSIS

All the sulfur groups in coal can be reduced by hydrogen to hydrogen sulfide, H_2S :



Each of these reactions has a given activation energy and a frequency factor which vary in a limited range for each group of sulfur compounds, when the structure of the organic radical is changed. Other reducing agents which contain hydrogen can be used with the same effective results:

These observations lead to the following important deductions: 1. If the activation energy E_{ai} and the frequency factor A_i for the rate of reduction of the i -th functional group are determined, the i -th group is uniquely characterized. In other words, a particular value of E_{ai} and A_i can belong only to the i -th group, and therefore they define the i -th group and 2. The exact amount of H_2S that evolves when the i -th group is reduced is proportional to the amount of the i -th sulfur group that has been reduced. If all the amount of the i -th group in the sample was reduced, then the amount of H_2S that evolved is proportional to the amount of the i -th group in the sample.

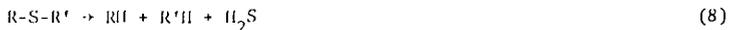
In order to be able to determine the total amount of each sulfur group in a fixed sample of coal, the following problems have to be solved:

1. How to determine the activation energy and the frequency factor for each sulfur group.
2. How to quantitatively reduce all the sulfur in a coal sample to H_2S and how to determine its amount.

The activation energies and the frequency factors can be determined using Juntgen method. Juntgen method and the methods which we proved that can be used to quantitize the H_2S are discussed in the next sections.

3.1 JUNTGEN METHOD FOR THE DETERMINATION OF E_{ai} AND A_i

Consider a sample which contains a fixed quantity of sulfur in the form of different functional groups. Let us assume that each group can be reduced to H_2S by a first order reaction. For example, consider the reduction of the aliphatic sulfides:



$$\frac{d[H_2S]_1}{dt} = k_1 [R-S-R'] \quad (9)$$

The index 1 was used to denote the sulfidic functional group; $R-S-R'$. Let's assume further that the rate constant, k_1 , depends on the temperature according to Arrhenius equation:

$$k_1 = A_1 c^{-\frac{E_{a1}}{RT}} \quad (10)$$

where A_1 is the frequency factor and E_{a1} the activation energy for the reduction. Then:

$$\frac{d[\text{H}_2\text{S}]_1}{dt} = A_1 c^{-\frac{E_{a1}}{RT}} [R-S-R'] \quad (11)$$

The rate constant of the reduction becomes larger at higher temperatures. That means that the rate of depletion of sulfide becomes larger at higher temperatures. The rate of evolution of H_2S from a sample with a fixed amount of the sulfide, which temperature is gradually increased, will increase initially due to the increase in the temperature, but since the concentration of the sulfur is depleted in the process, due to the evolution of H_2S , the rate will begin to decrease after most of the sulfur was reduced. The mathematical equation which describes the rate of evolution of gas as a function of the temperature of the sample, where the temperature is increased linearly with the time were developed by Juntgen (13)(14). Suppose that the temperature is increased according to:

$$T = T_0 + \alpha t \quad (12)$$

where T_0 is the initial temperature ($^{\circ}\text{K}$), α the rate of heating, $^{\circ}\text{K}/\text{min}$, and t the time, min. Then the volume of H_2S , V_i , that evolves when the i -th group is reduced, follows the equation:

$$\frac{dV_i}{dt} = \frac{A_i V_{i\infty}}{\alpha} \exp \left[-\frac{E_i}{RT} + \frac{A_i RT^2}{E_i} \left(1 - \frac{2RT}{E_i} \right) c^{-\frac{E_i}{RT}} \right] \quad (13)$$

where $V_{i\infty}$ denotes the total volume of H_2S that will evolve as a result of the complete reduction of the i -th group. The graph of this function is sketched in Figure 1.

The temperature at which the rate of evolution of H_2S from the i -th group reaches its maximum is denoted by T_{mi} , and is a unique function of E_{a1} and A_1 and the rate of heating, α :

$$\frac{RT_{mi}^2}{\alpha} \frac{A_i}{E_{a1}} = c^{-\frac{E_{a1}}{RT_{mi}}} \quad (14)$$

Equation (14) means that if the sample is heated at the constant rate α , the apex of the H_2S peak from the i -th group, which is reduced with activation energy E_{a1} and frequency factor A_1 , will be different from that of the j group which is reduced with different parameters, E_{aj} and A_j .

When a mixture which contains several functional groups is reduced, the behavior of each sulfur group is similar, except that each peak will appear at a different T_m . Figure 2 shows the graph for a mixture of several groups.

The reduction curve, or the "kinetogram" can be used to derive the following data:

1. The location of T_{mi} is characteristic of the i -th functional group.
2. The integral of the peak of each group is the exact stoichiometric equivalent of the sulfur group that has been reduced. The activation energy and the frequency factor of the reaction can be determined by curve pitting of the data to equation 12.
3. Slightly different variations of this method were used by Juntgen and co-workers to study the rates of coal pyrolysis and gasification (13)(14)(15),

by Campbell and Stephen (16) to study the rates of coal pyrolysis, and by Yerger et al. (17) and Bauman et al. (18) to study the rate of evolution of H₂S during coal hydrogenation. In the latter studies, not all the sulfur was removed from the coal, therefore, quantitation of the sulfur groups cannot be done from the data. A more detailed discussion of the quantitation is presented below.

5.2 QUANTITATION OF THE DATA

The most important problems that should be solved so that the analysis of the sulfur groups in coal will be quantitative are:

1. COMPLETE reduction of each sulfur group.
2. COMPLETE recovery of all the H₂S from each sulfur group.

The major difficulty on the road to obtain complete reduction of the sulfur groups are mass transfer limitations. The diffusion of the reducing agent into the coal particle is slow and so is the diffusion of the H₂S out of the coal particles. These processes result in incomplete reduction of the sulfur and in the spreading of the peak from one group over a large interval of temperature. To reduce the effect of mass transfer, we used finely divided coal particles and conducted the reduction in a solvent which partially liquefies the coal. In addition, we added Co-Mo catalyst to the cell to enhance the rate of reduction of sulfur groups.

Complete recovery of all the H₂S was impossible when lignite with a large content of calcium carbonate was examined. Apparently, some of the H₂S reacted with the carbonate according to:



Most of the basic carbonates in coal, e.g., calcite, dolomite, and sidrite can, however, be easily dissolved in dilute hydrochloric acid and removed from the sample.

The application of the special solvent permitted us to reduce most of the organic sulfur below 370°C and 100 psi.

4. EXPERIMENTAL SYSTEM

The experimental system consists of five parts: 1) reduction cell, 2) hydrogen sulfide detectors, 3) gas flow systems, 4) heater and temperature programmer, and 5) recording and signed processing device.

Figure 3 shows the functional relation among the units. All the components except for the reduction cell are standard. Several prototypes of cells were built and tested in our laboratory. The first prototype is described in Figure 4.

One commercial detector and two modified detectors were tested: 1) the lead-acetate detector*, 2) the flame photometric detector, and 3) electrolytic detector. The first two are differential detectors, while the third is an integral detector. The data that are reported in this manuscript were derived using the lead acetate detector.

5. RESULTS AND DISCUSSION

Two questions are addressed: 1. the identification peaks which belong to a specific functional group. 2. the variation in the distribution of sulfur groups in different coals.

5.1 IDENTIFICATION OF PEAKS

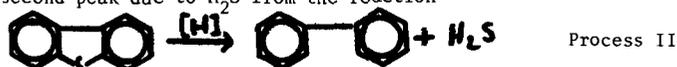
The philosophy of the identification technique is that when solids are reduced peaks that belong to a specific sulfur group will appear at the same temperature, T_{mi}, provided that the same rate of heating is used, and that the mass

* The courtesy of Mr. C. Kimbell, President of Houston Atlas, who loaned us the equipment and helped us in its modification is greatly appreciated.

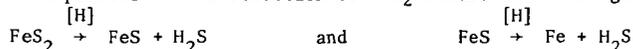
transfer does not limit the rate of reduction. Therefore, solid polymers that contain only one sulfur group, will produce one peak of sulfur only, the peak that corresponds to the sulfur group which they have. Thus, polythiophenes produce a peak which corresponds to the group ---S--- . Rubber produces a peak which corresponds to R-S-R and R-S-S-R, etc. Figure 5 shows the kinetogram of rubber. Figure 6 shows the kinetogram of thianthrenes . Note that two different peaks appear. The authors believe that the first peak is due to H_2S from the reaction



and the second peak due to H_2S from the reaction



The reduction of the first sulfur appear to be kinetically equivalent to the reduction of aromatic sulfides. However, the reduction of dibenzothiophene occurs at a higher temperature. The reduction of FeS_2 occurs in two stages as expected:



However, the "sharpness" of the peak depends on the particle size of the FeS_2 . Small FeS_2 produce very sharp peaks and larger FeS_2 particles produce a "sluggish" peak. The FeS and Fe produce resistance to mass transfer.

6.2 TESTS OF COAL AND LIGNITE SAMPLES

Table 2 gives the distribution of sulfur in Illinois No. 6 coal, and in Texas lignite. Figure 7 shows the kinetogram of the Illinois No. 6 coal. A tentative assignment of functional groups to the peaks is given on the chart. Extraction of the coal with nitric acid removes the pyritic sulfur altogether, and slightly affects the organic sulfur as well. The latter is expected because nitric acid oxidizes organic sulfur to the corresponding sulfoxides (19). Figure 8 shows the kinetogram of HNO_3 extracted Illinois No. 6 coal. Table 2 shows a quantitative estimate of the distribution of sulfur groups in Illinois No. 6 and in Texas lignite.

Texas lignite (Milam Co.) is more porous than bituminous coal, and therefore its resistance to mass transport is smaller than that of bituminous coal. Most of the sulfur in the samples that were tested was organic. The kinetogram in Figure 9 shows that the organic sulfur in the lignite was essentially in the form of isolated single thiophenic rings, and not in the form of dibenzothiophenes or aliphatic sulfides. This indicates that the thiophenic structures are formed in coals in early stages of the geological coalification of wood. This thiophenic structure condenses latter to dibenzothiophenic structures etc. The latter observation was unexpected, and we searched for reaction mechanisms which may lead to the same experimental observation. One such mechanism involves the reaction:



This reaction shows that isolated thiophenic structures can be produced from unstable sulfur-containing groups due to thermal decomposition. Thermally unstable sulfur groups are reduced to H_2S at much lower temperatures than stable groups, (see discussion in Ref. 6). However, if not all the unstable sulfur was reduced while the temperatures were still low, part of it may be converted into a more stable form during the analysis. Thus, if mass transfer limits the rate of reduction, the result of the analysis of coal samples will be biased, and will show a larger fraction of single-thiophenic rings.

Another observation which seems interesting is that the fraction of sulfidic sulfur is about the same in the lignite and in the bituminous coal. This observation can be accidental, however, similar results were noted by others (20).

6. CONCLUSION

A method has been developed which permits to conduct detailed quantitative analysis of the distribution of sulfur groups in coal. The method permits to determine qualitatively and quantitatively the distribution of organic sulfur groups in coal samples. Illinois No. 6 bituminous coal and Texas lignite were tested, and the results are consistent with accepted theories on the sulfur in coal.

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Table 1: Sulfur Classes in Illinois #6 and in Texas Lignite

	Illinois #6	Texas Lignite
Total Sulfur	4.05	1.03
FeS ₂ wt%	1.56	0.19
SO ₄ wt%	0.38	0.07
Organic wt%	2.09	0.77

Table 2: Wt% of the Organic Sulfur in Different Functional Groups
 Tentative assignment. ±15% error is possible.

Structure	Illinois No. 6 (Bituminous)	Texas Lignite
-SH	present in small amounts	
aliphatic or alicyclic 	27.4	26.6
-S- or 		
Dibenzothiophenic	41.8	16.3
Single thiophenic or other very stable group.	30.8	57.1

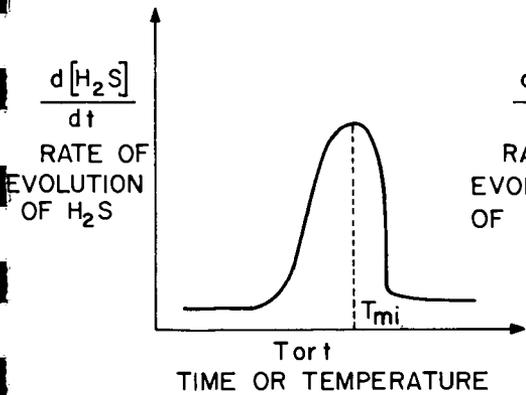


FIGURE 1: ANALYSIS OF MATERIAL WITH A SINGLE FUNCTIONAL GROUP

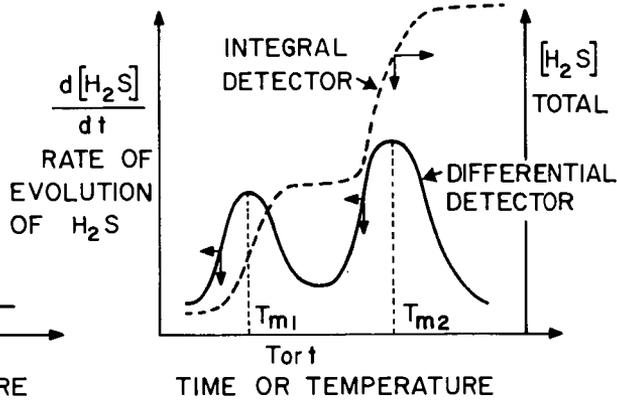


FIGURE 2: ANALYSIS OF A MIXTURE CONTAINING TWO GROUPS USING A DIFFERENTIAL AND AN INTEGRAL DETECTORS.

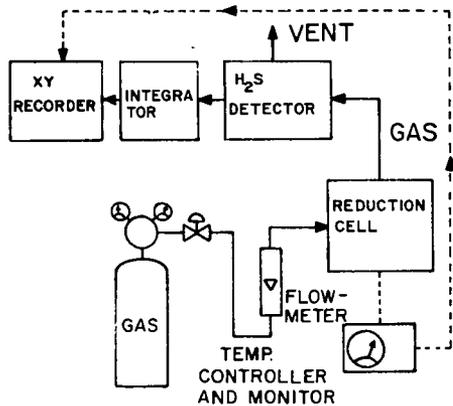


FIGURE 3: SCHEMATIC DIAGRAM OF EXPERIMENTAL SYSTEM.

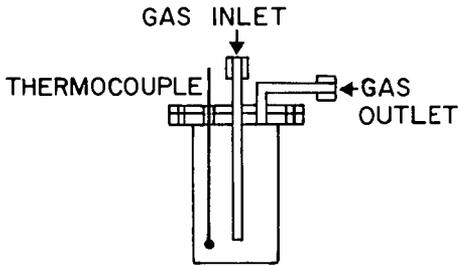


FIGURE 4: PROTOTYPE OF REDUCTION CELL.

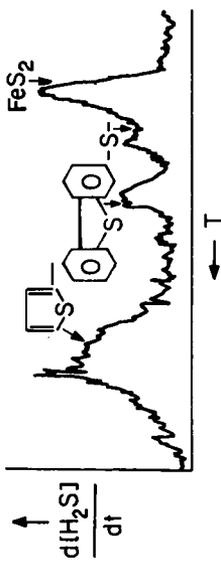


FIGURE 7: KINETOGRAM OF 32.6 mg ILLINOIS No. 6 BITUMINOUS COAL. THE GROUP ASSIGNMENT IS TENTATIVE.

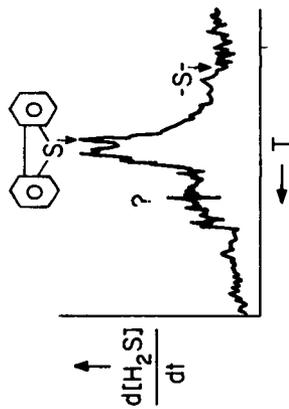


FIGURE 8: KINETOGRAM OF ILLINOIS No. 6 - EXTRACTED WITH HNO₃.

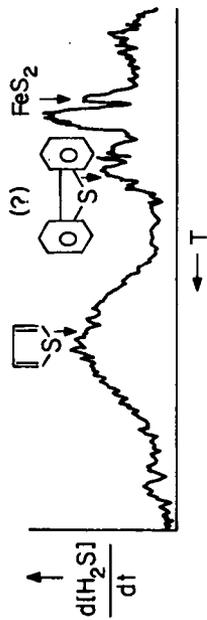


FIGURE 9: KINETOGRAM OF TEXAS LIGNITE. THE GROUP ASSIGNMENT IS TENTATIVE.

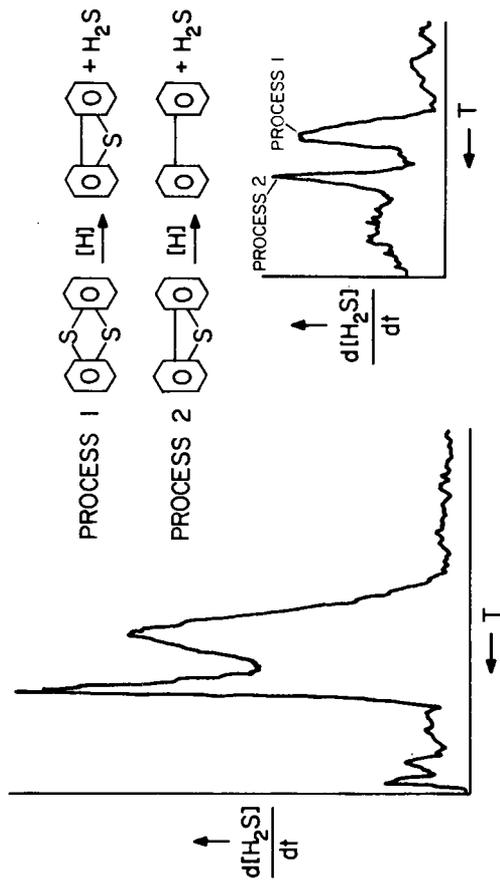


FIGURE 5: KINETOGRAM OF RUBBER.

FIGURE 6: KINETOGRAM OF THIANTHRENE.