DETERMINATION OF ORGANIC SULFUR-CONTAINING STRUCTURES IN COAL BY FLASH PYROLYSIS EXPERIMENTS

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Introduction

The sulfur in coal exists as both organic and inorganic forms. The inorganic forms are predominantly iron pyrite, although other metal sulfides and sulfates such as gypsum may also be present. ASTM tests [12,13] allow us to determine the total sulfur content of coals and the inorganic sulfur forms present. The total sulfur in organic structures is usually determined by difference, although electron microprobe can be used to determine it directly.

Despite its importance, there is only limited information in the literature on the chemical structures of sulfur in the organic components of coal. Attar [1,2,3,4,] has developed an interesting approach to determining the organic chemical structures of sulfur in coals by the programmed temperature reduction to H_2S. Discrete H_2S peaks are detected at various temperatures which presumably come from different sulfur entities. However, recovery of the sulfur has been low and interpretation of the results is difficult. LaCount [5] has developed a similar approach based on the programmed temperature oxidation to SO_2. SO_2 peaks are obtained at specific temperatures but assigment to particular sulfur structures is difficult and uncertain.

It was to see whether flash pyrolysis would provide an independent and new insight into coal sulfur structures that this research was undertaken.

Preliminary Experiments

Pyroprobe Pyrolysis

To identify pyrolysis products which might be expected from a more controlled pyrolysis of high sulfur coals, a Pyroprobe [6] programmed temperature solids pyrolyzer was connected to a GC/MS spectrometer (a Varian 3700 gas chromatograph with DB-5 column programmed from 60-230°C at 6°C min^{-1} coupled to a Micromass 16 mass spectrometer. Approximately 0.5 mg of coal was inserted into a 1 mm thin walled quartz tube and held in place with plugs of quartz wool. The tube was inserted in the pyroprobe and the temperature programmed from 250 to 1000°C at 20°C/millisec. The resulting mass patterns were resolved to identify the volatile sulfur compounds. Their yields were determined as area percent of total volatiles area. Results for one high sulfur coal - Pittsburgh 8-R&F - as the raw coal and as coal with most of the pyrite removed are shown in Table 1.

It can be seen by examination of Table 1 that a number of volatile or gaseous sulfur compounds are formed including H_2S, COS, CS_2, CH_3SH, and SO_2. In addition, many thiophenic compounds including thiophene, thianaphthene, and dibenzothiophene and most of the possible methyl derivatives of these three heterocyclic compounds are observed. No doubt many higher molecular weight heterocyclic compounds are formed which do not reach the mass spectrometer detector.

Removal of the mineral matter including the pyrite apparently reduces the SO_2, CS_2 and COS formed. With those exceptions, the products from the raw and low pyrite coals are qualitatively similar.

Solvent Extraction

To determine whether the sulfur species in coal are extractable or chemically bound into the coal structure, batch extraction experiments were carried out with four different solvents representing a range of solubility parameters (9.5-11.75). The extractions were run in 10 ml Hastalloy shaker tubes containing metal mesh baskets on the top sections to contain the coal. With solvent in the bottom section, the extractions were run at $100^{\circ}C$ for 4 hours with vertical shaking. The results are shown in Table 2.

As can be seen in the table, based on sulfur contents of the extracts, only a small fraction of the sulfur in the coal is solvent extractable.

Constant Temperature Flash Pyrolysis

A number of coals were pyrolyzed in the continous flash pyrolysis equipment shown in Figure 1. A Sigma 3B Perkin Elmer gas chromatograph equipped with a 3-column system and flame photometric sulfur detector provided sensitive analyses for the volatile sulfur products of coal pyrolysis.

The coal particles are entrained into the nitrogen stream in the feeder and carried over into the fluidized sand bed at the flash pyrolysis temperature. The coal pyrolyses in the sand bed and the volatile products are carried out of the reactor through a cellulosic thimble filter and much of the light char formed is entrained in the exit gas and carried into the filter also. Depending on the coal type, some of the coal is converted to coke in a process, going through a fluid or soft stage which remains on the sand particles or adhering to the reactor walls. Many of the high sulfur coals of particular interest in this study are so called "caking coals" which tends to make the sand particles adhere to each other. This creates problems in running the pyrolysis experiment by defluidizing the sand bed and plugging the inlet system to the reactor. While this often makes long pyrolysis runs difficult or impossible, in most cases, conditions can be used to provide adequate run life to get valid and useful data.

It is of interest to know how the sulfur in coal distributes itself among the various pyrolysis products. Not surprisingly, this depends upon the rank and sulfur components of the coal as well as the pyrolysis conditions. Table 3 shows the distribution of pyrolysis

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products and sulfur containing products (as sulfur) of a typical high sulfur bituminous coal and a low sulfur lignite at 850°C. It will be noted that material recovery is good, despite the small amount of coal pyrolyzed. Sulfur recovery from the caking bituminous coal, however, is not as good. The pyrolysis products coat the reactor system and cannot be recovered for sulfur analysis. Also much of the coke remains on the sand and relatively large amounts of sand have to be analyzed for low levels of sulfur with some loss in accuracy.

Twenty-five to 50% of the sulfur in the coal (depending on the pyrolysis temperature) appears in the gaseous products as H_2S, CS_2, COS, and SO_2. The remainder of the sulfur appears in the tar, char, and coke, probably as stable thiophenic sulfur which remains in the coal structure or is released as heterocyclic compounds in the tar.

Preliminary Conclusions

One can surmise from these preliminary results that the organic sulfur in coal is largely chemically bound in the macromolecular structure of the coal, in part as labile, probably pendent, sulfur-containing side chains, and partly as heteroatoms in clusters of aromatic rings (thiophenic). Decomposition of the pendent groups probably accounts for much or all of the gaseous sulfur compounds (H_2S, COS, CS_2 and CH_3SH). The sulfur structures in the heterocyclic rings are stable at the temperatures used, but are partly broken away from the coal structures by rupture of other weaker carbon-carbon bonds: attaching these rings in the coal.

Continuous Flash Pyrolysis

Pyrolysis of Coal

To use pyrolysis to study the sulfur constituents of coal, it is necessary to know what sulfur containing products are produced and also what components in the coal are breaking down to produce them. The literature provides some clues as to the origins of some of these products:

When pyrite is pyrolyzed at temperatures of 550°C or higher, the initial breakdown[7] products are sulfur and pyrrhotite (FeS).

$$Fe\ S_2 \xrightarrow{\quad 550°C \quad} Fe\ S + S \qquad (1)$$
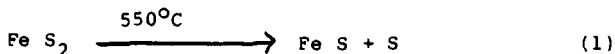
When the pyrite is in coal, the sulfur produced can react with hydrogen containing components of the coal (probably alkyl or hydroaromatic units) to form H_2S
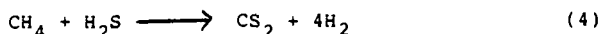
$$S + (Coal\ H) \longrightarrow H_2S + (Coal) \qquad (2)$$

Sulfur can also react with the coal matrix to form stable non-volatile products in the coal or coke[8,9].

At temperatures over 800°C, a significant amount of the H_2S or sulfur reacts with the coal to form carbon disulfide.

$$H_2S + (Coal) \longrightarrow CS_2 + H_2 \qquad (3)$$
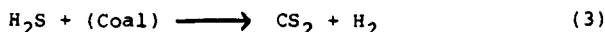
Similar reactions are observed when H_2S is reacted with methane,

$$CH_4 + H_2S \longrightarrow CS_2 + 4H_2 \qquad (4)$$

and since methane is produced in coal pyrolysis, this reaction may be a major route by which CS_2 is formed. The higher the pyrolysis temperature the larger the proportion of H_2S is converted to CS_2.

In most coal pyrolyses, a small amount of carbonyl sulfide is formed. Since COS is formed by reaction of CO and elemental sulfur, and substantial amounts of CO are formed on coal pyrolysis, it is likely that some sulfur formed by pyrite pyrolysis reacts with CO to form COS.

$$CO + S \longrightarrow COS \qquad (5)$$
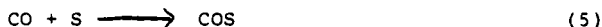
It will be noted that when pyrite is low, the amount of COS produced is also small.

COS is also produced by pyrolysis of organic sulfoxides. However, these appear to be low or absent in most coals.

Some coals contain small amounts of sulfur as sulfates, although most of the sulfur in coal is in the reduced state. If these inorganic sulfates in coal are pyrolyzed in the presence of coal containing pyrite, SO_2 is formed. While the stoichiometry of this reaction has not been adequately demonstrated, it appears that the following reaction or something similar to it is going on.

$$CaSO_4 + FeS_2 + H_2O \longrightarrow CaO + FeS + 2SO_2 + H_2 \qquad (6)$$
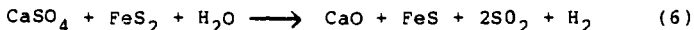
SO_2 is also formed in pyrolysis of organic sulfones. but these appear to be very low or absent in most coals.

Pyroprobe pyrolysis of coal shows formation of small amounts of methyl mercaptan, and model compounds containing $-SCH_3$ groups pyrolyzed at low temperatures ($600^\circ C$ and lower) do form methyl mercaptan. However, little of this compound is observed in our continuous coal pyrolysis experiments.

Pyrolysis of Model Sulfur Compounds

To learn the behavior of the various types of organic sulfur structures in pyrolysis, a series of solutions of low molecular weight sulfur compounds was prepared in benzene at concentrations roughly approximating the organic sulfur content in high sulfur coals. Using a precise piston pump and vaporizer, these compounds were introduced into the pyrolyzer at rates roughly comparable to the rates used in pyrolyzing coal. Pyrolysis temperatures of 600, 700, 800, 850, 900 and $950^\circ C$ were used. Some 16 model sulfur compounds were pyrolyzed at the various temperatures. Figure 2 shows conversion of some of these compounds at various temperatures. This shows that aliphatic and benzylic sulfides, mercaptans and disulfides split out H_2S at relatively low temperatures ($600-800^\circ C$). Aromatic sulfides and mercaptans require $900^\circ C$ to give high conversions to H_2S and CS_2. The three major thiophenic compounds, thiophene, thianaphthene, and dibenzo-thiophene show only a relatively low conversion even at $950^\circ C$. This provides a basis for differentiating between sulfur types in coal.

However, this assumes that the sulfur compounds in coal behave similarly to the model compounds investigated. There is no obvious way to show whether this is true or not. It was reasoned, however, that a polymeric sulfide would more nearly approximate the organic sulfur containing structures in coal. To test this, approximately 5% of Aldrich polyphenylene sulfide (10,000 mol wt) was added to anthracite and epoxy resin, cured, ground, sieved and fed to the pyrolyzer at 900, 910 and 920°C. Yields of pyrolysis products from this sample suggests that polymeric aromatic sulfides are perhaps slightly more stable than the corresponding monomeric sulfur compounds although not greatly different.

In continously pyrolyzing coal or model sulfur compounds it is important to establish a steady state condition with respect to all the pyrolysis products before meaningful results can be obtained. There appears to be a great difference between the various pyrolysis products in the rate at which this steady state is achieved. COS and CS_2 tend to level out quite rapidly after a steady coal feed rate is achieved; H_2S, on the other hand, is quite slow. This is probably due to chemi or physisorption on the walls of the system. Since H_2S is the largest single sulfur product of coal pyrolysis, it is extremely important that sufficient time be allowed to attain a steady state.

## Pyrolysis of a Typical High Sulfur Bituminous Coal

A raw Pittsburgh 8 R&F coal was pyrolyzed at 600, 775, 850, 900, 925, 950, 975 and 1000°C. The principal product was H_2S at all temperatures but over 850°C, CS_2 is formed at the expense of H_2S. Small amounts of COS were also formed at all temperatures. Unlike the pyrolysis in the pyroprobe and the pyrolysis of such model compounds as thiocresol at 600°C, no methylmercaptan was observed even at 600°C.

Figure 3 shows a plot of combined sulfur yield as COS, H2S, and CS_2 vs. pyrolysis temperature. It also shows individual yields of H_2S, and CS_2 vs. pyrolysis temperature. It is to be noted that sulfur yield appears to level off at 775 to 900°C and then drops precipitously. Also, H_2S is by far the major product up to 800°C but above that, the H_2S starts to drop as CS_2 is formed.

The drop above 900°C in the amount of total sulfur volatilized raises a number of questions concerning what is occuring. It does not appear to occur in the pyrolysis of the low molecular weight model compounds. To make sure the drop when coal is pyrolyzed was not associated with H_2S absorption of basic components in the coal mineral matter, the same coal was boiled with dilute HCl, washed with distilled water and dried. Pyrolysis of that coal at 1000°C gave roughly equivalent results as the untreated raw coal.

There is evidence in the literature that H_2S or sulfur can react with coal or coal char at high temperatures (4,8,9). Energetically, for this reaction to occur at such high temperatures, the product must be very thermally stable. It also raises the question whether this reaction consuming H_2S is affecting our results at 900°C. Table 4 shows the rate constants (assuming first order kinetics) for the high temperature reaction at various temperatures and Figure 4 is an Arrhenius plot of these data. The activation energy of 56 kcal suggests that chemical bonds are being made or broken. The data also indicates that the H_2S consuming reaction is

very slow indeed at 900°C and not likely to interfere significantly with the 900°C pyrolysis measurements. Attar[4] has observed this H_2S absorption phenomenon and explains it as reaction of the H_2S with coke or char to form thiophenic structures.
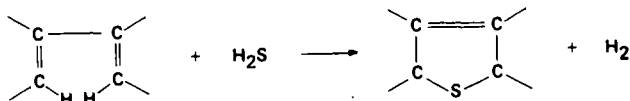
This is consistent with the known high stability of the thiophenic structures and the fairly high activation energy we observe.

Pyrite

While pyrolysis appears to be a promising approach to determining the composition of the organic sulfur components in coal, the presence of iron pyrite in such large amounts as are present in high sulfur coals, presents a serious problem as mentioned previously. Pyrite, like organic sulfur compounds, when pyrolyzed in the presence of coal also produces H_2S at temperatures around the decomposition temperature of pyrite (around 550°C) and H_2S and CS_2 at higher temperatures (over 850-900°C) An effort was therefore made to remove the pyrite and other inorganic sulfur from the coal ground to 1μ size, before the pyrolysis studies were carried out. However, even with combinations of both sink/float and the Otisca solvent agglomeration processes, about 10% of the original pyrite remained in the coal as indicated by iron analysis (atomic absorption). The reason for the difficulty in pyrite removal became apparent when STEM Scanning Transmission Electron micrographs were made of the fine particles after pyrite "removal". They showed pyrite particles in the range of 0.1 to 0.6μ size inside the coal particles. These could not be removed from the coal unless it was ground much finer than 1μ.

It was decided, therefore, for pyrolysis studies to prepare each coal with several known different pyrite concentrations by partial pyrite removal. The pyrolysis results would then be extrapolated to zero pyrite concentration.

A series of five (5) samples of Pittsburgh 8 R&F coal containing various levels of pyrite was pyrolyzed in the pyrolyzer (Figure 1). The sum of the yields of COS, H_2S, and CS_2 at 600, 775, 850 and 900°C are plotted against actual pyrite concentration in Figure 5. There is a fair amount of scatter in the data. This scatter is due in part to variations in gas rate and coal feed rate and in determining the pyrite concentration. However, a set of reasonably straight lines is defined which can be extrapolated to 0 pyrite concentration. Some conclusions can be drawn from these data. 1) There is little or no difference in the data obtained at 775°C and that obtained at 850°C, suggesting that all the aliphatic sulfur compounds are broken down by 775°C and either the aromatic sulfur species are low in concentration or have not yet started to break down at 850°C. 2) There is only a relatively small difference between the 900°C line and the 775°C and 850°C line, supporting the idea that the aromatic sulfur compounds are very low in concentration. 3) The slope of the 600°C line is about 0.21 gram sulfur/gram of pyritic

sulfur which is considerably under the theoretical value of 0.5 for the breakdown of pyrite to pyrrhotite. 4) In the 775-900°C temperature range, the slope increases to around 0.27-0.30. Apparently about 54 to 60% of the sulfur liberated in the pyrite pyrolysis reacts with the coal matrix at those temperatures to form H_2S. The rest forms COS or is trapped in the coal or coke structure. 5) The intercept of this 775-850°C line occurs at 0.82% sulfur which represents approximately 40% of the total organic sulfur in the coal as aliphatic sulfur. The 900°C intercept occurs at about 0.83% sulfur representing an additional approximately 1% as aromatic sulfur. Presumably, the remaining 59% of organic sulfur is thiophenic or stable sulfur compounds of some kind.

Another problem associated with the mineral matter of the coal was due to the basicity of some mineral matter. If the mineral matter of the coal contains a significant amount of basic material, it may absorb some of the sulfur containing acid gases (H_2S, SO_2) produced in pyrolysis and thereby prevent them from entering the analytical system. Acid treating of the coal, however, resulted in only slight increase in the H_2S produced on pyrolysis of the bituminous coals tested. The acid washed lignite gave approximately 20% higher sulfur volatile yield, however, than the untreated.

Pyrolysis of 3 Additional High Sulfur Coals

Three additional high sulfur coals were prepared at two or three pyrite concentrations each. These were pyrolyzed at two temperatures – 775°C and 900°C. They represent temperatures at which most of the aliphatic and most of the aromatic sulfur compounds should be broken down, respectively. Little or none of the thiophenic compounds should be affected at those temperatures.

The results of these pyrolyses are plotted in Figure 6. It will be noted that as was the case with Pittsburgh 8 R&F, the 775°C and 900°C lines are very close together indicating very little (only 1-4%) aromatic sulfur compounds present. However, in each case, a substantial portion (30-40%) of the organic sulfur is aliphatic sulfur. The rest is assumed to be thiophenic.

The slopes of the 900°C lines were approximately 0.27 gms of sulfur/gram of pyritic sulfur suggesting that this slope can be used in future determinations with other coals.

## Organic Structures Containing Sulfur in Coals of Various Ranks

Distribution of Sulfur Types

Four additional coals of various ranks were pyrolyzed and the zero pyrite point estimated using the slope of .27. An estimate of the distribution of organic sulfur types in 8 different coals is shown in Table 5. This of course assumes that all sulfur compounds obtained on pyrolysis at 775-850°C or lower is aliphatic mercaptan or sulfide, and that sulfur compounds obtained from 850-900°C are aromatic mercaptans or sulfides. Organic sulfur structures not pyrolyzing at 900°C or lower are assumed to be primarily thiophenic. These assumptions are challengeable as mentioned previously on the basis that sulfur in a macromolecular structure such as coal may behave

differently than model compounds on pyrolysis and that substituents of various types in coal may activate or deactivate the sulfur structures so that they pyrolyze somewhat differently. Nevertheless, these results do suggest that the organic sulfur in coal is mainly aliphatic and thiophenic. Low rank coals appear to have higher proportions of aliphatic sulfur and as rank increases, the thiophenic proportions increase.

Thioethers or Mercaptans?

This pyrolysis method does not distinguish between mercaptans and thioethers. In an effort to determine whether the sulfur is mercaptan, thioether, or both, an independent analytical method was resorted to. This method, first tried by Russian workers, depends on the reaction of methyliodide with mercaptans and thioethers[10,11].

$$RSR' + CH_3I \quad \text{------} \quad RSR'I^{+-} \qquad (8)$$

$$RSH + CH_3I \quad \text{------} \quad RSCH_3 + HI \qquad (9)$$
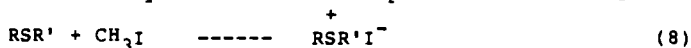
If there is mercaptan present, some titratable acid should be formed. If there is thioether present, iodide should remain in the coal and could be determined quantitatively. The results of this test on three high sulfur coals are shown in Table 6. While this reaction does not appear to be highly reproducible or quantitative, it does indicate that a significant amount of the organic sulfur in coal is present as thioether and there is little if any sulfur present as free mercaptan.

These experiments together with the pyrolysis runs, suggests that the sulfur in coal is present as aliphatic thioether side chains and as heteroatoms in the aromatic ring clusters.

Estimate of Pyrolysis Rates

The degradation rates of the model compounds studied were obviously quite high since almost complete conversion of the aliphatic sulfur compounds was obtained at $775^{\circ}C$ and of the aromatic sulfur compounds at $900^{\circ}C$ and the nominal hold-up time of about 0.5 seconds. With high sulfur coals, however, the coal melts and much of it remains as coke on the sand particles. Do the sulfur groups in the coal pyrolyze as fast as the model compounds did or do they break down more slowly? This would provide a clue as to whether the sulfur compounds in coal do behave like their low molecular weight models.

To try to answer this question, Pittsburgh 8 R&F coal was pyrolyzed at $900^{\circ}C$ and $775^{\circ}C$ by feeding the coal to the pyrolyzer at those temperatures until a steady state rate of H_2S, CS_2 and COS evolution was observed as had been seen previously. The coal input was then stopped suddenly and the evolution of H_2S, CS_2 and COS evolved determined at one minute intervals. In both experiments, the evolution of these compounds dropped abruptly with little or nothing observed even at the first minute.

A similar test run at 700°C when the aliphatic sulfur breakdown should be slower, showed roughly a third of the steady state H_2S coming off after one minute and small amounts of CS_2 and COS. The sample taken at two minutes show none of these compounds.

These results support the view that the labile sulfur compounds in coal break down at rates similar to those of the model compounds.

Acknowledgement

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Table 1

PYROPROBE GC/MS ANALYSIS OF
PITTSBURGH 8-R & F HIGH SULFUR COAL
(% of Total Area)

	Raw	90% of Pyrite Removed
H_2S	3.03	4.83
COS	0.48	0.31
CH_3SH	0.32	0.34
SO_2	2.13	0.02
CS_2	0.27	0.06
Thiophene	0.25	0.22
Methylthiophene-1	0.34	0.23
Methylthiophene-2	0.23	0.10
Dimethylthiophene-1	0.49	0.46
Dimethylthiophene-2	0.47	0.38
Dimethylthiophene-3	0.38	0.24
Dimethylthiophene-4	0.07	0.05
Trimethylthiophene-1	0.19	0.10
Trimethylthiophene-2	0.22	0.16
Tetramethylthiophene	low	0.04
Benzothiophene	0.29	0.24
Methylbenzothiophene-1	0.06	0.04
Methylbenzothiophene-2	0.13	0.15
Methylbenzothiophene-3	0.20	0.19
Methylbenzothiophene-4	0.15	0.14
Methylbenzothiophene-5	0.17	0.12
Methylbenzothiophene-6	?	0.02
Dimethylbenzothiophene-1	0.11	0.11
Dimethylbenzothiophene-2	0.06	0.05
Dimethylbenzothiophene-3	0.12	0.14
Dimethylbenzothiophene-4	0.07	0.10
Dimethylbenzothiophene-5	0.05	0.04
Dimethylbenzothiophene-6	0.07	0.08
Dimethylbenzothiophene-7	0.05	0.04
Dimethylbenzothiophene-8	0.05	0.03
Dimethylbenzothiophene-9	0.03	0.02
Dibenzothiophene	0.08	+

*Number does not denote chemical structure but an
 arbitrarily assigned isomer number.

Table 2

SOLVENT EXTRACTION OF COALS

Pittsburgh 8—R & F 200 mesh (4.65% S)
100°C/4 hrs w/shaking

	%S in Extract	% of S Extracted
Acetonitrile	0.10	4.7
Pyridine	0.09	4.3
Tetrahydrofuran	0.33	14.2
Ethylenediamine	0.07	3.3

Table 3

COAL PYROLYSIS PRODUCTS
MATERIAL AND SULFUR BALANCES

	850°C			
	Pittsburgh 8 R & F		Alcoa Texas Lignite	
	Wt %	% of the Sulfur	Wt %	% of the Sulfur
Gas	21.8	49.5	36.3	48.4
Tar	11.9	7.3	5.5	8.8
Char	6.4	1.7	31.1	31.4
On Sand & Reactor	43.0	24.5	29.1	1.3
Trap Head	6.5	?	.01	
TOTAL	89.6	81.1	101.7	90.0

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Table 4

RATE CONSTANTS FOR
HIGH TEMPERATURE ABSORPTION OF H_2S
(Assumes First Order Kinetics)

Temperature °C	Rate Constant (Sec^{-1})
900	ca 0
925	.167
950	.497
975	.801
1000	1.233

Table 5

ORGANIC SULFUR SPECIES IN COALS STUDIED

	Total Sulfur wt %	Organic Sulfur wt %	% of Organic Sulfur			BTU
			Aliphatic Sulfides & Mercaptans	Aromatic Sulfides & Mercaptans	More Internally Stable Types (Thiophenic) (By Diff.)	
Alcoa Texas Lignite (Wilcox)	1.30	.73	82	<1	18	10,555
Emery (Utah)	1.19	0.57	61	1-2	39	12,710
Pittsburgh 8-Shoemaker	4.00	1.36	53	<1	46	12,991
Pittsburgh 8-R & F	4.85	1.63	49	1-2	49	12,156
Pittsburgh 8-McElroy	5.47	1.58	49	<2	49	13,098
Ohio 9-Egypt Valley	2.49	1.46	44	<1	55	13,175
Illinois 6-Burning Star	3.24	2.04	39	2	59	12,165
Anthracite - Lehigh Valley	0.90	0.6	0	0	100	14,245

Table 6

THIOETHER AND MERCAPTAN GROUPS
IN HIGH SULFUR COALS

(By Reaction with CH_3I)

	% Organic Sulfur	% of Organic Sulfur	
		As RSR'	As RSH
Pittsburgh 8-R & F	1.63	33.0	4.3
Pittsburgh 8-Shoemaker	1.40	30.4	2.5
Illinois 6-Burning Star	2.04	22.4	4.9

Figure 1

Fluidized Bed Pyrolyzer
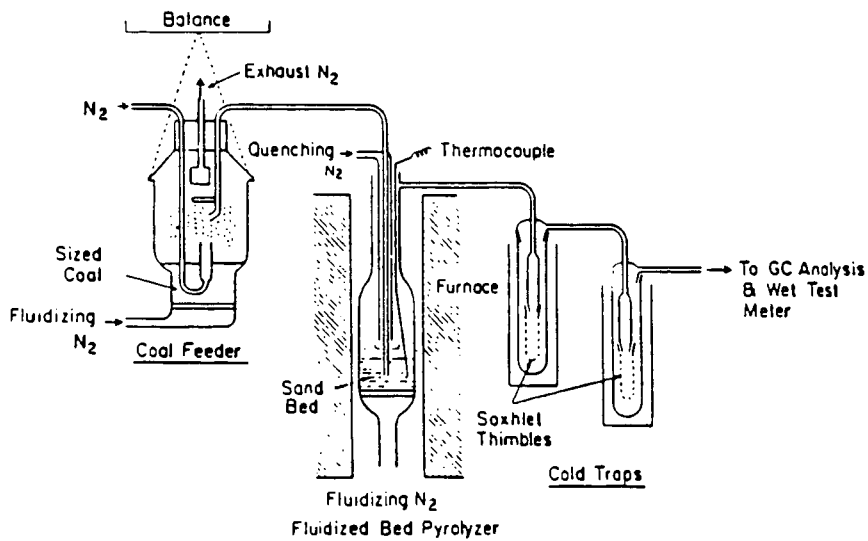
Figure 2

PYROLYSIS BEHAVIOR OF MODEL SULFUR COMPOUNDS
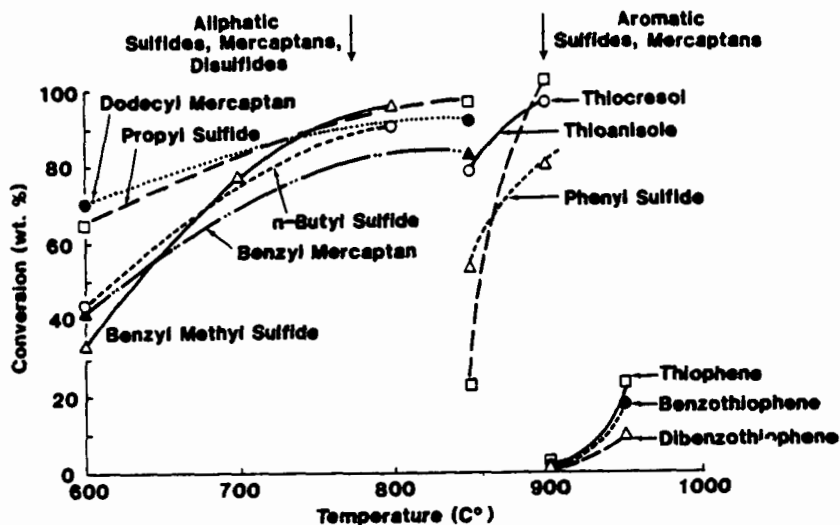### 0.5 SEC. CONTACT TIME

Figure 3

PYROLYSIS OF PITTSBURGH 8 – R & F
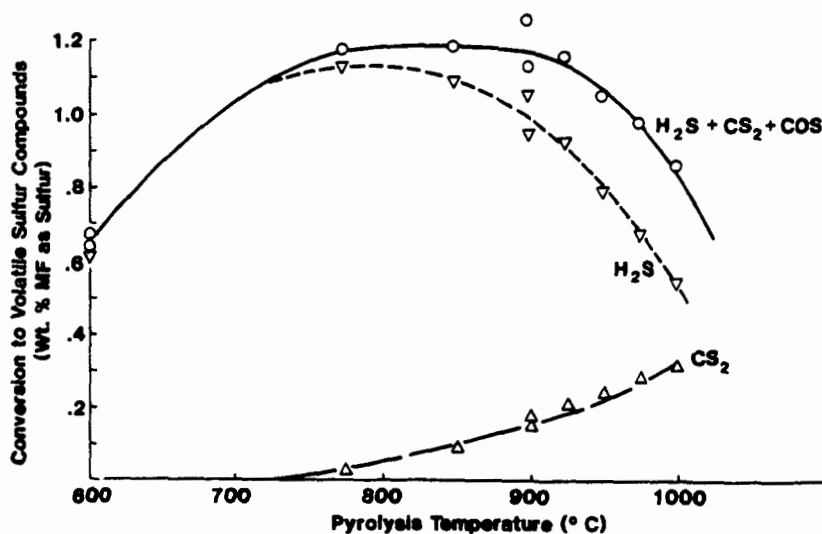### YIELD OF VOLATILE SULFUR COMPOUNDS vs TEMPERATURE

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Figure 4

PYROLYSIS OF PITTSBURGH 8 R & F
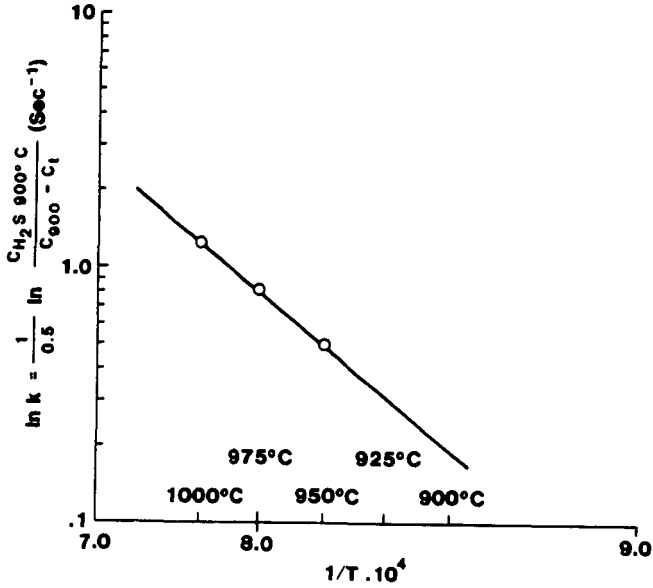## ARRHENIUS PLOT OF HIGH TEMPERATURE H_2S ABSORPTION

Figure 5

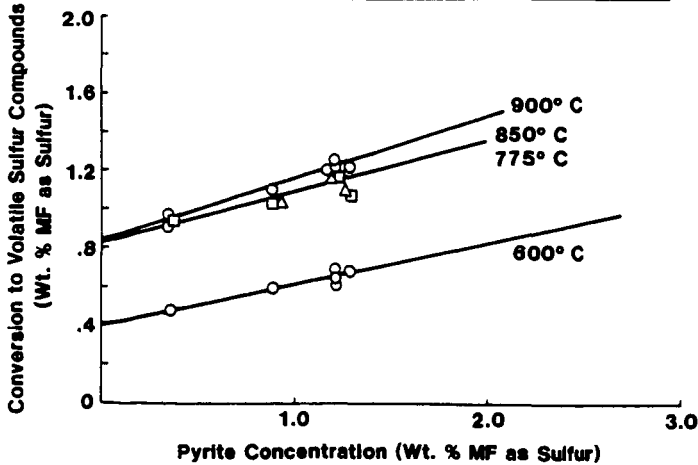## PYROLYSIS OF PITTSBURGH 8 R & F
VOLATILE SULFUR YIELDS vs PYRITE CONCENTRATION

Figure 6

VOLATILE SULFUR YIELDS vs PYRITE CONCENTRATION

PYROLYSIS OF PITTSBURGH 8 – SHOEMAKER

PYROLYSIS OF PITTSBURGH 8 – McELROY

PYROLYSIS OF ILLINOIS 6 – BURNING STAR

Conversion to Volatile Sulfur Compounds (Wt. % MF as Sulfur)

Pyrite Concentration (Wt. % MF as Sulfur)