

TRANSFORMATION OF SULFUR FUNCTIONAL GROUPS DURING PYROLYSIS OF COAL

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INTRODUCTION

Three classes of sulfur compounds in coal are traditionally considered: (1) the inorganic sulfides, most of which are iron pyrites, FeS_2 ; (2) the inorganic sulfates, most of which are iron and calcium sulfates; and (3) the organic sulfur which includes the sulfur that is bound to the organic matrix of the coal. During processing, transformation of sulfur from one class to another, elimination of sulfur as hydrogen sulfide, or changes in the sulfur functional groups within the same class may occur.

Some of the facts that have been reported on the behavior of the sulfur functional groups during pyrolysis are given as follows:

- 1) Hydrogen sulfide is released.
- 2) Coking at temperatures up to 800°C cannot remove all the sulfur (3)(4). Coking at 1400°C removes up to 95 per cent of the sulfur; however, considerable volatilization of the coal occurs (5).
- 3) The inorganic sulfur remaining in the coke corresponds to 66 per cent of the inorganic sulfur in the original sample. Organic sulfur left in the coke corresponds to 72 per cent of the initial organic sulfur (6). More detailed distribution into classes is given by Given and Jones (7).
- 4) The degree of desulfurization relates to the volatilized fraction (3). The larger the volatilization, the larger will be the desulfurization.
- 5) A larger ash content increases the amount of sulfur that is retained in the coke (7).
- 6) The distribution of sulfur may change during pyrolysis. Inorganic sulfur is incorporated into the organic matrix (4)(8).

From our study, additional conclusions may be developed:

- 7) The release of H_2S at different times of the pyrolysis is due to different processes. Loose FeS_2 crystals, when pyrolyzed with coal, cause release of H_2S by two new processes. The first new H_2S peak is from the FeS_2 that was added to the coal. It has different mass-transfer limitations from the H_2S coming from the FeS_2 that was originally present in the coal. The other new H_2S peak appears at a higher temperature and is from the organic sulfur compounds. The first new H_2S originates in the reaction of H_2 with FeS_2 without mass-transfer limitations. The H_2S from the organic source appears to be by way of catalysis of the hydrodesulfurization of organosulfur compounds by the FeS crystals.
- 8) The total amount of organosulfur compounds of the thiophene class in the tar decreases as a result of adding FeS_2 . The decrease is probably the result of hydrodesulfurization of the compounds, probably catalyzed by the FeS crystals.

EXPERIMENTAL RESULTS

Different samples of bituminous coal were examined. A list of properties is given in Table 1. The coals were crushed to -100 mesh, and variable amounts of iron pyrites, FeS_2 at -170 mesh, were added. The components were thoroughly mixed until a constant total-sulfur reading was obtained for samples of 60-80 mg. The iron pyrites was supplied by Matheson-Coleman and Bell and used as received.

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Experimental System and Procedure

A LECO Model 571-018 resistance furnace was used both to pyrolyze the coal samples and to combust samples for total-sulfur analysis. Pyrolysis was performed at 1300°F in a stream of argon (1250 ml/min) in a standard zirconia boat, LECO Cat. No. 528-051. The gas was bubbled in a chilled solution of $\text{Cd}(\text{BO}_2)_2$ whose pH and $\log[\text{S}^-]$ were followed electrochemically. A radiometer pH meter Model 26 was used with Radiometer electrodes G-202C for pH and F1212S for $[\text{S}^-]$ vs. SCE K401. Carbon dioxide was found to have a small influence on the measurement when it was injected into the argon stream. The aqueous solutions were extracted twice with benzene and then separated. The benzene phase was concentrated approximately 50 times by evaporation and then analyzed by means of an HP Model 5700 gas-chromatograph which was equipped with a flame-photometric detector. Two columns were used. One was 3 ft x 1/8 in. with 1 per cent OV-1 on Gas Chrom Q (Applied Science Laboratories) 80/100 mesh. The other was 6 ft x 1/8 in. 10 weight % diethylene glycol succinate on Gas Chrom Q 80/100 mesh.

Results

Table 2 shows the distribution of the total sulfur between the volatiles and the coke after the carbonization. The sulfur content of the coke increased as a result of adding FeS_2 , but the fraction that remained in the coke did not show an obvious correlation with the content of FeS_2 . In particular, samples C4 and C6 indicate that a smaller fraction of the total sulfur pool was retained when pyrites were added to the sample. The phenomenon can be explained if it is assumed that the iron (or FeS) catalyzes the decomposition of organosulfur compounds.

Figures 1-6 show how the rate of evolution of H_2S and the total amount of H_2S that was evolved vary with the pyrolysis time. Examination of the figures suggests the following points:

- 1) Adding FeS_2 to the samples caused added evolution of H_2S at two points where H_2S was not evolved otherwise. One was between the peaks of the original coal sample and caused them to merge. Compare Figures 1 with 2 and 3 with 4.
- 2) The additional peaks that appeared when FeS_2 was added did not coincide with existing peaks in the H_2S of the evolution.
- 3) The differences between samples C1, C4, and between C2 and C5 was mainly in the particle size and the amount of sulfur. The original microstructure was assumed to stay. When the coarse material was pyrolyzed, however, a third peak resulted which did not appear when the fine coals were pyrolyzed. Mass-transfer may have been controlling.

In Table 3, gas-chromatographic data for the organosulfur compounds that were collected in the solution are given. The peaks of the alkyl-thiophene isomers were lumped together as were the peaks of the alkyl-thianaphthene isomers and the alkyl-dibenzothiophene isomers. Separation was affected by a column with a very low polarity (OV-1), and a sulfur-specific flame-photometric detector was used. Sulfur compounds lighter than methyl thiophene were not analyzed. Moreover, some of the methyl thiophene may have been lost during the concentration by evaporation. The alkyl-thiophene peaks may include also some alkyl and aryl sulfides which are not separated on the column used. When a polar column was used for separation, 2- and 3-methyl thiophene, 2- and 3-ethyl thiophene, smaller amounts of propyl and butyl thiophene, and at least seven thianaphthenes were identified. The chromatograms from a polar column were very much the same as those reported by Martin and Grant (14) who analyzed the sulfur compounds in gas oil. Out of sixteen samples that were analyzed, a moderate increase in the organosulfur was observed for one sample only (#C6).

The data in Table 3 show that the addition of FeS_2 to the coal samples caused a decrease in the amount of the benzene-soluble thiophene derivatives in the oil. This observation is consistent with the result that relatively more H_2S is emitted when FeS_2 is added.

DISCUSSION

The H_2S and the organosulfur compounds that were emitted during the coking of coal were the result of reactions in both the dense phase and in the gas phase. The addition of FeS_2 to the coal was more likely to affect the gas-phase reactions. Such an effect could be either a reaction with components of the gas or catalysis or inhibition of reaction of components in the gas phase.

The following reactions were believed to be the most important in the system of FeS_2 and coal at temperatures below $800^\circ C$.

- 1) Decomposition of iron pyrites (7)



- 2) Hydrogen elimination



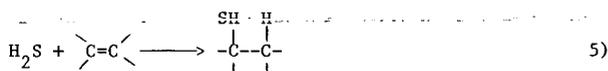
- 3) Production of olefines both in the gas and the condensed phase:



- 4) Desulfurization of iron pyrites by hydrogen (12)



- 5) Incorporation of sulfur via hydrogen sulfide into an organic molecule in the gas or in the condensed phase,

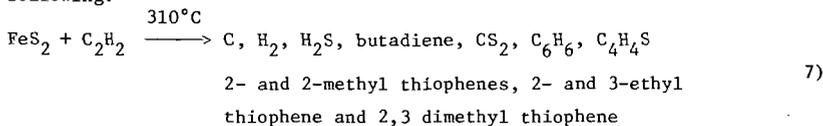


via sulfur by means of crosslinking

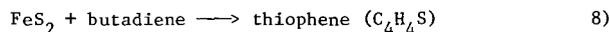


The above reactions can explain the incorporation of sulfur from the pyrites into the char (8).

- 6) Catalysis of ring-closure by reactions among H_2S , S, and unsaturated hydrocarbons. From references 9 and 10 we have reactions in accord with the following:



from reference 10,



Thiophene is a very stable compound and does not thermally decompose in homogeneous media up to temperatures as high as $950^\circ C$. So once formed, it is unlikely that it will decompose at the experimental conditions that were used. In the presence of hydrogen, however, catalytic reduction of the organosulfur compounds may occur even at temperatures lower than $1300^\circ C$. As a result of adding FeS_2 to the coal, the total amount of organosulfur compounds that was produced decreased. One must

conclude that FeS acts to a certain extent like CoS and MoS₂ and catalyzes the hydrodesulfurization of thiophenes. The use of iron in hydrodesulfurization catalysts was mentioned by McKinley (11).

The two additional peaks of hydrogen-sulfide emission that showed as a result of adding FeS₂ to the coal sample are believed to be due to the following:

- 1) The reaction of hydrogen with the FeS₂ crystals that were added to the sample. Such a peak, because of diffusion and mass-transfer limitations, appears a little before the peak of H₂S from the same reaction of FeS₂ that was previously in the coal reactions.
- 2) The hydrodesulfurization of the organosulfur compounds which adsorbed on the FeS crystals at lower temperatures. Hydrodesulfurization on FeS of thiophenic sulfur compounds may be the source of the "organic III" peak reported by Yergey et al. (13). Thiophenic compounds are known to be components of coal tar; however, the mechanisms of their source can be gas-phase or solid phase dehydrocyclation.

The following arguments imply that the thiophenic compounds indeed exist in the coal as such:

- 1) At 300-310°C, FeS₂ reacts with hydrocarbons to form thiophenic compounds; however, FeS₂ decomposes at 450-500°C, and FeS is formed.
- 2) FeS catalyzes the hydrodesulfurization of organosulfur compounds, and when coal is pyrolyzed at 700°C their concentrations in the tar are smaller when FeS₂ is added to the coal than for untreated coal.
- 3) Because thiophenes are found in the pyrolysis tar at temperatures like 700°C, their source must have been the coal itself. Their amounts in the tar will depend on their amounts in the original coal, on the amount of FeS, and on the efficiency of the hydrogenation that takes place which depends on the mass-transfer constraints of the coking reactor.

CONCLUSIONS

Preliminary data on the kinetics of the transformations of sulfur functional groups in coal shows that:

- 1) Hydrogen sulfide from loose FeS₂ crystals evolves at different rates than hydrogen sulfide from FeS₂ that was in the original sample.
- 2) Pyrolysis of coal in the presence of FeS₂ causes a decrease in the benzene-soluble, thiophenic organosulfur compounds in the oil.

The difference in the kinetics of the release of H₂S is probably due to different mass-transfer limitations. This assumption is supported by the fact that the ratio of the amount of sulfur that is released to the gas and that which remains in the char depends on the particular equipment in which the pyrolysis is made.

The reduction in the benzene-soluble organosulfur compounds is probably due to catalysis of the hydrodesulfurization on the FeS surface. Although the H₂ pressure is very small, the rate of reaction may still be large because of the high temperature of the pyrolysis (1300°F).

Since thiophene derivatives are found in the oil, even when FeS₂ is added to the coal, their source must be the organic matrix and not dehydrocyclation reactions on the sulfide surface.

ACKNOWLEDGMENT

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Table 1
Properties of the Coals Used

Coal Source	Supplied By	Notation	Total % S	Pyrites % S	Organic % S	% Volatile	Size Mesh
Jefferson Co., Ohio	U.S. Bureau of Mines	C1	1.698	1.234	0.464	38.0	65-100
Jefferson Co., Pittsburgh Seam		C2	3.233	2.261	0.972	34.3	-100
Washington State	Jet Propulsion Laboratory	C3	0.363	0.363	0.0		-100
As C1 + FeS ₂		C4	3.938				coal -100 FeS ₂ -170
As C2 + FeS ₂		C5	4.650	3.90	0.75		coal -100 FeS ₂ -170
As C3 + FeS ₂		C6	2.689	2.685	0.0		coal -100 FeS ₂ -170

Table 2
Distribution of the Total Sulfur Between the Volatiles and the Coke

Sample	No.	Weight % Volatiles	Weight % Sulfur in Coal	Weight % Sulfur in Coke	mg Sample Size	Fraction of total sulfur weight % <u>in coke</u> <u>in volatiles</u>	
C1	25	33.27	1.698	1.052	49.9	41.34	58.66
C2	23	30.35	3.233	0.724	40.2	15.60	84.40
C3	26	37.58	0.363	0.358	79.3	61.56	38.44
C3*	27	34.36	0.363	0.242	74.5	43.76	56.24
C4	32	30.95	3.938	2.040	33.6	35.77	64.23
C5	28	27.84	4.650	2.009	25.5	31.18	68.82
C6	30	35.04	2.689	0.538	25.4	13.00	87.00

*Coked 24 minutes. All the rest 12 minutes at 1300°F.

Table 3
Organosulfur Compounds in the Pyrolysis Products

Relative amount/mg coal. Note that some of the light sulfur compounds might have been lost.

Sample	No.	C_1-C_2 Alkyl Thiophenes**	C_3-C_4 Alkyl Thiophenes**	Thianaphthenes	Dibenzothiophenes
C1	25-55	0.316	1.97	4.03	3.36
C1*	24-52	0.729	1.42	1.30	0.077
C3	23-54	0.154	0.248	0.204	0.0063
C3*	27-49	0.399	0.77	0.624	0.012
C4	32-56	0.0997	0.459	0.399	0.0399
C5	28-48	0.314	0.251	0.0637	0.0078
C6	30-50	0.0484	0.387	0.436	<0.001

*Deeply carbonized plus mildly carbonized.

**Includes also some non-thiophenic sulfides.

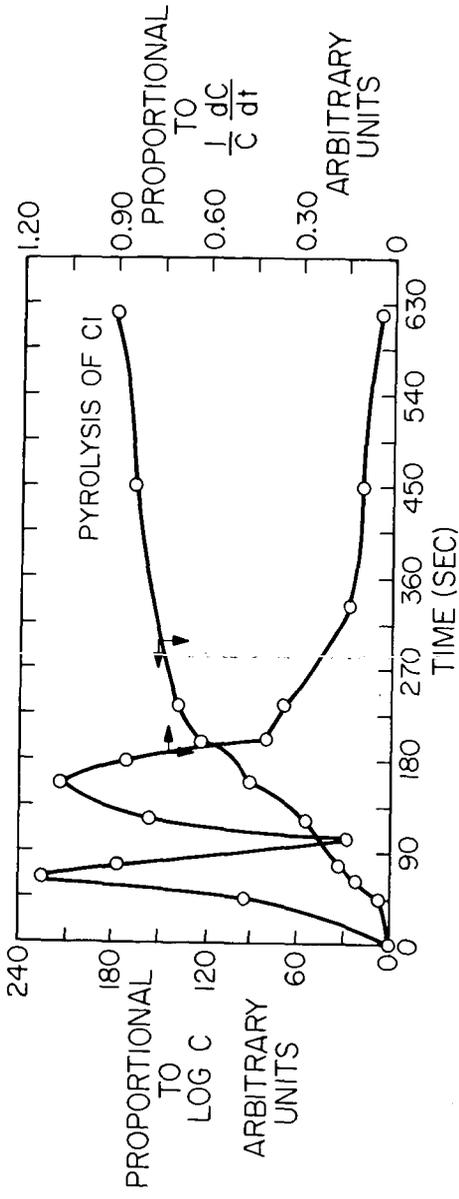


Fig. 1 Relative amount and rate of evolution of H₂S in pyrolysis of coal sample C1

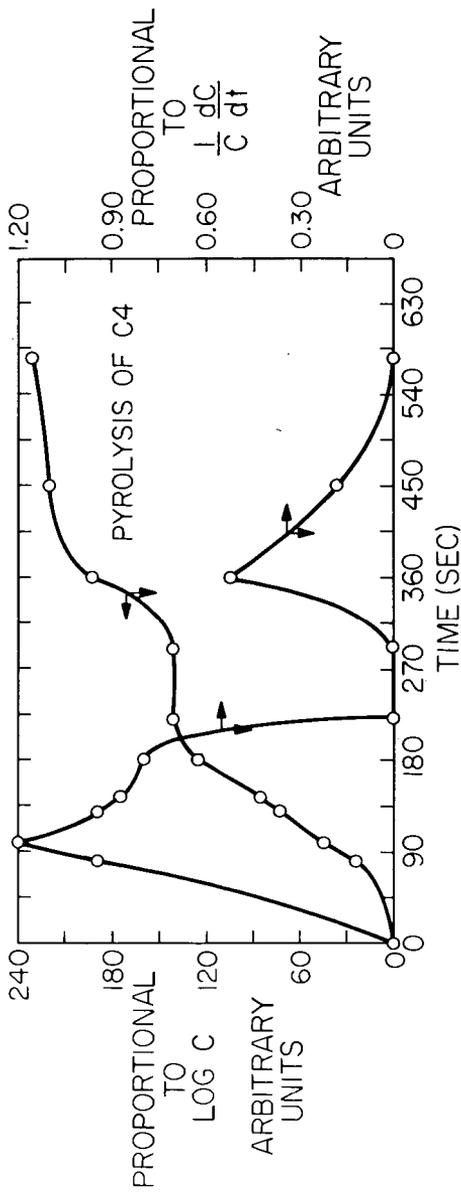


Fig. 2 Relative amount and rate of evolution of H_2S in pyrolysis of coal sample C4

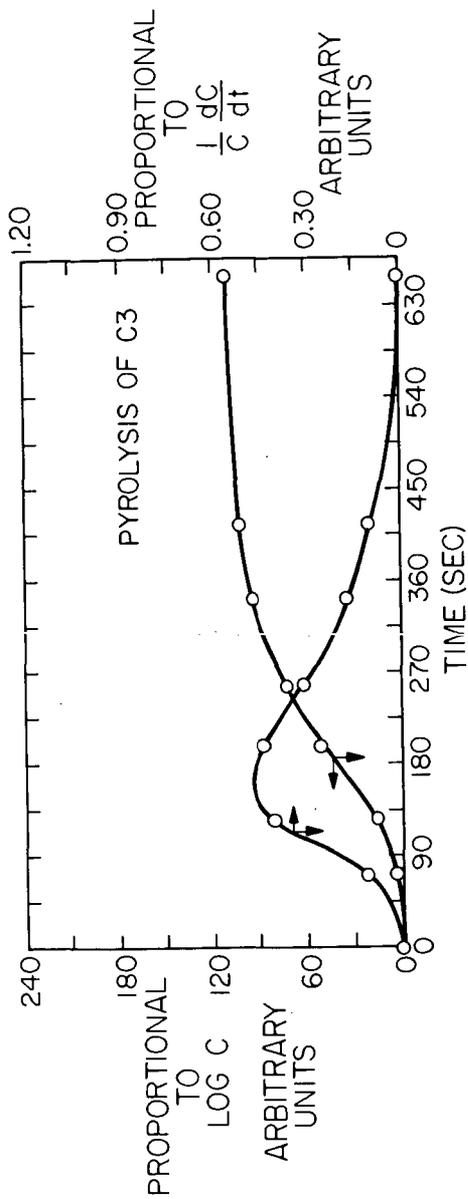


Fig. 3 Relative amount and rate of evolution of H_2S in pyrolysis of coal sample C3

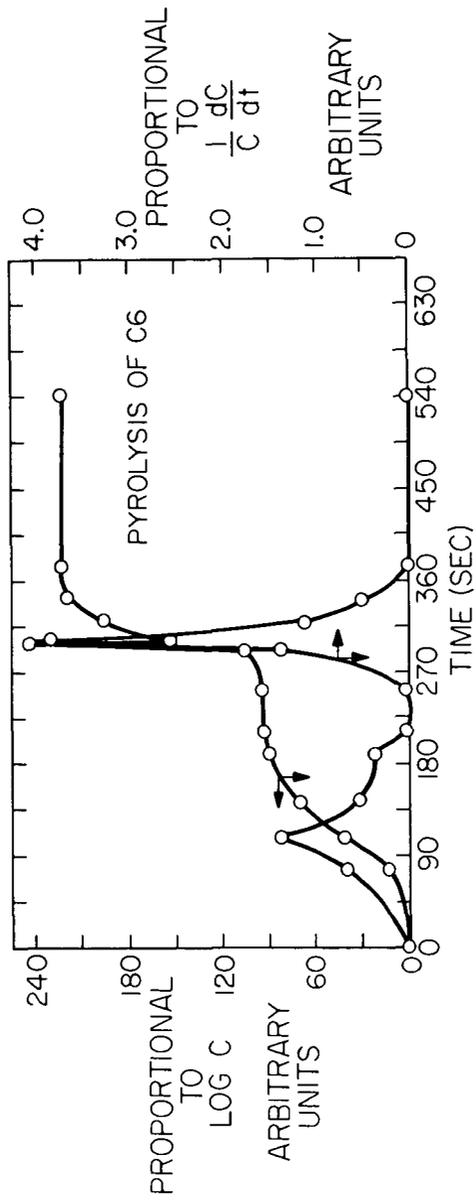


Fig. 4 Relative amount and rate of evolution of H_2S in pyrolysis of coal sample C6

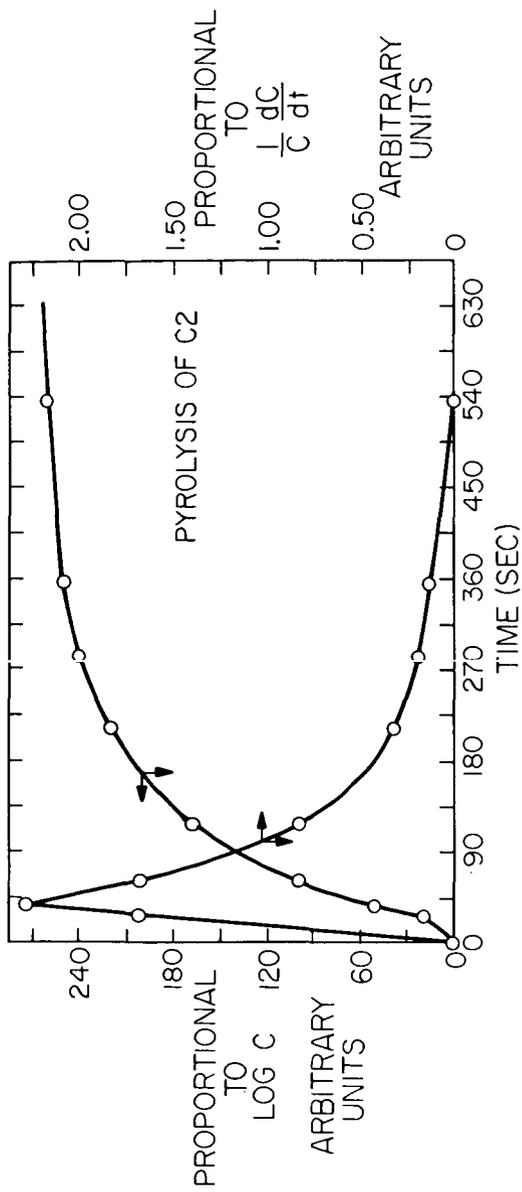


Fig. 5 Relative amount and rate of evolution of H₂S in pyrolysis of coal sample C2

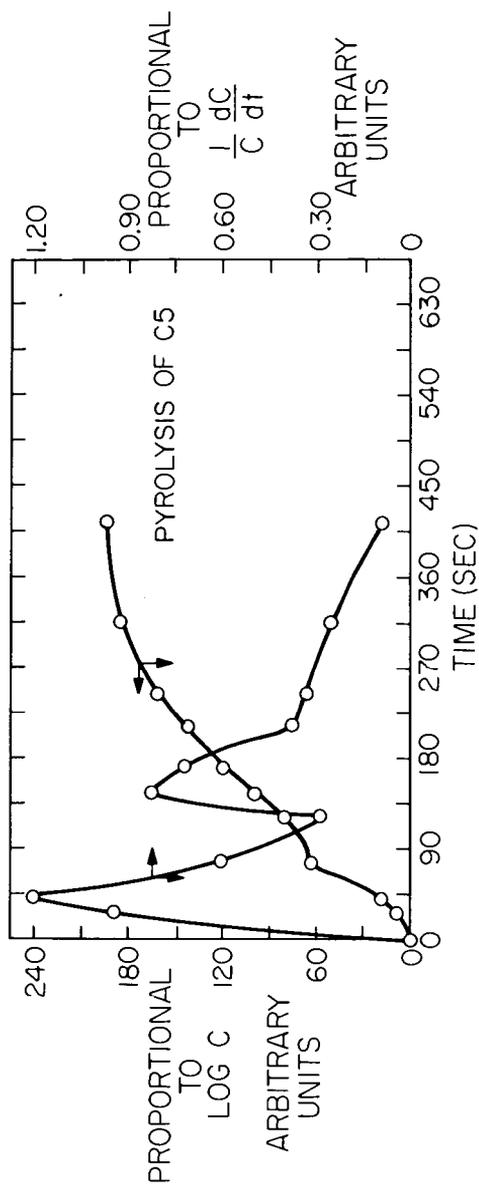


Fig. 6 Relative amount and rate of evolution of H₂S in pyrolysis of coal sample C5