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STUDIES IN COAL LIQUEFACTION
WITH APPLICATION TO
THE SRC AND RELATED PROCESSES

Quarterly Report for the
Period July- September 1976

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James A. Guin
Arthur R. Tarrer

450 5374

Coal Conversion Laboratory
Auburn University
Department of Chemical Engineering
Auburn, AL 36830

PREPARED FOR THE UNITED STATES ENERGY RESEARCH AND DEVELOPMENT ADMINISTRATION

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W. C. Neely
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C. Y. Chang
D. N. Bush
J. F. Martin
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J. K. Nicholson
C. D. Hathaway
G. A. Thomas
R. D. Wilson
F. A. Brewer
M. T. Price
L. C. Davis
T. S. McClanahan

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ABSTRACT

This report presents work performed in a program designed to further the understanding of Solvent Refined Coal Process chemistry and to further process improvements. Several differences in the liquefaction behavior of Kentucky and Wyodak coals have been noted. Coal conversion and hydrodesulfurization kinetics data have been obtained and models constructed. A theoretical model for the continuous SRC process reactor has been inititated. Liquid and gas chromatography procedures have been further refined and utilized to examine steady state SRC recycle solvents.

Objective and Scope

Scope:

The Auburn Coal Conversion Laboratory is engaged in a research program designed to investigate fundamental aspects of the Solvent Refined Coal (SRC) and other closely related coal liquefaction processes. The SRC process provides a method for liquefaction of coal, and removal of sulfur and ash pollutants which would result from direct combustion of the raw coal. If successful, the SRC process will permit the use of high sulfur coals as a boiler fuel, which otherwise could not be used under EPA regulations. This research program seeks to improve the economic attractiveness of the SRC process through the application of chemical engineering techniques.

Objective:

The objective of this research program is to systematically investigate, characterize, and delineate the effects of changes in process operating conditions, equipment configuration, and nature of raw materials upon the kinetics, mechanism, and extent of coal dissolution, heteroatom removal, and hydrogenation in the SRC and closely related processes, for the purpose of providing an increased fundamental understanding of SRC process chemistry as well as guidelines and recommendations leading to economic and technical improvements in SRC technology. The program objectives are being carried out in cooperation with the Southern Services' SRC pilot plant operation at Wilsonville, Alabama, and with the Rust Engineering subsidiary of Wheelabrator-Frye, Inc.

The research program is divided into three major tasks with several subtasks within each area. An outline of the program by tasks and subtasks is presented on the following page.

Program Task Outline

Task 1. Mechanistic Studies of Coal Particle Dissolution

- A. Dissolution Behavior as a Function of Coal Characteristics
- B. Effect of Initial Particle Size and Agitation Rate on Particle Dissolution
- C. Effect of Solvent Type and Gas Phase Composition on Particle Dissolution
- D. Direct Visual Observation of In-situ Particle Dissolution
- E. Particle Structural Strength Evolution During Dissolution
- F. Effect of Pretreatment on Dissolution Behavior
- G. Slurry Viscosity During Particle Dissolution

Task 2. Reaction Kinetics and Process Variables Studies

- A. Bench-Scale Batch Autoclave Experiments
- B. Bench-Scale Continuous Reactor Experiments
- C. Catalysis by Coal Mineral Matter

Task 3. Application of High Pressure Liquid Chromatography To Coal Liquid Analysis And Reaction Kinetics Studies

- A. Development of HPLC Methodology
- B. Characterization of Coal Liquefaction Products
- C. Application: Reaction Kinetics and Process Variables Studies

Executive Summary

As noted on the included milestone chart, the project is on or ahead of schedule in virtually all tasks, with the single exception of the continuous reactor experiments. These have been purposely deferred until a later time period, for reasons given later. The experiments which are currently being performed included the dissolution behavior of various types of coal, effects of solvent type and hydrogen donor ability on coal dissolution rate, catalysis by iron minerals on hydrodesulfurization, effects of hydrogen sulfide partial pressures on desulfurization, and characterization of solvents and SRC product by high pressure liquid chromatography and by gas chromatography.

Personnel:

Three new research associates have been added to the coal conversion team this quarter. They are:

1. Dr. J. M. Lee, University of Utah, Fuels Science and Catalysis
2. Dr. Christine Curtis, Florida State University, Chromatographic, IR and NMR Specialist
3. Dr. M. H. Lee, University of Toledo, Mathematical Modeling and Analysis

Equipment:

Major items of equipment ordered during this quarter include:

1. Brookfield viscometer,
2. High temperature fluidized sand bath,
3. X-Ray Fluorscence Analysis System,
4. High Pressure Liquid Chromatograph,
5. Gas Chromatograph Data System,
6. C,H,N,O,S, Analyser,
7. High Pressure Batch Autoclave.

None of this equipment was received during this quarter.

Major Accomplishments this Quarter:

Major accomplishments this quarter include:

1. Detailed compound analysis of several Wilsonville SRC recycle solvents.
2. Effects of iron and hydrogen sulfide concentrations on hydrodesulfurization rates.
3. Development of a Coulter Counter technique for measuring coal particle size during SRC reactions.
4. Analysis of reactor geometry effects on SRC conversion, and development of theory for continuous reactor modeling.
5. Determination of coal conversion and desulfurization kinetics for SRC process conditions.

Paper and Presentations

Three papers were presented at the September San Francisco Meeting of the American Chemical Society.

1. Tarrer, A. R., Guin, J. A., Prather, J. W., Pitts, W. S., and Henley, J. P., "Effect of Coal Minerals on Reactions Rates in Coal Liquefaction", ACS Div. of Fuel Chem. Preprints, 21 (5) 59 (1976).
2. Guin, J. A., Tarrer, A. R., Pitts, W. S., and Prather, J. W., "Kinetics and Solubility of Hydrogen in Coal Liquefaction Reactions", ACS Div. of Fuel Chem. Preprints, 21 (5) San Francisco, Ca, 1976.
3. Prather, J. W., Tarrer, A. R., Guin, J. A., Johnson, D. R., and Neely, W. C., "High Pressure Liquid Chromatographic Studies of Coal Liquefaction Kinetics," ACS Div. Fuel Chem. Preprints, 21, (5) San Francisco, CA, 1976.

In addition, a short talk was presented by J. A. Guin at the ERDA Principal Investigators Conference held at Golden, Colorado, in September, 1976.

Two manuscripts have been prepared this quarter. These are:

1. Guin, J. A., Tarrer, A. R., and Pitts, W. S., "Reaction Mechanisms and Coal Conversion Kinetics in the Solvent Refining of Coal" prepared for the ACS Southeastern Regional Meeting, Gatlinberg, Tennessee, October 27-29, 1976.

2. Pitts, W. S., Tarrer, A. R., Guin, J. A., Prather, J. W., "Hydrodesulfurization in the Solvent Refined Coal Process" to be presented at the New Orleans, ACS Meeting, March, 1977.

A third manuscript entitled "A Coulter Counter Technique for Coal Particle Dissolution Monitoring in the SRC Process," is under preparation.

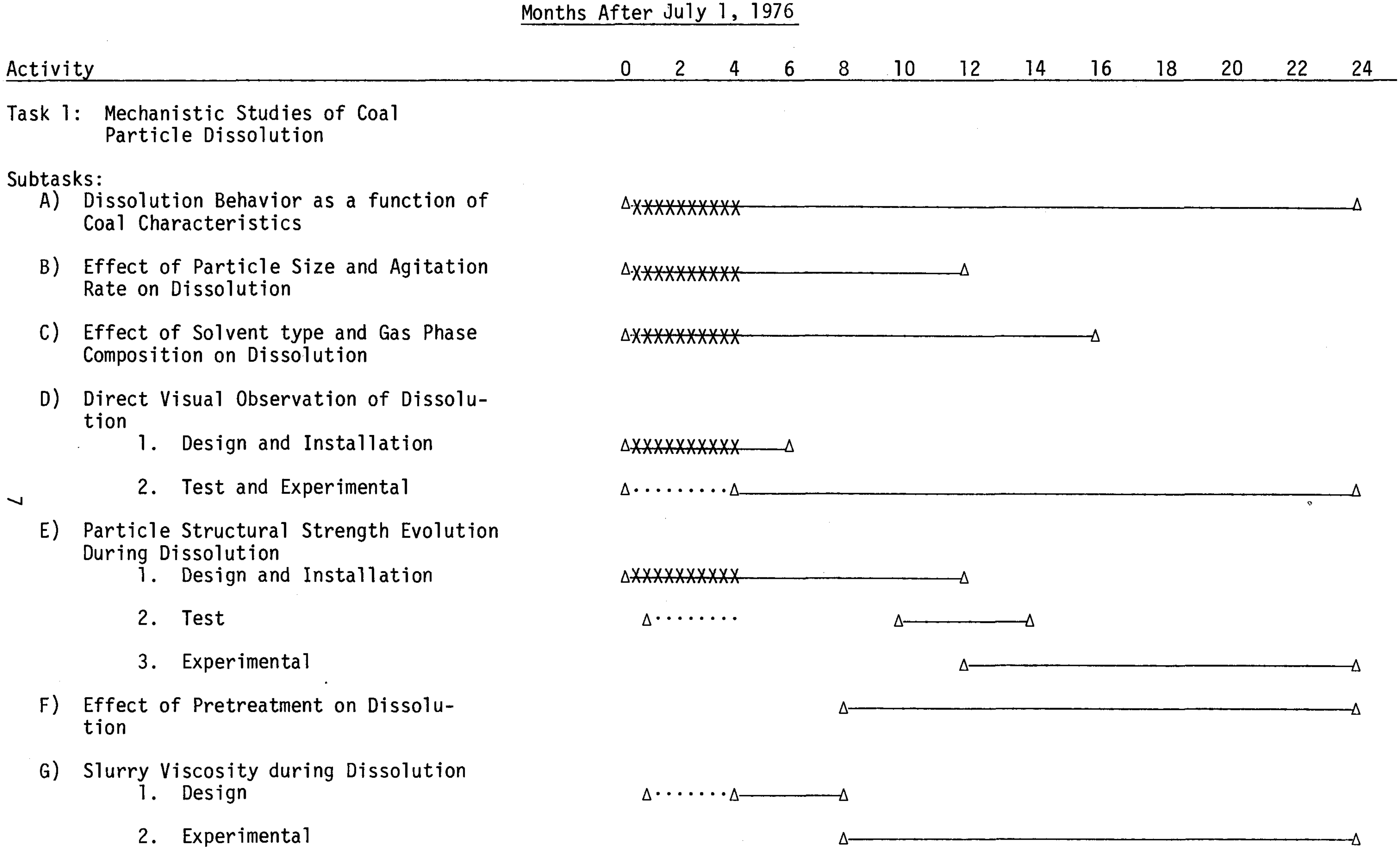


Figure 1. Work Schedule

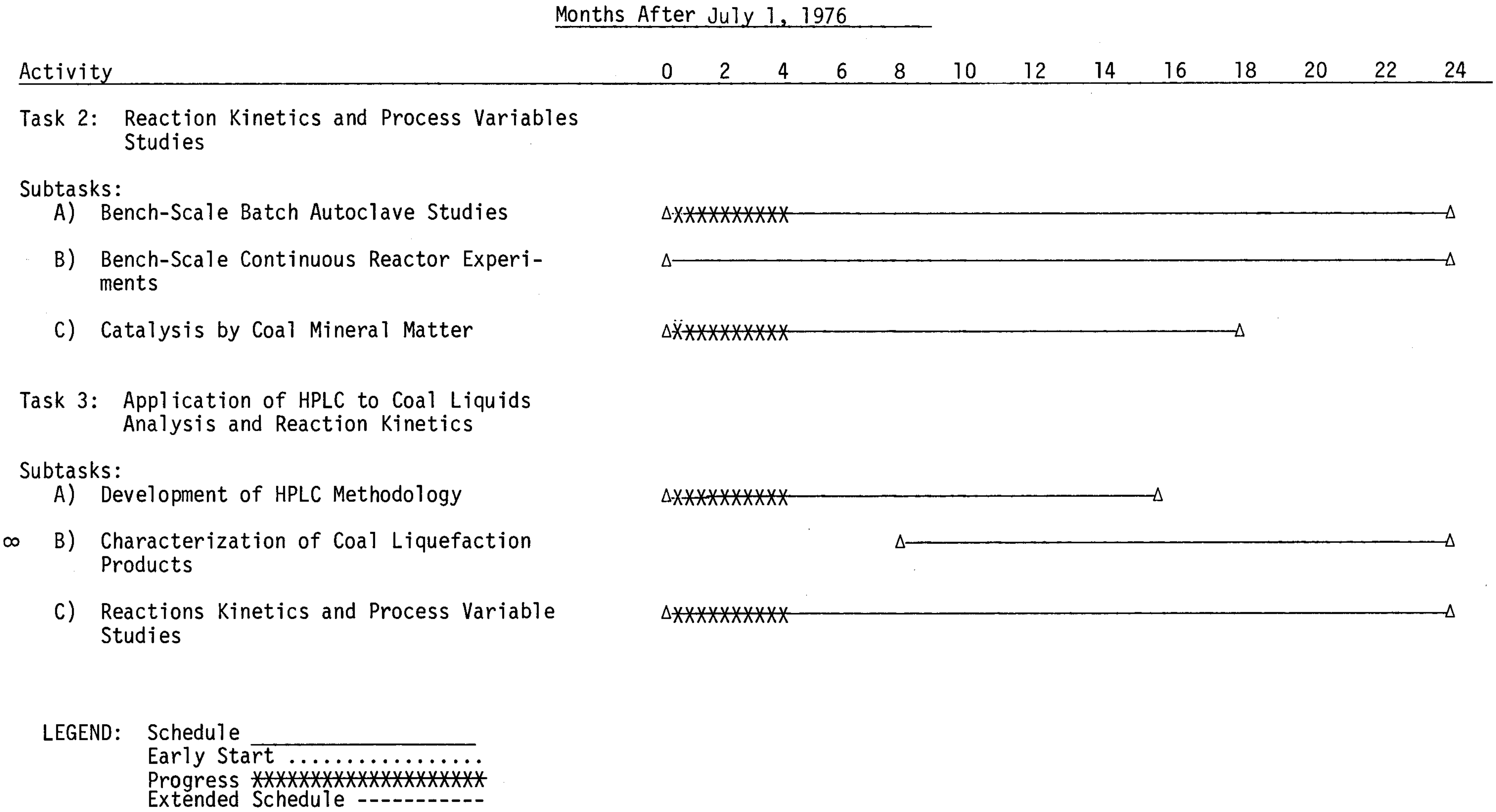


Figure 1 (continued)

TECHNICAL PROGRESS BY TASKS

Task 1. Mechanistic Studies of Coal Particle Dissolution

Objective: The objective of this task is to examine the effects of significant variables upon the initial rate and mechanism of coal particle dissolution, in order to obtain an understanding of the initial stages of particle dissolution, to provide a guide to the suitability of different types of coals for SRC processing, and to provide operational guidelines for such processing.

1.A. Dissolution Behavior as a Function of Coal Characteristics

Objective: The objective of this subtask is to investigate experimentally the changes in particle size distribution of several coals during the early stages of coal particle dissolution.

Progress: Two types of coals have been investigated: a Kentucky No. 9/14 bituminous coal and a Wyodak sub-bituminous coal. Samples of these coals were obtained from Southern Services, Inc., and were collected from feed stock used at the Wilsonville, Alabama, SRC pilot plant. (Detailed analysis of these coals are given in Wilsonville SRC Tehnical Reports No. 5 through 8.) The dissolution behavior of each type of coal in different solvents was observed in situ at reaction conditions (400^{o}C and 1000 psig) using a microreactor with transparent walls. Experimental studies in 300 cc batch reactors were made to confirm observations made in the microreactor and to study further the dissolution behavior of each coal. Dissolution behavior was found to be highly dependent on coal and solvent type. For example: the Wyodak coal behaved much differently during dissolution than the Kentucky coal; both types dissolved at much faster rates in hydrogenated creosote oil than in creosote oil or tetralin. A technique was developed for performing size analysis of particulate matter in a reaction mixture using the Coulter counter -- a paper describing this technique and an evaluation thereof is now under preparation. The Coulter counter was used to monitor changes in particle size distribution with reaction time for both types of coal. The Wyodak coal solids were observed to first decrease markedly in size and then to increase in size with reaction; whereas the Kentucky coal solids continuously decreased in size. Most interestingly, at Wilsonville, significant accumulation of solids in the dissolver/reactor occurred while processing the Wyodak coal, creating a major operational problem. Presumably accumulation of solids resulted because of particle growth during reaction as was observed in our studies. Also, at Wilsonville, accumulation of solids in the dissolver/reactor presented no major operational problem while processing the Kentucky coal; for no significant particle growth occurred during its reaction -- as also was observed in our studies.

A detailed discussion of the progress made during this past quarter in three areas -- in situ studies, batch reaction studies, and development/ application of a technique for particle size analysis using the Coulter counter -- will now be given, followed by a discussion of the studies planned for the forthcoming quarter:

1) In Situ Studies: A microreactor with transparent walls was used for these studies. A detailed description of this reactor is given in the discussion under Subtask 1.D. In each experiment a representative sample of either the Wyodak or the Kentucky coal - consisting usually of one, two, or three large particles -- was placed in the microreactor; the reactor was filled with creosote oil and heated to reaction temperature (400^0 - 430^oC). During the heat-up and

reaction, the oil was maintained under a pressure of 700 to 1000 psi to prevent the oil from boiling. In Figures 1.A.1.a and 1.A.1.b a particle of the Kentucky coal is shown before and after heat-up to 410°C. Apparently no changes occurred in the shape and size of the particle during heat-up; in fact, after four hours of reaction at 410°C no significant changes were observed to occur in the shape and size of the particle. To study the structural strength of the Kentucky coal at reaction temperature, in a different experiment, a sliding rod (or penetrator) was used to push the particle against the thermocouple well mounted in the microreactor, applying a pressure on the particle. When only a small amount of pressure was so applied on the particle, the rod penetrated the particle; and as shown in Figures 1.A.2.a and 1.A.2.b, in addition to being soft, the particle appeared to be very sticky, almost like chewing gum. When a particle of Wyodak coal submerged in creosote oil (Figures 1.A.3.a, 1.A.3.b, and 1.A.3.c) was heated to 410°C, it remained also essentially the same in appearance. However, a significant amount of pressure was required to crush the particle of Wyodak coal at reaction temperature (410°C); and when crushed, the particle of Wyodak coal broke up into discrete particles,like sand or salt particles.

The inactivity of the coals in creosote oil at 410°C was confusing, since at this temperature these coals are known to liquefy at an appreciable rate. Since the solvent is not agitated in the microreactor, one reason for the inactivity could be lack of agitation, or poor mass transfer. In one experiment, however, a particle of the Kentucky coal was heated to reaction temperature (410°C) in the presence of tetralin, a known hydrogen donor; and to promote mass transfer, i.e. for stirring purposes, the pressure exerted on the oil was reduced so that the oil boiled profusely, stirring the oil; yet still no significant change in appearance of the

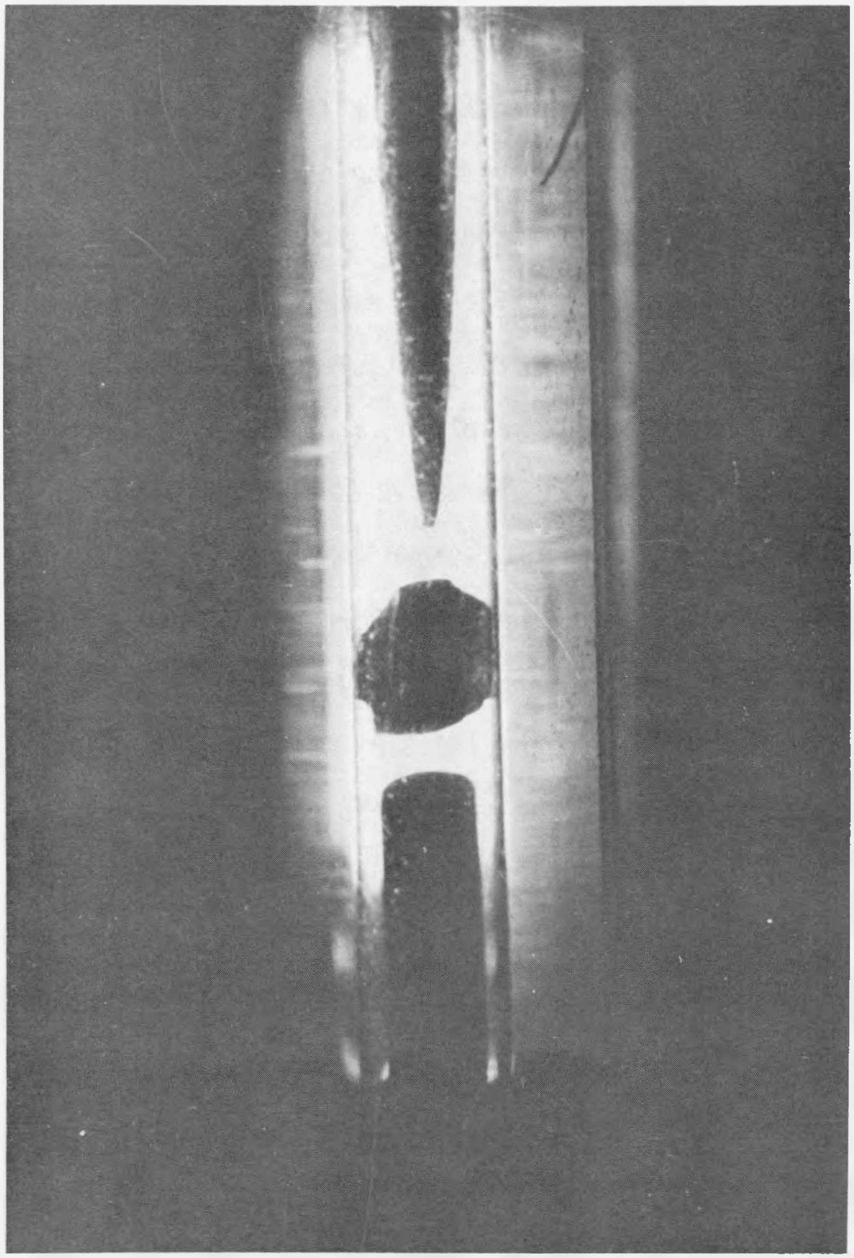


Figure 1.A.1.a Original Particle of Kentucky Coal in Tetralin

Note: The pointed rod at the top is the penetrator; the flat-edged rod at the bottom is the thermocouple well; and the particle is the object in the center.

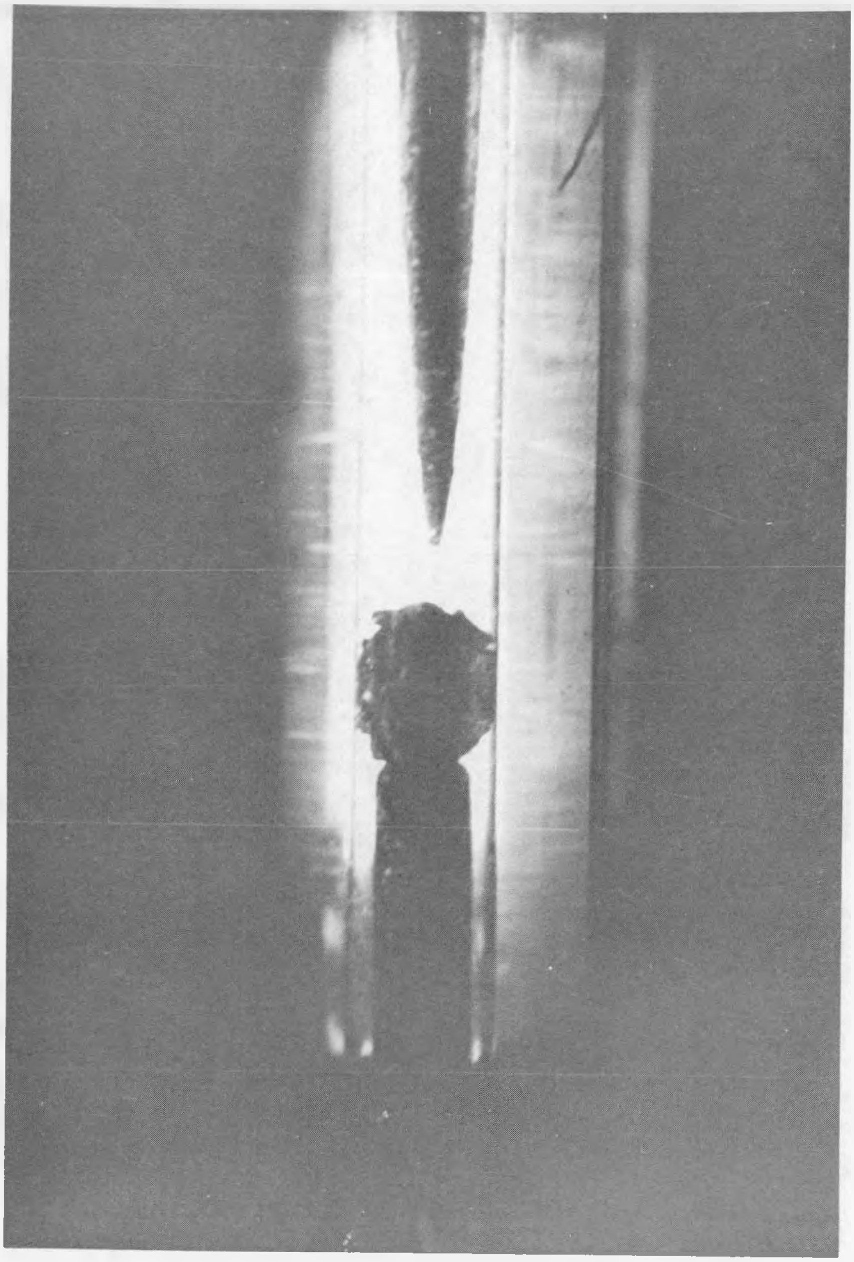


Figure 1.A.1.b Particle of Kentucky Coal at 410^{o}C After 15 Minutes of Reaction.

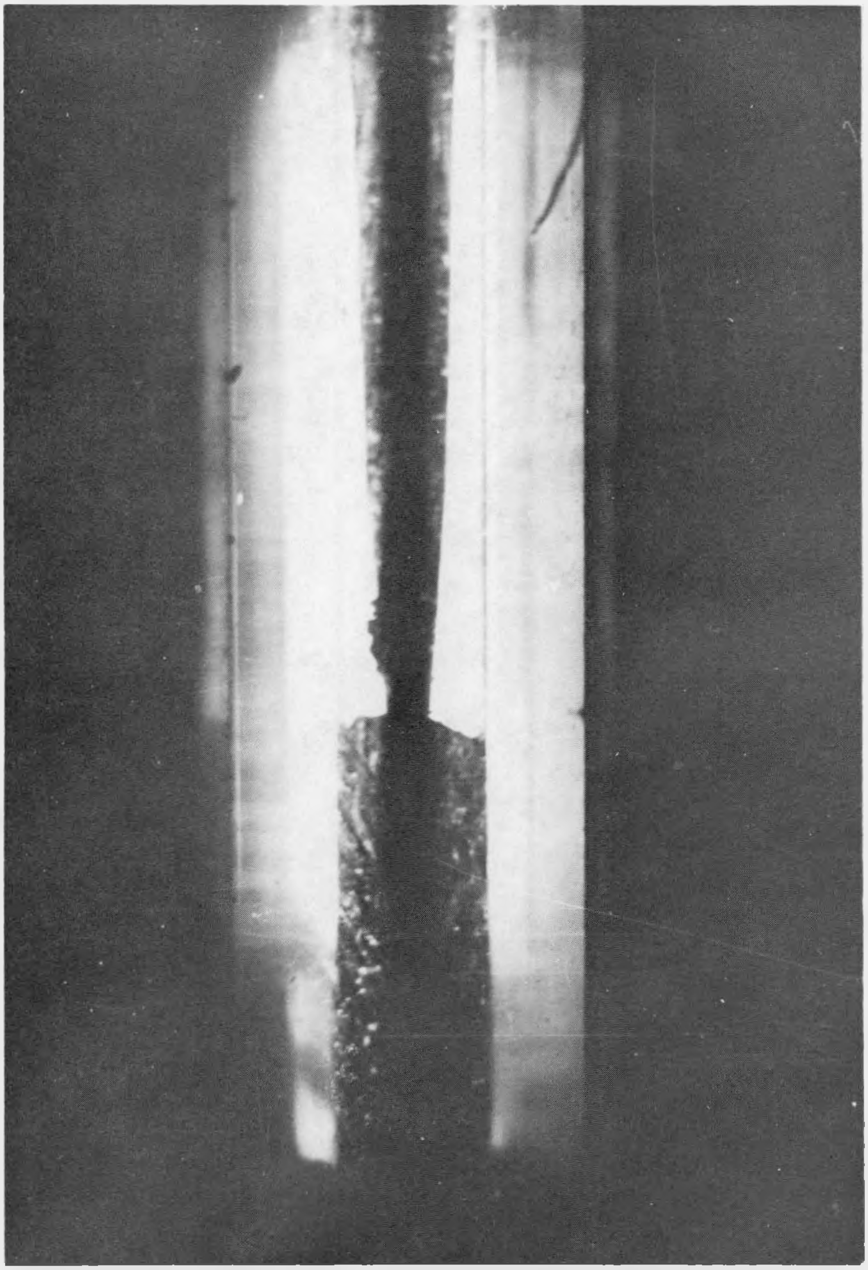


Figure 1.A.2.a Particle of Kentucky Coal at 410^{o}C after pentration.

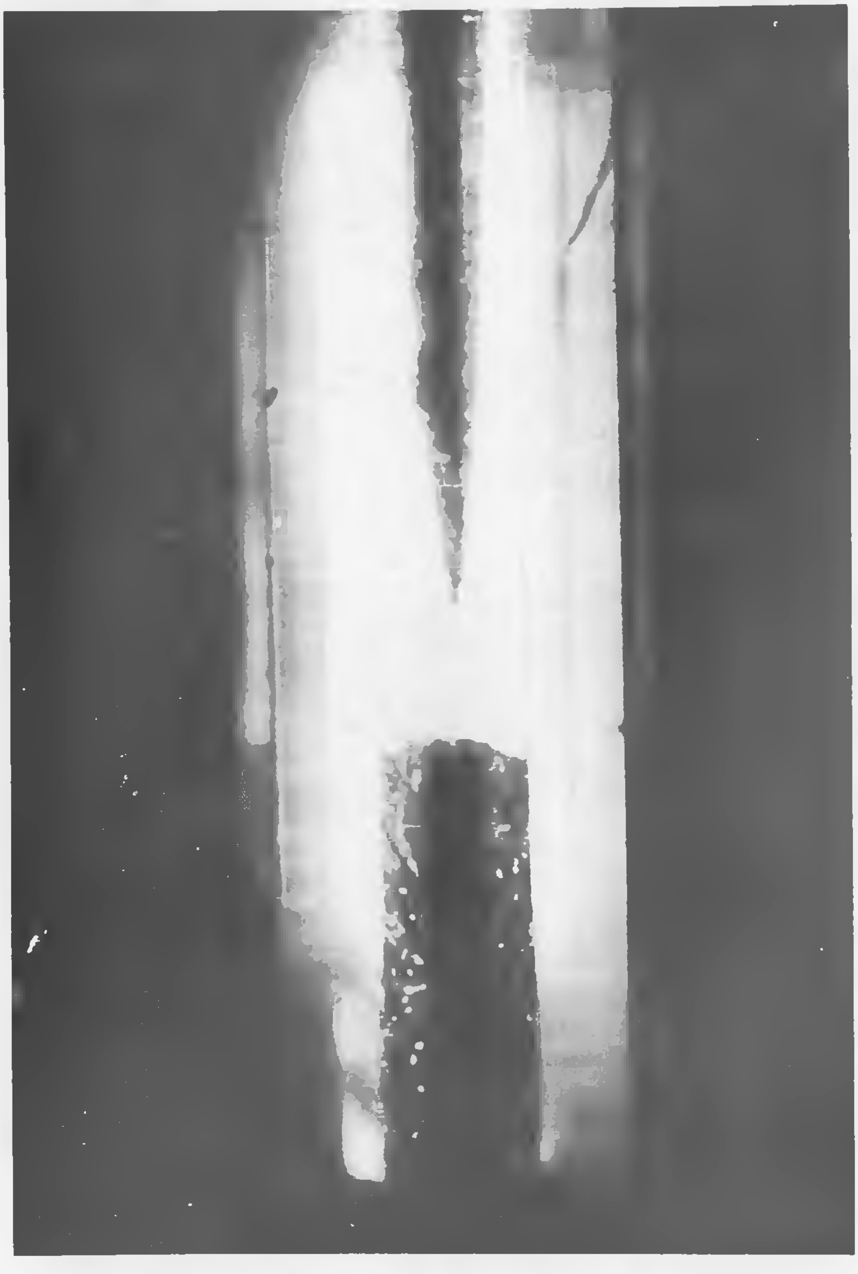


Figure 1.A.2.b Particle of Kentucky Coal at 410^{0}C After Removal of the Penetrator.

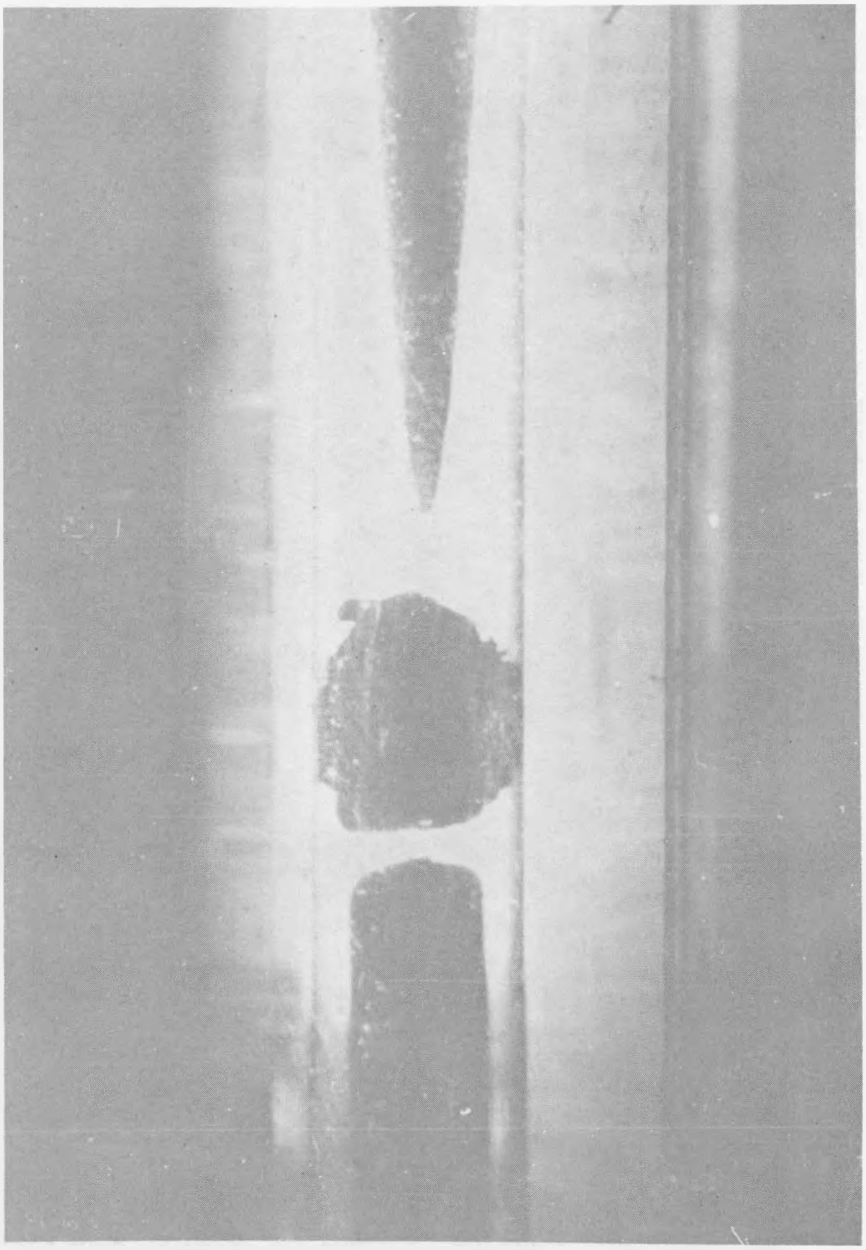


Figure 1.A.3.a Original Particle of Wyodak Coal in Tetralin

Note: The pointed rod at the top is the penetrator; the flat-edged rod at the bottom is the thermocouple well; and the round-shaped object between these two rods is the coal particle.

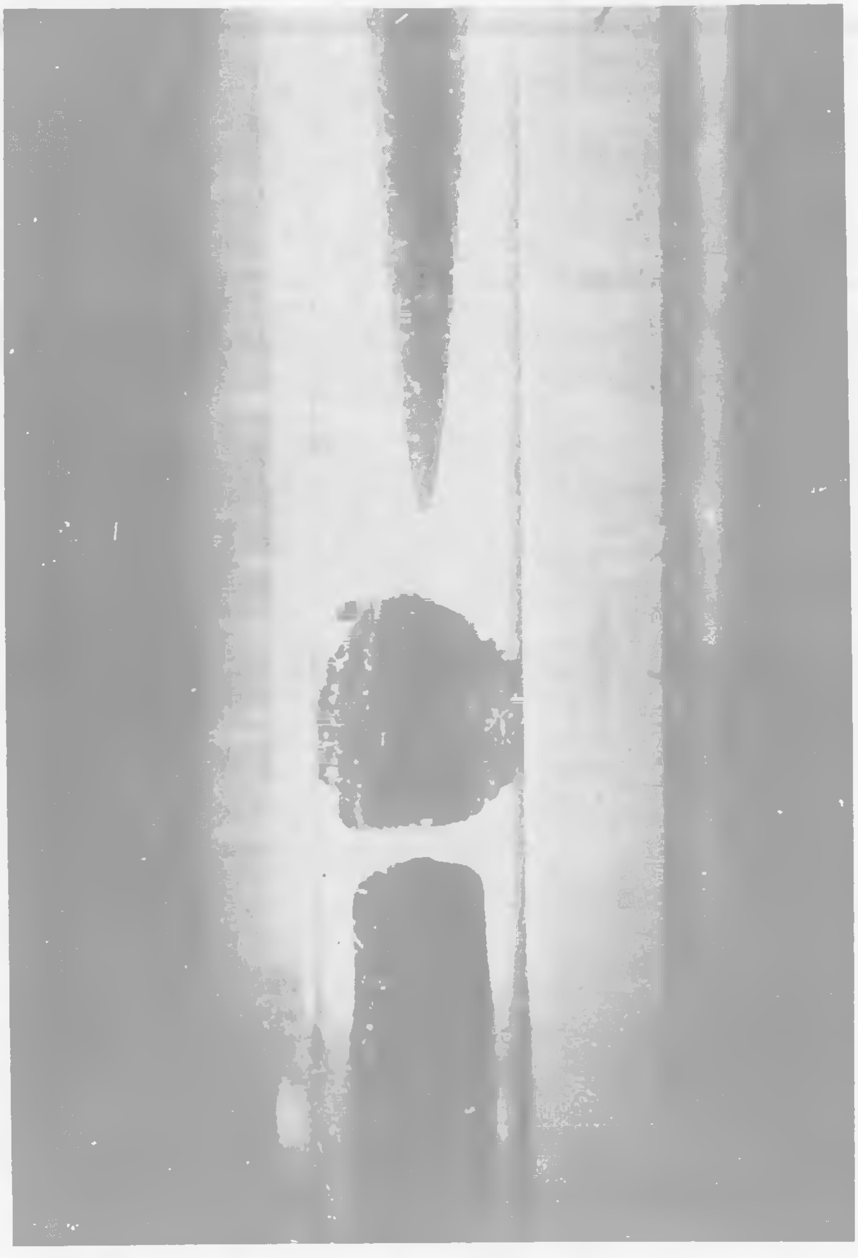


Figure 1.A.3.b Particle of Wyodak Coal in Tetralin at 410°C After Five Minutes of Reaction.

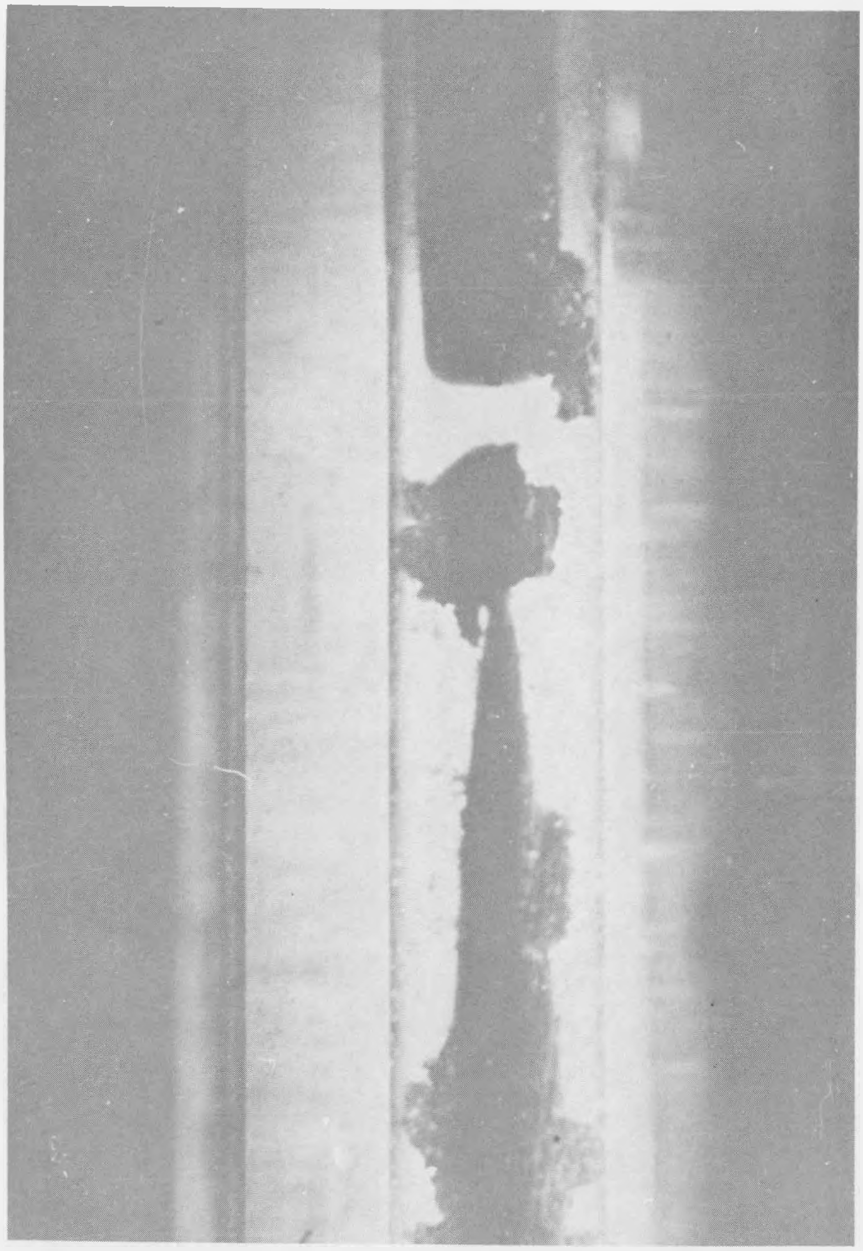


Figure 1.A.3.c Particle of Wyodak Coal in Tetralin at 410°C After it Broke Up into Smaller Units During Attempted Penetration.

particle was observed after an hour of reaction. In another experiment, furthermore, hydrogen gas was even bubbled past the particle while maintaining the temperature of the tetralin, in which the particle was submerged, at 410^{o}C, and no changes in appearance of the particle were observed. The tentative conclusion was thus made that, in addition to the effect of solvent type as discussed in the following paragraph and in Subtask 1.C, agitation of the particle itself must play an important role in its dissolution, probably by preventing a coating that is impermeable to the solvent from forming around the particle -- for instance, by mechanically breaking the particle into smaller units prior to reaction. Size analysis of particulates in reaction mixtures, showed that particulates did indeed change drastically in size during the early stages of dissolution, supporting this tentative conclusion.

In an earlier work (refer to discussion under Task 2), the rate of liquefaction of coal solids was shown to be very sensitive to hydrogen concentration in the solvent: coal solids dissolved at a significantly higher rate when hydrogenated in the presence of hydrogenated creosote oil or a hydrogen atmosphere than when hydrogenated in the presence of creosote oil or an inert atmosphere, respectively. To verify these earlier observations then, a particle of the Kentucky coal was heated in the microreactor to 410^{o}C in the presence of hydrogenated creosote oil. Before reaching reaction temperature (specifically at about 360^{o}C), the particle dissolved almost instantaneously, with the oil becoming very discolored in the vicinity of the particle and no traces of the particle remaining after flushing with fresh solvent. When a particle of the Wyodak coal was heated in the presence of hydrogenated creosote oil, on the other hand, the particle did not dissolve instantaneously; instead, it dissolved in a shrinking core manner at an appreciable rate; but compared to the almost instantaneous dissolution of the Kentucky coal, its rate of dissolution was extremely slow, requiring about an hour before most of the particle dissolved.

2) Batch Reaction Studies. To confirm results of the in situ studies, to study the changes in particle size distribution with reaction, and to evaluate differences in rate of dissolution between the two types of coals, several batch reaction experiments were made. A 300 cc magnedrive autoclave from Autoclave Engineers, Inc., was used. The general experimental procedure was the same as that described in Task 2.A.

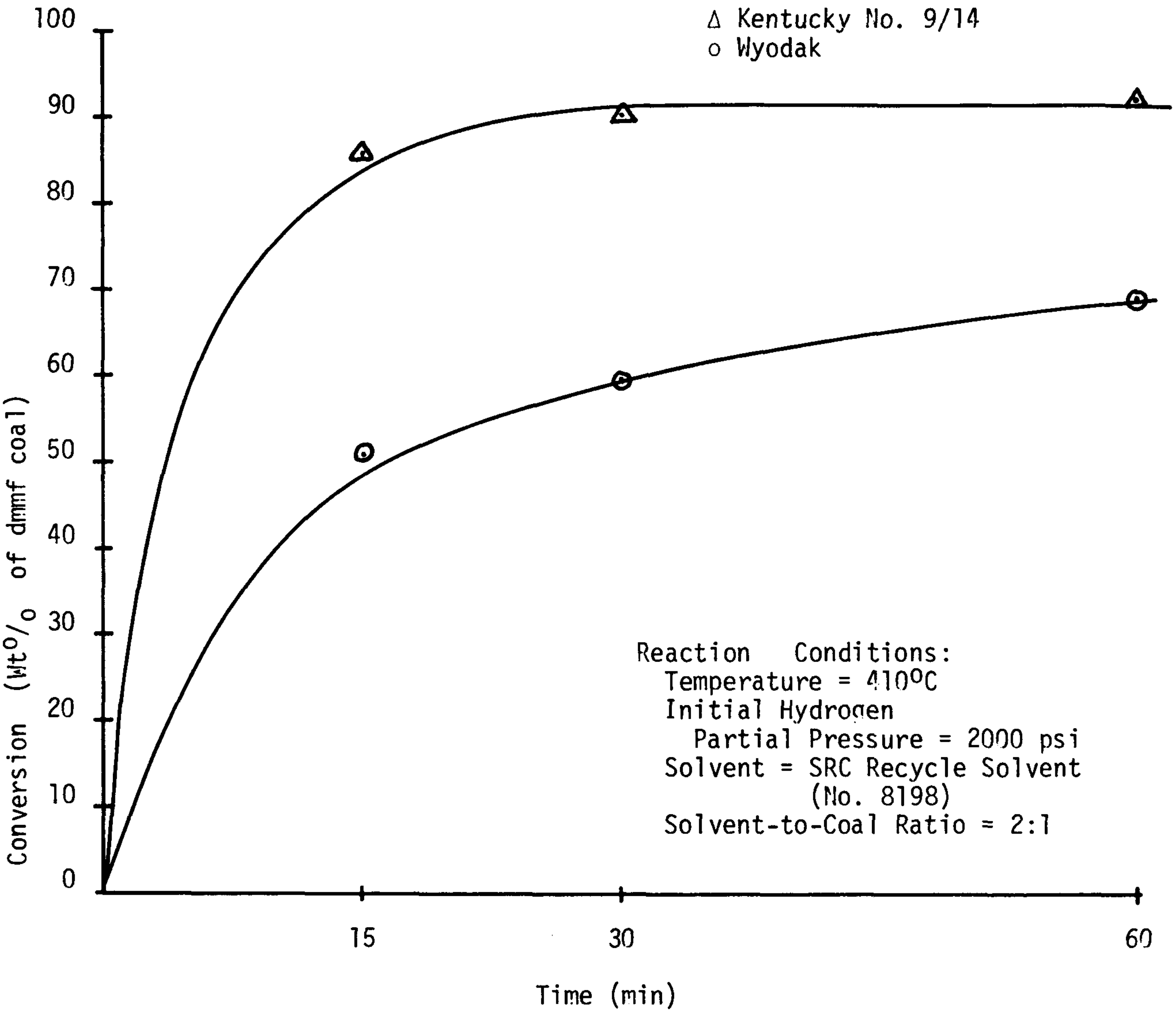
The rate of dissolution of both the Kentucky coal and the Wyodak coal was found in the in situ studies to be very sensitive to the concentration of hydrogen, either in the form of dissolved hydrogen gas or transferable hydrogen such as that attached to donor species, in the solvent. As shown in Table 1.A.1, indeed, the rate of liquefaction (or conversion) was significantly higher in hydrogenated creosote oil than in creosote oil for the Kentucky coal. (For a more detailed discussion of the effect of solvent composition on the rate of liquefaction refer to the discussion under Subtask 1.C.). Also, the rate of liquefaction of the Wyodak coal was observed to be significantly less than that of the Kentucky coal in the in situ studies. This observation also agreed with the results of the batch reaction experiments; for example, as shown in Figure 1.A.4, the reactivity of the Wyodak coal was significantly less than that of the Kentucky coal.

The Coulter counter was used to monitor variations in size distribution of particulates in reaction mixtures at different reaction times. The results of the associated batch reaction studies is given in the following discussion.

Table 1.A.1 Comparions of Hydrogenation and Hydrodesulfurization Activity of Coal in Different Solvents

Solvent	Temperature (°C)	Atmosphere (psi)	Reaction Time (min.)	Solvent-to-Coal Ratio	Conversion (Based on Cresol Solubles) (%)	Total Sulfur (%)
Creosote Oil	410	2000 N_2	15	3/1	42.13	.904± .023
Hydrogenated Creosote Oil	410	2000 N_2	15	3/1	83.10	.487± .030
Recycle Oil (Pitts, Seam Coal; Sample No. 8189)	410	2000 N_2	15	3/1	76.35	.733± .024
Recycle Oil (Sample No. 16171)	410	2000 N_2	15	3/1	78.88	.732± .013
Creosote Oil	410	2000 H_2	15	3/1	61.03	.912± .054
Hydrogenated Creosote Oil	410	2000 H_2	15	3/1	90.70	.506± .026
Recycle Oil (Pitts. Seam Coal; Sample No. 8198)	410	2000 H_2	15	3/1	82.78	.634± .028
Recycle Oil (Sample No. 16171)	410	2000 H_2	15	3/1	85.78	.745± .015
Cresol/Creosote-Oil Mixture (1:1 wt. ratio)	410	2000 N_2	15	3/1	53.2	

Figure 1.A.4 Effect of Coal Type on Conversion to Cresol-Solubles



3) Development/Application of a Technique for Particle Size Analysis Using the Coulter Counter.

The Coulter counter has been shown in past studies to offer a reliable means for rapid analysis of pulverized coal and fly ash; however, its use for analyzing complex SRC reaction mixtures -- which contain coal-derived solvent, undissolved coal, and mineral matter -- had not been previously reported. A technique thus had to be developed to use our Coulter counter to monitor size distribution of particulate matter in a SRC reaction mixture.

The most difficult task confronted in the development of the technique was the selection of an acceptable solvent/electrolyte system. After numerous screening studies, a solvent/electrolyte with the necessary characteristics was found. As shown in Figures 1.A.5 and 1.A.6, the reproducibility obtained using the resulting technique was excellent. As was recommended by Coulter, Inc., Xerox toner was used as a calibration standard. And as shown in Figure 1.A.5, our analysis of the Xerox toner agreed very well with that by Coulter, Inc.

Particle stability during dispersion and analysis was found to be adequate (Figure 1.A.6). However, since prior to analysis particulates were dispersed using an ultrasonic bath, only those agglomerates strongly bonded together could be assumed to remain intact during analysis. For this reason the Coulter counter has limited usefulness for monitoring particle agglomeration during reaction, etc.

Using the technique developed for performing size analysis, the effects of reaction temperature and reaction time on particle size distribution were studied:

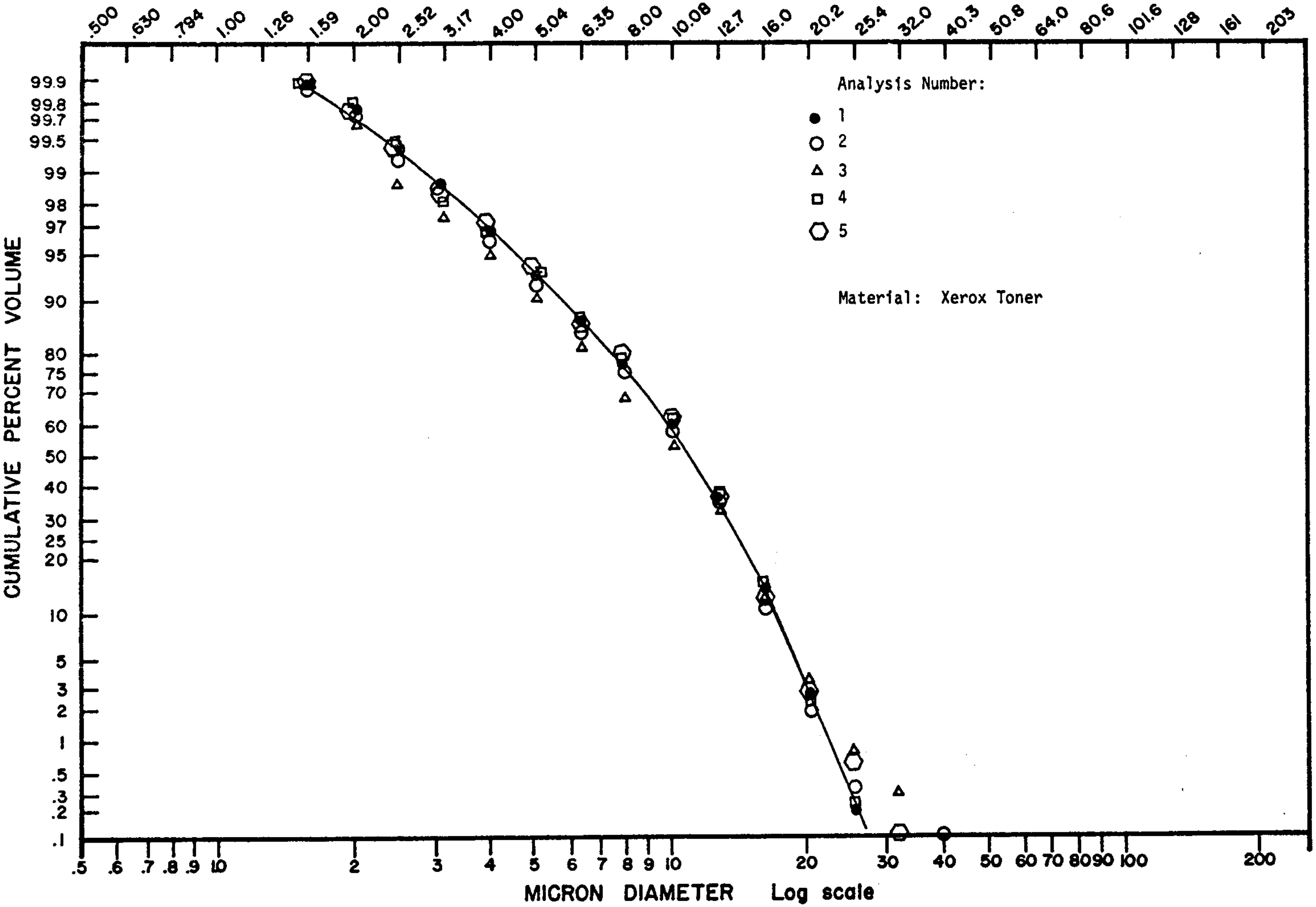
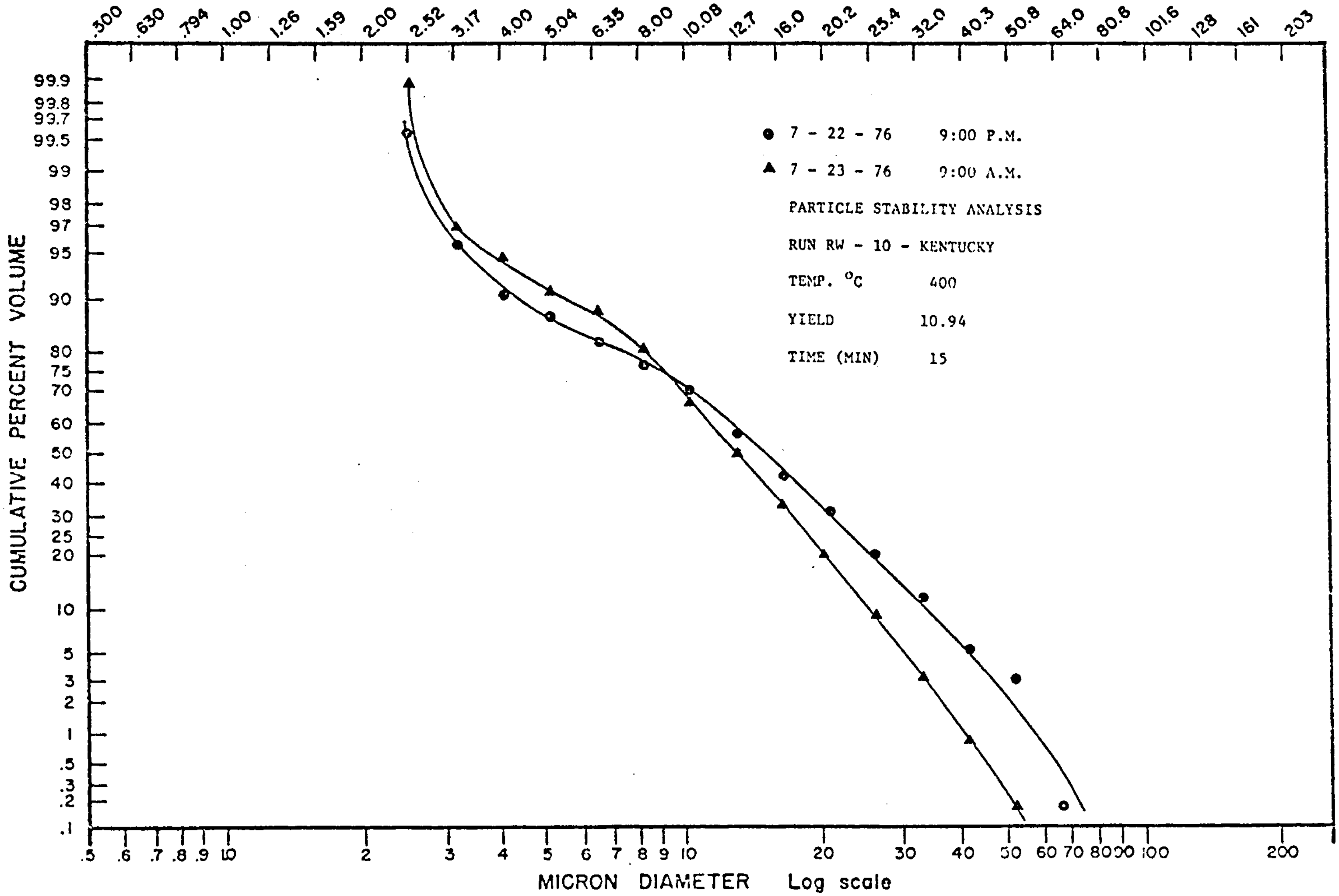


Figure 1.A.5 An Evaluation of Degree of Internal Duplication Obtained for Size Analysis of Calibration Standard.


.300 .630 .794 1.00 1.26 1.59 2.00 2.52 3.17 4.00 5.04 6.35 8.00 10.08 12.7 16.0 20.2 25.4 32.0 40.3 50.8 64.0 80.8 101.6 128 161 203
99.9
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CUMULATIVE PERCENT VOLUME
● 7 - 22 - 76 9:00 P.M.
▲ 7 - 23 - 76 9:00 A.M.
PARTICLE STABILITY ANALYSIS
RUN RW - 10 - KENTUCKY
TEMP. °C 400
YIELD 10.94
TIME (MIN) 15
.5 .6 .7 .8 .9 10 2 3 4 5 6 7 8 9 10 20 30 40 50 60 70 80 90 100 200
MICRON DIAMETER Log scale

Figure 1.A.6

a) Reaction Temperature. The reaction conditions for the experiments used for investigating the effect of reaction temperature on particle size distribution are summarized in Table 1.A.2.

Size analysis for experiments RW-11 and RW-12 are given in Table 1.A.3. And log-probability plots of these data are given in Figure 1.A.7. For the Kentucky coal used, the mean size of residual particulates was significantly lower after reaction at 410°C than that of the original coal and, more importantly, than that after reaction at 400°C.

b) Reaction Time. The reaction conditions for the experiments used for investigating the effect of reaction time on particle size distribution are summarized in Table 1.A.4.

For the Kentucky coal used, the particle size distribution shifted toward smaller sizes with each incremental increase in reaction time from 0,15,30 to 60 minutes. A duplicate experiment with a reaction time of 15 minutes was made, showing reasonable agreement between the two size distributions. Size analyses for these experiments are given in Table 1.A.5; corresponding log-probability plots and photomicrographs are given in Figures 1.A.8 and 1.A.9, respectively. The photomicrographs agreed well with size analyses by the Coulter Counter.

The variation in particle size distribution with reaction time was not the same for the Wyodak coal as that for the Kentucky coal. As shown in Figure 1.A.10, as with the Kentucky coal, the particle size distribution did shift toward smaller sizes after 15 minutes of reaction; but with further reaction, the particle size distribution actually shifted toward larger sizes, indicating an overall growth in size of the particulates. These observations were most surprising,

Table 1.A.2 Reaction Conditions for the Experiments Used to Investigate the Effect of Reaction Temperatureon Particle-Size Distribution.

Run	Coal	Ratio	°C Temp	Time Minutes	C.I. Yield-%
RW-11	Kentucky	3:1	350	15	46.24
RW-10	Kentucky	3:1	400	15	10.94
RW12	Kentucky	3:1	410	15	85.78
MJ-58	Wyodak	2:1	410	15	51.24
MJ-59	Wyodak	2:1	410	15	50.29
RW-43	Kentucky	2:1	385	15	5.20
MJ-66	Kentucky	2:1	410	15	85.90

Note: SRC recycle solvent no. 8189 and an initial hydrogen partial pressure of 2000 psi were used in all experiments.

TABLE 1.A.3

COULTER COUNTER PARTICLE SIZE ANALYSIS

3:1 Solvent to Coal Ratio, 15Minutes, 2000 psig H_2

Kentucky 9/14 Coal-Pittsburg Seam Solvent

Run	RW-10		RW-11		RW-12	
Temperature°C	350		400		410	
Yield-%	10.94		46.24		85.78	
Particle Size (Microns)	DIF	CUM	DIF	CUM	DIF	CUM
2.52	1.3	99.9	2.2	99.9	5.9	99.9
3.17	1.5	98.6	2.4	97.8	7.7	94.2
4.00	1.8	97.1	2.7	95.4	8.2	86.9
5.04	2.9	95.2	3.1	92.7	8.7	79.0
6.35	6.8	92.3	4.7	89.6	9.7	70.7
8.00	14.2	85.7	6.8	85.1	10.9	61.4
10.08	19.1	72.1	9.3	78.5	11.7	50.6
12.70	16.0	53.6	12.2	69.4	10.6	39.0
16.00	14.6	37.8	15.1	57.5	9.4	28.3
20.20	12.3	23.1	17.1	42.6	6.3	18.8
25.40	7.5	10.7	14.0	25.5	5.4	12.4
32.00	1.7	3.0	6.0	11.4	4.4	6.8
40.30	0.3	1.0	1.7	5.1	1.2	2.1
50.80	0.0	0.4	0.7	3.2	0.3	0.7
64.00	0.3	0.3	2.4	2.4	0.2	0.2
Particle Count	140794		179817		395676	

Table 1.A.4 Reaction Conditions for the Experiments Used to Investigate the Effect of Reaction Time on Particle-Size Distribution.

Run	Coal	Ratio	°C Temp	Time Minutes	C.I.-% Yield
RW-04	Kentucky	3:1	400	15	81.69
RW-05	Kentucky	3:1	400	15	82.68
RW-08	Kentucky	3:1	400	30	87.12
RW-07	Kentucky	3:1	400	60	89.68
MJ-58	Wyodak	2:1	410	15	51.24
MJ-59	Wyodak	2:1	410	15	50.29
MJ-63	Wyodak	2:1	410	30	60.50
MJ-67	Wyodak	2:1	410	30	58.32
MJ-61	Wyodak	2:1	410	60	68.59
MJ-62	Wyodak	2:1	410	60	69.71

Note: SRC recycle solvent no. 8189 and an initial hydrogen partial pressure of 2000 psi were used in all experiments.

TABLE 1.A.5

COULTER COUNTER PARTICLE SIZE ANALYSIS
3:1 Solvent to Coal Ratio, 400°C, 2000 psig H_2
Kentucky 9/14-Pittsburg Seam Solvent

Run	RW-04		RW-05		RW-08		RW-07	
Time-Minutes	15		15		30		60	
Yield-%	81.69		82.68		87.12		89.68	
Particle Size (Microns)	DIF	CUM	DIF	CUM	DIF	CUM	DIF	CUM
1.59	6.5	99.5	3.5	99.7	4.8	99.7	6.1	99.7
2.00	6.3	93.4	3.9	96.3	5.8	95.1	7.5	93.9
2.52	4.9	87.4	3.6	92.5	6.7	89.6	8.3	86.8
3.17	5.0	82.5	4.0	89.1	8.1	83.1	9.6	78.9
4.00	6.2	77.8	5.4	85.2	10.2	75.3	11.2	69.6
5.04	8.2	71.7	7.5	79.8	12.1	65.4	12.2	58.1
6.35	11.0	63.5	10.1	72.6	13.5	53.5	12.4	46.8
8.00	12.6	52.9	12.8	62.7	14.1	40.2	11.5	34.4
10.08	14.3	40.4	14.5	50.1	13.3	26.1	9.8	22.9
12.70	13.0	26.1	13.2	35.7	8.0	12.6	6.6	12.9
16.00	8.9	12.9	18.9	22.4	2.8	4.4	3.6	6.2
20.20	3.2	3.8	2.1	3.4	0.7	1.3	0.8	2.2
25.40	0.3	0.3	0.0	1.1	0.4	0.4	0.7	0.7
32.00			0.7	0.7			0.2	0.2
Particle Count	364052		266482		370202		325460	

TABLE 1.A.6.a

COULTER COUNTER PARTICLE SIZE ANALYSIS

2:1 Solvent to Coal Ratio, 410°C, 2000 psig H_2

Wyodak Coal-Pittsburg Seam Solvent

Run	MJ-58		MJ-59		MJ-63	
Time-Minutes	15		15		30	
Yield-%	51.24		50.29		60.50	
Particle Size (Microns)	DIF	CUM	DIF	CUM	DIF	CUM
1.59	2.2	99.9	2.5	99.9		
2.00	3.2	97.8	3.8	97.7		
2.52	4.0	94.6	4.8	93.9	1.8	99.7
3.17	4.7	90.6	6.0	89.1	3.5	98.0
4.00	5.9	85.9	7.3	83.1	4.8	94.5
5.04	6.8	80.0	7.5	75.8	5.5	89.9
6.35	7.6	73.2	8.2	68.3	7.2	84.7
8.00	9.1	65.6	9.3	60.1	8.2	77.7
10.08	9.5	56.5	10.7	50.8	9.3	69.7
12.70	10.2	47.0	10.5	40.1	10.3	60.6
16.00	10.5	36.8	12.1	29.6	12.3	50.5
20.20	11.3	26.3	10.1	17.5	12.3	30.2
25.40	8.3	15.0	5.1	7.4	13.3	25.9
32.00	5.1	6.8	2.1	2.3	9.3	12.5
40.30	1.6	1.6	0.2	0.2	2.7	2.7
Particle Count	178781		241487		175136	

TABLE 1.A.6.b

COULTER COUNTER PARTICLE SIZE ANALYSIS

2:1 Solvent to Coal Ratio, 410°C, 2000 psig H_2

Wyodak Coal-Pittsburg Seam Solvent

Run	MJ-67		MJ-61		MJ-62	
Time-Minutes	30		60		60	
Yield-%	58.32		68.59		69.71	
Particle Size (Microns)	DIF	CUM	DIF	CUM	DIF	CUM
2.52	4.4	99.6	3.4	99.9	3.6	99.9
3.17	5.7	95.4	4.9	96.2	5.3	96.4
4.00	5.9	90.0	5.3	91.5	6.3	91.4
5.04	6.0	84.4	5.5	86.3	6.9	85.3
6.35	7.0	78.6	6.6	80.9	8.2	78.6
8.00	8.2	71.8	7.6	75.5	8.4	70.6
10.08	9.9	63.5	8.4	67.0	9.4	62.5
12.70	10.3	54.0	9.6	58.7	9.8	53.1
16.00	11.6	43.9	10.0	49.3	10.4	43.4
20.20	11.2	32.3	11.2	39.3	10.3	33.0
25.40	11.4	21.0	11.9	27.9	10.3	22.6
32.00	6.8	9.4	8.8	15.9	6.7	12.1
40.30	1.7	2.3	5.4	6.8	3.9	5.2
50.80	0.4	0.4	1.2	1.2	0.6	1.0
64.00	0.0	0.0	0.0	0.0	0.2	0.2
Particle Count	288408		279910		285258	

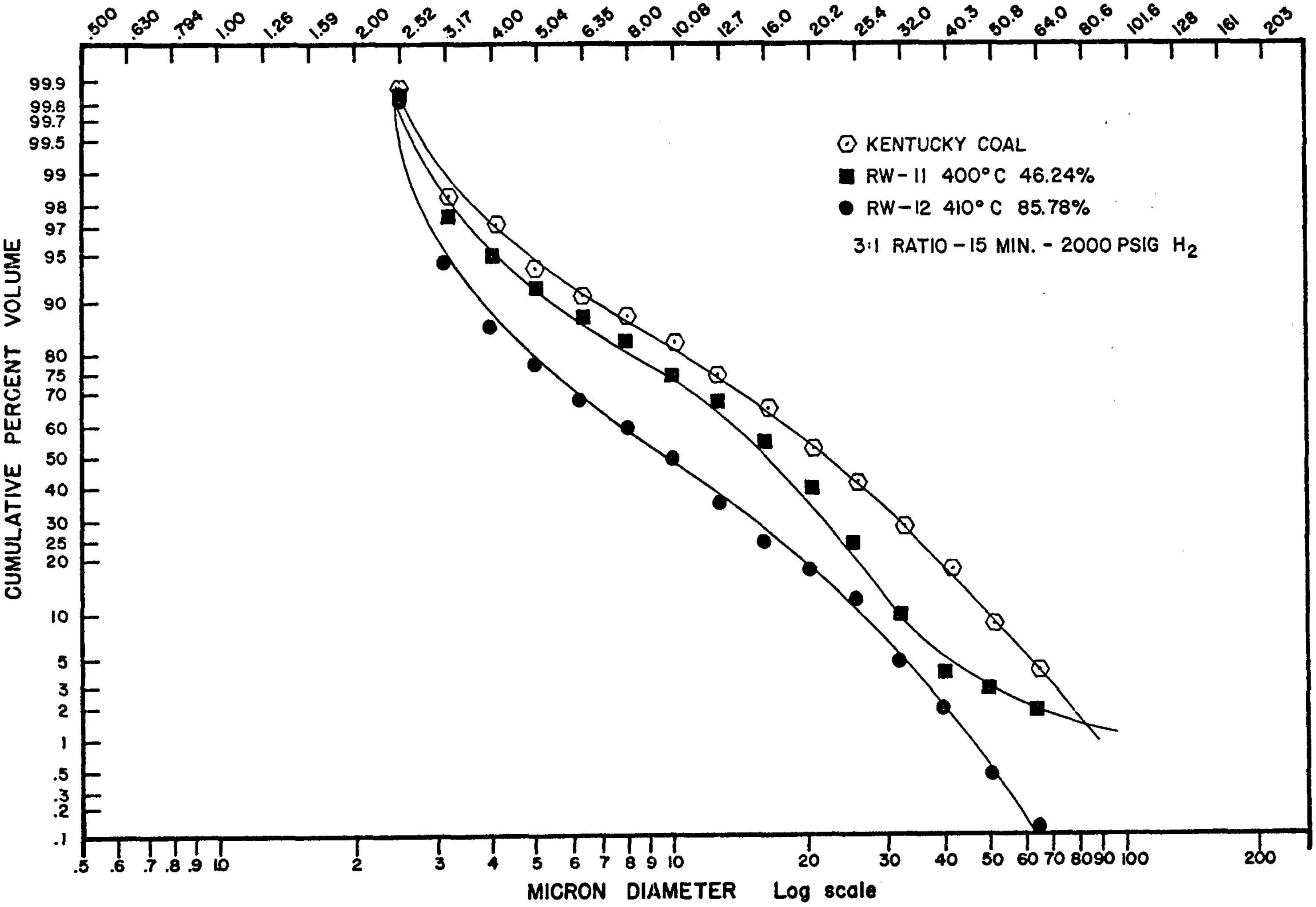

.500
.630
.794
1.00
1.26
1.59
2.00
2.52
3.17
4.00
5.04
6.35
8.00
10.08
12.7
16.0
20.2
25.4
32.0
40.3
50.8
64.0
80.6
101.6
128
161
203
CUMULATIVE PERCENT VOLUME
99.9
99.8
99.7
99.5
99
98
97
95
90
80
75
70
60
50
40
30
25
20
10
5
3
2
1
.5
.3
.2
.1
KENTUCKY COAL
RW-11 400° C 46.24%
RW-12 410° C 85.78%
3:1 RATIO - 15 MIN. - 2000 PSIG H_2
.5
.6
.7
.8
.9
1.0
2
3
4
5
6
7
8
9
10
20
30
40
50
60
70
80
90
100
200
MICRON DIAMETER Log scale

FIGURE I.A.7

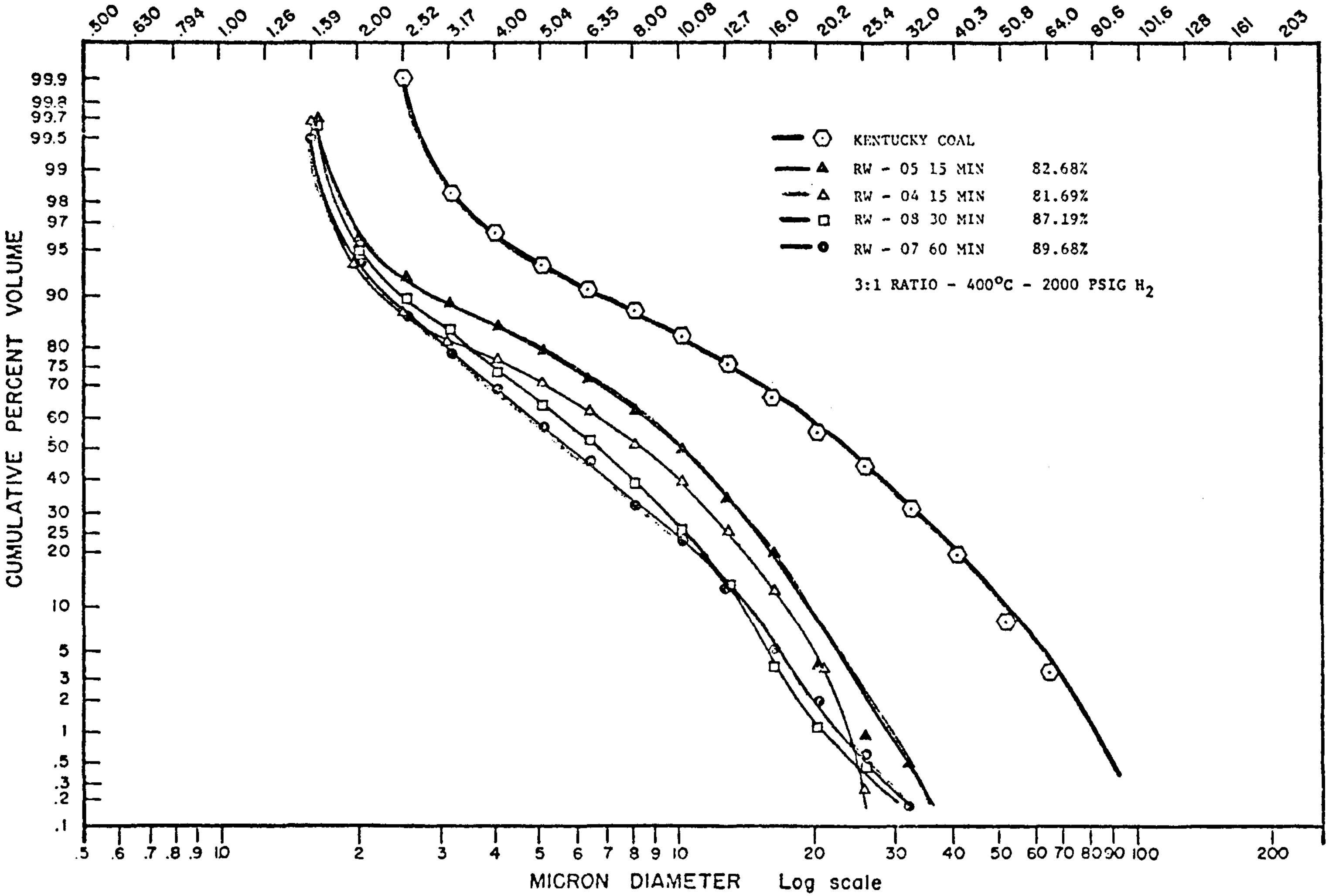

.500
.630
.794
1.00
1.26
1.59
2.00
2.52
3.17
4.00
5.04
6.35
8.00
10.08
12.7
16.0
20.2
25.4
32.0
40.3
50.8
64.0
80.6
101.6
128
161
203
KENTUCKY COAL
RW - 05 15 MIN 82.68%
RW - 04 15 MIN 81.69%
RW - 08 30 MIN 87.19%
RW - 07 60 MIN 89.68%
3:1 RATIO - 400°C - 2000 PSIG H_2
CUMULATIVE PERCENT VOLUME
99.9
99.8
99.7
99.5
99
98
97
95
90
80
75
70
60
50
40
30
25
20
10
5
3
2
1
.5
.3
.2
.1
.5
.6
.7
.8
.9
10
2
3
4
5
6
7
8
9
10
20
30
40
50
60
70
80
90
100
200
MICRON DIAMETER Log scale

Figure 1.A.8

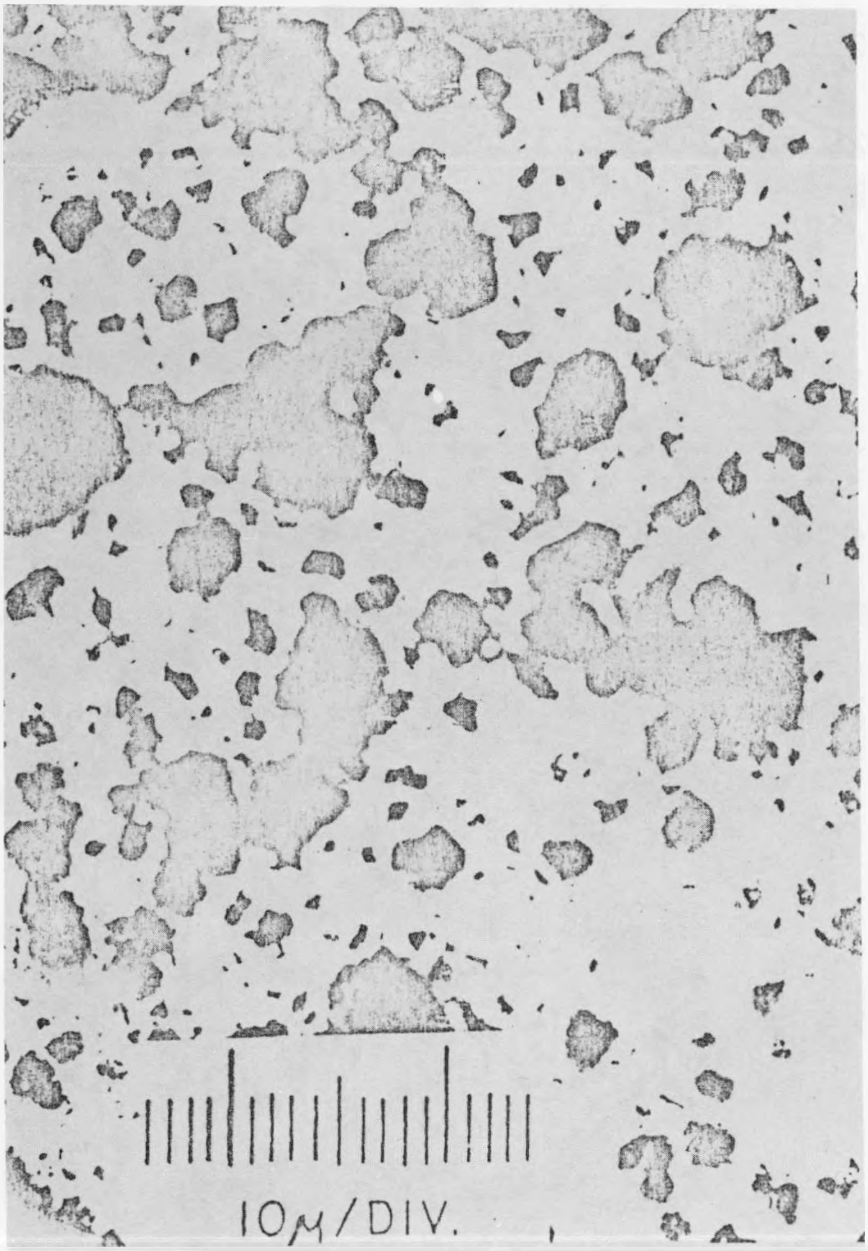


Figure 1.A.9.a Photomicrography-200X RW-04, Solvent Refined Coal Autoclave Mixture, 3:1 Ratio, 400°C, 81.69% Yield, 15 Minutes, Kentucky Coal

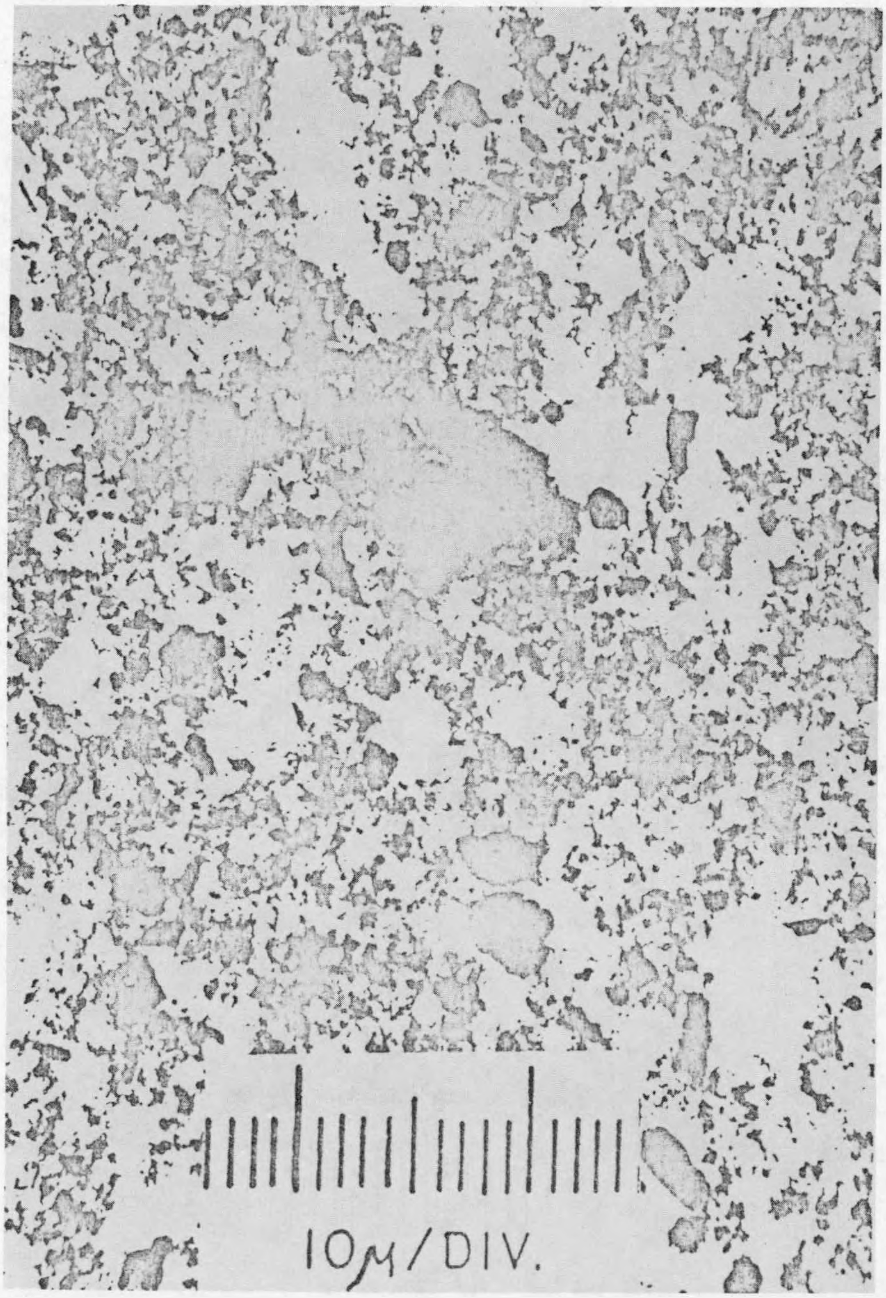


Figure 1.A.9.b Photomicrograph-200X RW-05, Solvent Refined Coal Autoclave Mixture, 3:1 Ratio, 400°C, 82.68% Yield, 15 Minutes, Kentucky Coal

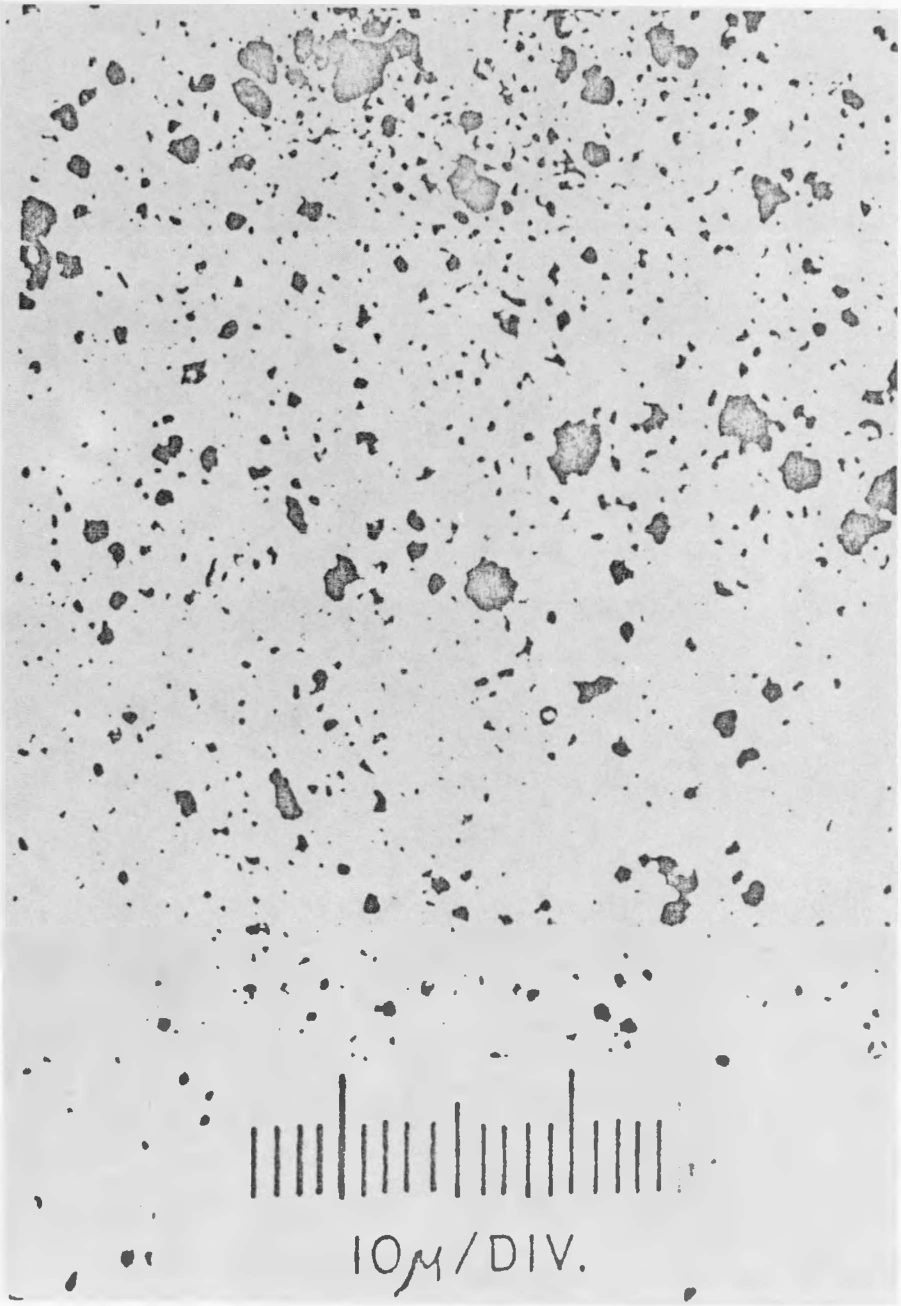


Figure 1.A.9.c Photomicrograph-200X RW-08, Solvent Refined Coal Autoclave Mixture, 3:1 Ratio, 400°C, 87.12% Yield, 30 Minutes, Kentucky Coal

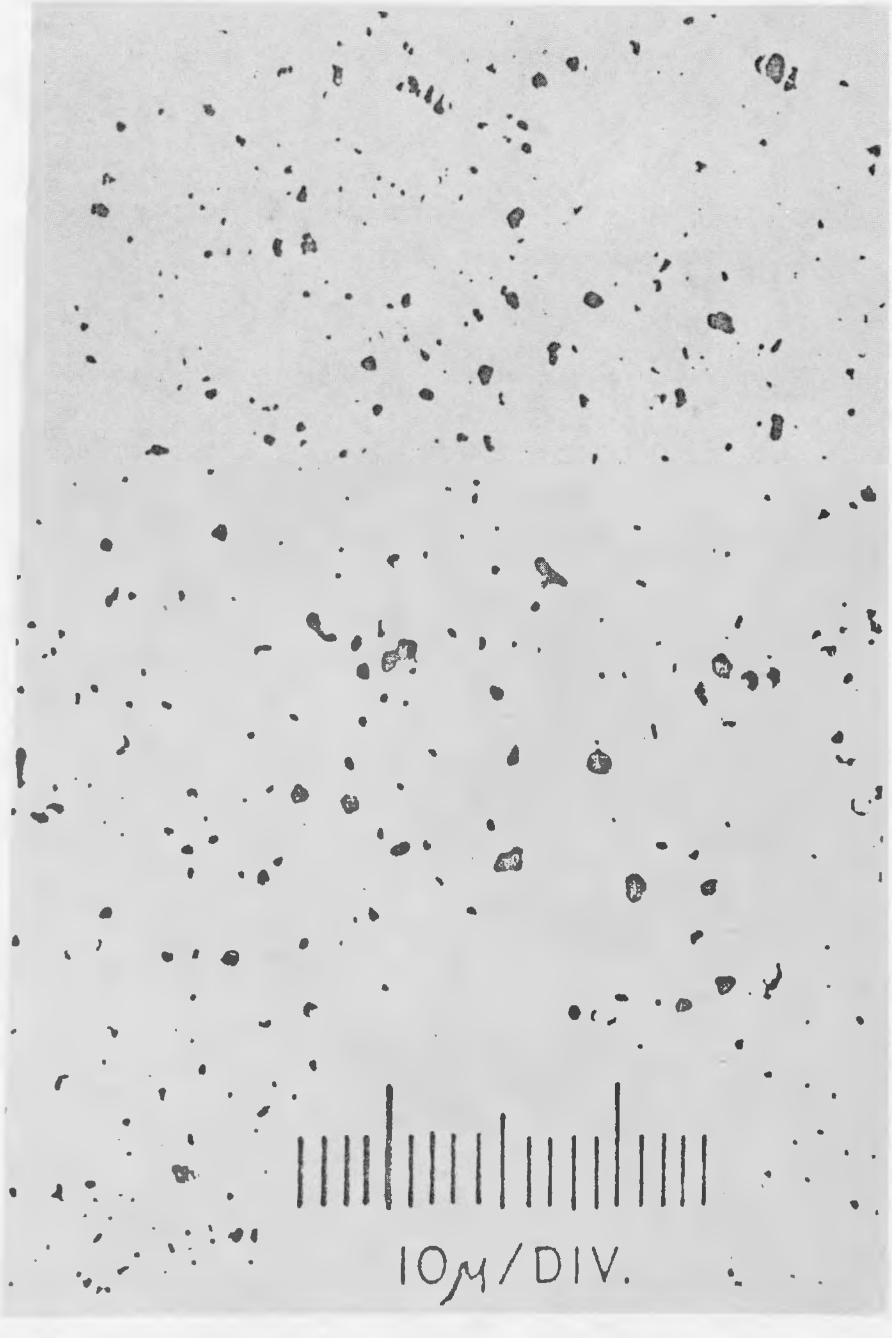


Figure 1.A.9.d Photomicrograph-200X RW-07, Solvent Refined Coal Autoclave Mixture, 3:1 Ratio, 400°C, 89.68% Yield, 60 Minutes, Kentucky Coal

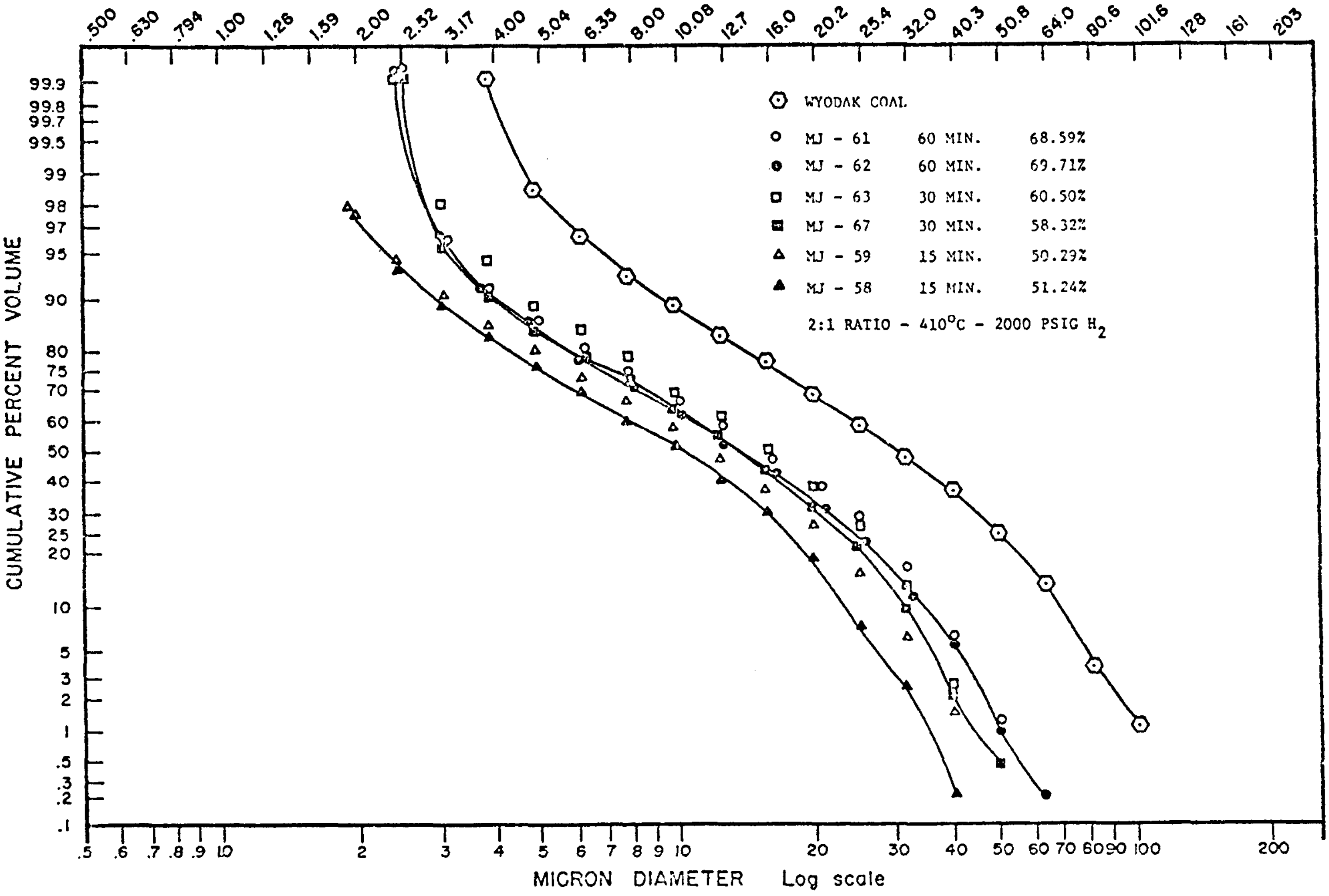

.500
.630
.794
1.00
1.26
1.59
2.00
2.52
3.17
4.00
5.04
6.35
8.00
10.08
12.7
16.0
20.2
25.4
32.0
40.3
50.8
64.0
80.6
101.6
128
161
203
99.9
99.8
99.7
99.5
99
98
97
95
90
80
75
70
60
50
40
30
25
20
10
5
3
2
1
.5
.3
.2
.1
CUMULATIVE PERCENT VOLUME
WYODAK COAL
MJ - 61 60 MIN. 68.59%
MJ - 62 60 MIN. 69.71%
MJ - 63 30 MIN. 60.50%
MJ - 67 30 MIN. 58.32%
MJ - 59 15 MIN. 50.29%
MJ - 58 15 MIN. 51.24%
2:1 RATIO - 410°C - 2000 PSIG H_2
.5
.6
.7
.8
.9
1.0
2
3
4
5
6
7
8
9
10
20
30
40
50
60
70
80
90
100
200
MICRON DIAMETER Log scale

Figure 1.A.10

yet consistant with findings at the Wilsonville SRC pilot plant, as was stated earlier.

The entire populace of the particulates is not analyzed by the Coulter counter; actually, for the aperture used in the above studies, only those particles in the size range of 1-2 to 80 microns were effectively counted. Recognizing then that only a fraction, presumably the major fraction, of the particle populace of the sample is counted by the Coulter counter -- some particles being too large to pass through the aperture and some too small for detection -- a least squares routine was developed to approximate the size distribution of the entire particle populace, assuming it to be log-normally distributed. This routine computes adjusted values for the mean particle size and standard deviation so as to force the particle size distribution to be log-normally distributed, while minimizing the sum of squares deviation between measured values in the relative size frequency density, as determined by Coulter counter analysis, and corresponding predicted values, as determined from the approximate log-normal distribution.

Planned Work: The two types of studies -- in situ and batch reaction -- used so far shall be continued to better establish some of the observations discussed above. The Coulter counter shall be used standardly in analyzing reaction mixtures. Also, an attempt shall be made to correlate size analysis of particulates in a reaction mixture, as determined by the Coulter counter, to its filterability. To do so, reaction mixtures shall be obtained from the Wilsonville SRC pilot plant, their mean particle size shall be determined and correlated with their filterability, or cake resistivity during their filtration.

In past batch reaction studies, coal solids were charged to the reactor mixed with solvent at room temperature, and rapidly heated to reaction temperature. Based on our past studies, C-C bonds and other (e.g. C-S) bonds are felt to thermally rupture almost instantaneously upon reaching reaction temperature. The free radical products may recombine (i.e. reploymerization may result) to form more stable compounds than those existing originally. Consequently, batch reaction experiments in which coal solids are injected at reaction temperature shall be performed to determine if there is any increase in activity of the coal over that resulting with rapid heat-up of the solvent/coal mixture.

1.B Effect of Initial Particle Size and Agitation Rate on Particle Dissolution

Objective: The objective of this subtask is to assess the effects of initial coal particle size and agitation rate upon particle dissolution.

Progress: No evaluation was made during this quarter of the effect of particle size upon particle dissolution. However, some very interesting observations were made concerning the effect of agitation rate upon particle dissolution. For example, without agitation of the particle itself, the rate of dissolution of a particle of both the Kentucky and the Wyodak coals in creosote oil was extremely slow, with no appreciable dissolution occurring over a four hour period (refer to the above discussion under Subtask 1.A.) With agitation, on the other hand, both the Kentucky coal and the Wyodak coal dissolved at an appreciable rate in creosote oil (refer to the discussion of the kinetics of coal liquefaction in Subtask 2.A.) Yet, above a critical amount of agitation -- which is yet to be determined -- additional agitation was observed to have little, or no effect on the reactivity of the coals; for

Table 1.B.1 Effect of Type of Agitator on Coal Conversion to Cresol Solubles

Solvent	Initial Atmosphere (1000 psi)	Cresol-Solubles (%)	
		Turbine Agitator	Propeller Agitator
Creosote Oil	H_2	89.30	81.40
Hydrogenated-Creosote Oil	H_2	96.25	95.71
50% Cresol/45% Tetralin/5% 9,10 Dihydroanthracene	H_2	97.40	93.82
(Ditto)	H_2	99.03	94.64
Hydrogenated-Creosote Oil	N_2	94.47	95.16
50% Cresol/45% Tetralin/5% 9,10 Dihydroanthracene	N_2	98.08	97.27

Reaction Conditions:

Temperature = 410^{o}C
Time = 15 min.
Stirring Speed = 1000 rpm
Solvent-to-Coal Ratio = 3:1
Type of Coal = Kentucky 9/14 Mixture

example, the rate of hydrogen consumption during liquefaction of coal solids in creosote oil remained essentially the same when the stirring rate was increased from 1000 to 2000 rpms.

Also, as shown in Table 1.B.1, the type of stirrer used had a significant effect on the rate of liquefaction. At first, this effect was assumed to be simply a sampling problem; but four batch reaction experiments, having final cresol soluble yields of about 0% (no reaction), 75%, 85%, and 95%, were performed, and for each experiment the percentage cresol solubles in the sample collected at reaction temperature at the end of the experiment was essentially the same as that of the remaining contents of the reactor after quenching to room temperature.

Based on the experimental results collected so far, then, agitation does appear to be of importance in dissolution. Its specific role in accelerating the dissolution of coal solids, although it must be related in some manner to mass transfer, has not yet been determined.

Planned Work: Further experiments shall be performed to evaluate the effect of agitation on the rate of dissolution. A technique has been developed for determining conversion based on an ash balance rather than on cresol solubles. The ash balance should be valid even if sampling problems do exist; therefore, it can be used to determine whether the observed effect of stirrer type on dissolution is an experimental artifact or a real effect. To do so, several batch reaction experiments shall be performed using a turbine and a propeller type of agitator, and the ash content of both a sample collected at reaction temperature and of the remaining autoclave contents shall be determined and compared.

Based on the above results for the Wyodak coal, since with no agitation it dissolves in a shrinking-core manner, initial particle size may indeed have a significant effect on reaction rates. Using this type of coal then, coal samples having significantly different initial particle sizes, as determined by the Coulter counter, shall be reacted in batch reactors, and variations in size distribution of residual particulates after a certain period of reaction shall be monitored using the Coulter counter.

1.C. Effect of Solvent Type and Gas Phase Composition on Particle Dissolution

Objective: The objective of this task is to study the dissolution behavior of the coals of Subtask 1.A as a function of solvent character; and to assess the relative roles of dissolved hydrogen versus donor hydrogen from solvent species in promoting particle dissolution.

Progress: As shown in Table 1.A.1, numerous batch reaction experiments were conducted to evaluate the effects of solvent composition on rate of dissolution of coal solids; for further details refer also to the discussion under Subtask 2.A. As was stated earlier, the degree and rate of liquefaction of coal solids was found to depend strongly on the concentration of hydrogen - donor species in the solvent. The rate of liquefaction was also shown to depend on the concentration of dissolved hydrogen gas; in fact, the rate controlling step in liquefaction was found to be the transfer of hydrogen to replenish hydrogen donor species. In addition, when the concentration of hydrogen donors in the solvent was low (e.g., as is true for creosote oil), the addition of a phenolic compound having a high solvating action caused an increase in the rate of liquefaction. For example, when cresol was added to an equal weight percentage of creosote oil, the amount of conversion of coal solids after fifteen minutes of reaction in a nitrogen atmosphere in the resulting cresol/creosote solvent was 26% higher than that resulting under the same reaction conditions except in creosote oil alone. When cresol was added to recycle solvent obtained from the Wilsonville SRC pilot plant, which has a much higher hydrogen donor concentration than creosote oil, the amount of conversion remained practically the same.

To allow quantification of the effect of hydrogen donor concentration on dissolution of coal solids, we have initiated an effort to improve our gas chromatographic (GC) procedure for analysis of liquid products in reaction mixtures. Considerable effort has been dedicated to evaluating different packing materials for the GC column, to determining response factors for different major constituents, and for developing a computer data logging and interpretation procedure. For example, we have almost completed the development of a computer routine for deconvoluting overlapping peaks in the GC output -- a necessary tool for GC analysis when complete separation of constituents cannot be achieved as is the case here.

Planned Work: The development of a better procedure for GC analysis of liquid products shall be completed or, at least, advanced to the stage that it can be used to support on-going studies. A series of batch reaction experiments in which different weight percentages of 9,10 dihydroanthracene (or some other known hydrogen donor species) is added to paraffin oil (or some other relatively inert solvent) shall be performed to further evaluate the effect of donor concentration on rate and degree of conversion. Also, the effect of phenolic addition (i.e., solvating action as opposed to hydrogen donor activity of the solvent) on conversion shall be further explored.

1.D. Direct Visual Observation of In-Situ Particle Dissolution

Objective: The objective of this task is to design, construct, and employ a sight glass apparatus suitable for direct visual observation of particle dissolution at temperature to a maximum of 450^{o}C and pressures to 1000 psig.

Progress: An apparatus has been designed and constructed to allow direct visual observation of particle dissolution at reaction temperatures. An overall schematic for the apparatus, or transparent wall microreactor, is given in

Figure 1.D.1. As stated earlier in the discussion under Subtask 1.A, the microreactor has proven to be very instrumental in studying the effect of coal and solvent type on particle dissolution. In fact, the transparent wall microreactor provides a useful tool for monitoring the activity of different solvents and coal feeds.

Planned Work: Dissolution studies shall be continued using the transparent wall microreactor. Its dependability as a tool for monitoring differences in activity between different types of coals and solvents shall be investigated more thoroughly. For example, duplicate experiments shall be performed using the Kentucky coal and a constant heat-up rate; and differences in dissolution temperature between different experiments shall be compared. Developmental efforts shall also be dedicated to improving the microreactor design and experimental technique so as to allow dissolution rate to be effectively measured. Attempts shall also be made to develop better sampling and sample preparation procedures.

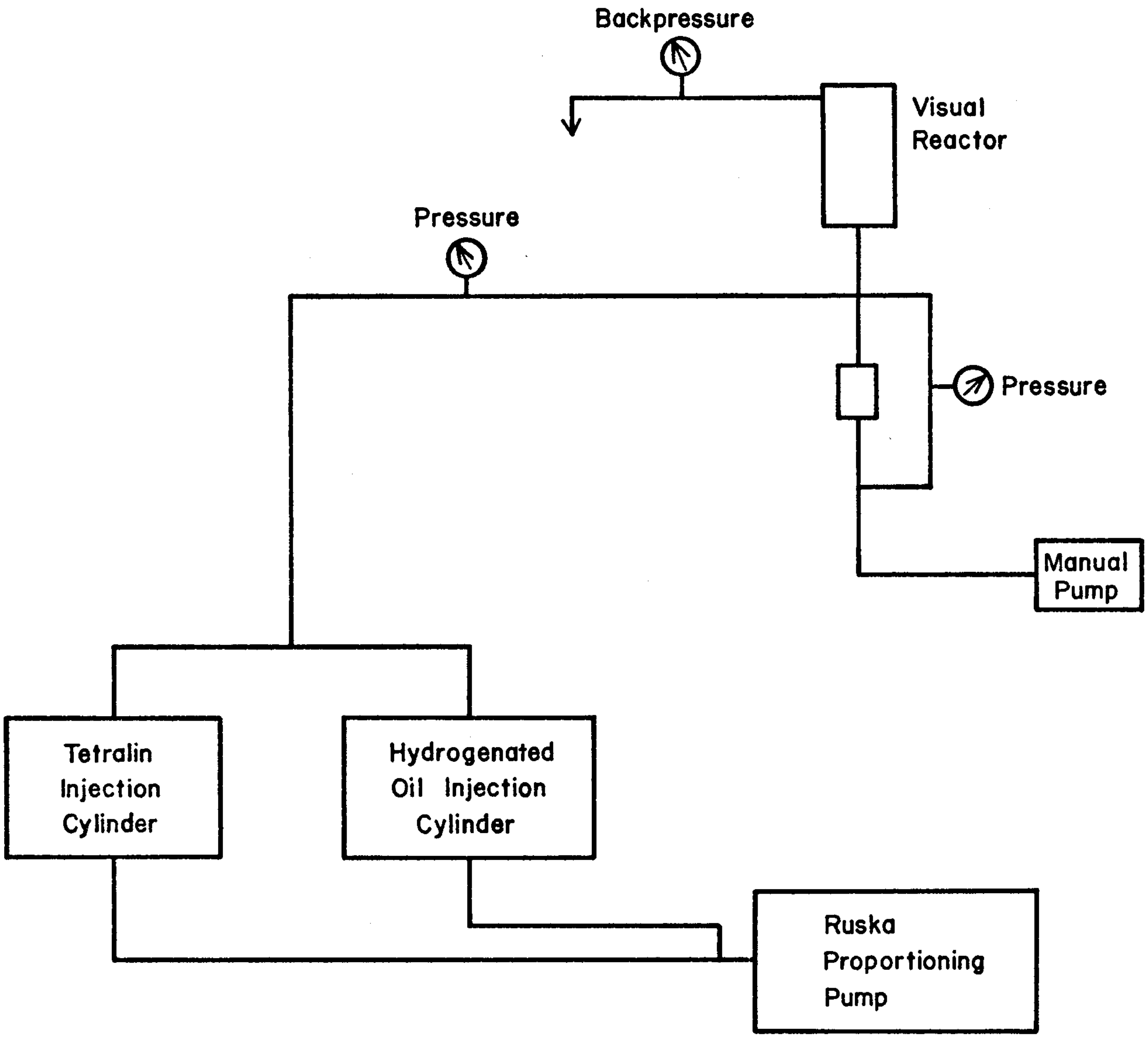
Subtask 1.E. Particle Structural Strength Evolution During Dissolution.

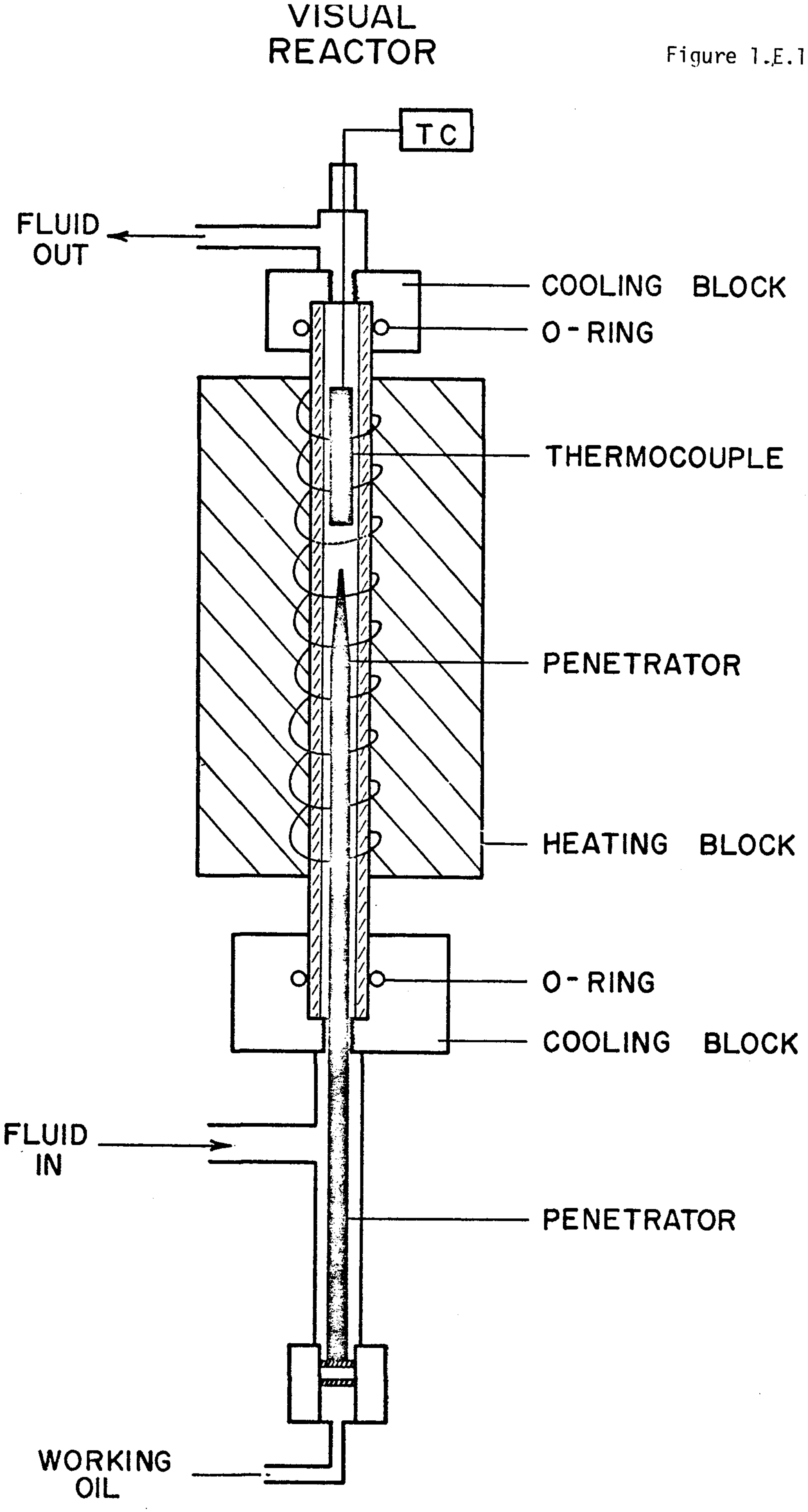
Objective: The objective of this task is to design, contruct, and employ a unique high pressure, high temperature penetrometer capable of allowing measurement of temporal evolution in particle structural strength during actual dissolution while submerged in solvent at pressures ranging up to 1000 psig and temperature at 450°C.

Progress: The transparent wall microreactor has been modified by adding a movable penetrator in the microreactor as shown in Figure 1.E.1. The penetrator is driven by a hydraulic system; by applying pressure to the working oil the piston end of the penetrator can be driven forward pressing the coal particle between the pentrator and the flat-surfaced thermocouple well. By monitoring the pressure on the working oil required to penetrate a particle, the

Figure 1.D.1

VISUAL REACTOR SYSTEM




VISUAL
REACTOR
Figure 1.E.1
TC
FLUID OUT
COOLING BLOCK
O-RING
THERMOCOUPLE
PENETRATOR
HEATING BLOCK
O-RING
COOLING BLOCK
FLUID IN
PENETRATOR
WORKING OIL

structural strength of a particle can be measured. As stated earlier in the discussion under Subtask 1.A, this appartus has been used to compare the structural strength of a Kentucky coal with that of a western sub-bituminous (Wyodak) coal. However, these two coals had a large difference in structural strength: the Kentucky coal was soft like chewing gum at reaction conditions; whereas the Wyodak coal was hard like table salt. And if the difference had not been large, the penetrometer would not have been capable of distinguishing the difference; for the pressure required to overcome inertia and initially displace the pentrator is significantly large, greatly limiting applicability of the existing penetrometer.

Planned Work: Developmental work on the design of the penetrometer shall continue, in search of a design that allows more sensitivity to differences in structural strength. Also, attempts shall be made to develop a procedure for monitoring the rate of penetration. One approach under consideration is the monitoring of the displacement of a marked point on the penetrator using a cathetometer.

1.F. Effect of Pretreatment on Dissolution Behavior

Objective: The objective of this subtask is to assess the effects of various oxidative and chemical pretreatments upon coal liquefaction.

Progress: During the quarter, experiments to determine the effect of oxidation upon coal conversion under SRC process conditions were initiated. Also, a literature review of various methods of coal oxidation was completed.

Planned Work: The oxidation experiments will be carried forward during the next quarter and results presented in the next quarterly progress report.

1. G. Slurry Viscosity During Particle Dissolution

Objective: The objective of this subtask is to investigate slurry viscosity changes occuring during the heat-up period of the coal/solvent slurry. Such viscosity variation is of importance to the design of preheaters for the SRC process feed slurry. In addition, viscosity is a major variable determining the flow regime, pressure, drop, and rate of heat transfer in the preheater tubes.

Progress: The initial approach to this problem during this quarter has been to monitor the torque on the stirrer shaft of the magnedrive batch autoclave during the heat-up period. In laminar flow, the stirrer torque is directly proportional to the fluid viscosity and hence provides a convenient indication of this variable. Unfortunately this method of measurement has been unsuccessful due to the large residual torque required to turn the magnedrive stirrer, even in the absence of any fluid in the autoclave. That is, the torque required to overcome stirrer friction in the bearings completely overshadowed any viscosity variations of the slurry itself. Although this might be alleviated to some degree by modification of the stirrer impeller, so as to produce a larger fluid drag, it is believed that a completely new approach to the problem is necessary.

Planned Work: Our attention is now focused on a method in which slurry samples will be withdrawn from the autoclave during heating and the viscosity of each sample measured externally with a Brookfield viscometer. A viscometer for this purpose has now been ordered and delivery is expected during the next quarter. The viscosity of each sample will be measured at several temperatures, the activation energy determined and from this, an expression for the viscosity at any temperature will be found. In addition, the Brookfield method provides a better indication of viscosity behavior than the torque reading, since it allows detection of non-Newtonian behavior, upon varying the shear rate of a truly viscometric flow.

Task 2. Reaction Kinetics and Process Variables Studies

Objective: The objective of this task is to conduct bench scale kinetics and process variables experiments using Wilsonville coals to (1) better understand SRC process chemistry (2) extend the range of variable space beyond the convenient limits of pilot plant operation and (3) obtain kinetics data which can be used to construct process design models.

2.A. Bench-Scale Batch Autoclave Experiments

Objective: The objective of this subtask is to perform batch autoclave experiments to determine the effects of temperature, hydrogen partial pressure, solvent/coal ratio, hydrogen/coal ratio, agitation rate, and reaction time upon such phenomena as coal conversion (yield), desulfurization, denitrogenation, and hydrogenation rate of vehicle/coal mixtures.

Progress: A considerable number of batch autoclave experiments were performed during the quarter. As a result of these experiments it has been possible to propose a preliminary overall mechanism for the solvent refining of coal. In addition, kinetic rate expressions have been developed for the conversion of Kentucky 9/14 coal in creosote oil with hydrogen atmosphere. This progress is reported in detail in the manuscript "Reaction Mechanisms and Coal Conversion Kinetics in the Solvent Refining of Coal" and is contained in the appendix of this report.

Planned Work: The batch autoclave experiments will continue next quarter using different recycle solvents and a different coal. The effect of hydrogen donor concentration on dissolution rate will be examined in detail. Additional kinetics experiments will be performed in batch tubing bombs for comparison with the results in the larger batch autoclaves currently used.

2.B. Bench Scale Continuous Reactor Experiments

Objective: The objective of this subtask is to better define the differences in SRC process performance which may occur because of differences in reactor designs, eg. stirred tank versus tubular reactor.

Progress: The continuous tubular reactor in the Auburn Laboratory was not operated during this quarter. It is believed that these experiments, because of their relatively high cost, will be more profitable being conducted after more data have been obtained under the batch conditions (Task 2.A.). This is because the batch data can be utilized to select better conditions for the continuous reactor runs. Even though no continuous reactor experiments were performed this quarter, a theoretical analysis of the continuous reactor system was made. This analysis is necessary to interpret and account for certain phenomena occurring in continuous reactor systems which do not appear in batch systems. For economic reasons, and ease of operation, continuous, rather than batch reactors will be used in large scale SRC processing. Thus, the SRC pilot plants at Wilsonville, Alabama, and Fort Lewis, Washington, both use continuous tubular reactors (dissolvers) and preheater tubes. Because of heat and mass transfer effects, and the complexities of three phase flow, it is difficult to extrapolate batch autoclave experiments to predict the performance of continuous reactors. Two factors which cause difficulty in the calculation of performance of tubular reactors are (1) the residence time of the liquid and (2) the extent of mixing in the liquid phase. In two-phase vertical tubular flow, such as in the Wilsonville and Fort Lewis dissolvers, the gas phase occupies a certain portion of the reactor, thus decreasing the liquid phase residence time as calculated on the basis of the total dissolver volume. Calculations based on literature correlations (1) indicate that roughly half of the dissolver volume would be occupied by the vapor phase and therefore the actual liquid phase residence time would be only about half of that calculated based on the total dissolver volume. Further calculations also based upon literature correlations (2) indicate that the reciprocal Peclet number for the liquid phase is greater than unity, which indicates that the tubular dissolvers actually approach well-mixed reactors in practice, rather than plug-flow behavior as might be expected from the reactor geometry. If one is willing to ignore mixing effects for the moment (an axial dispersion term can always be included later), then a mathematical model can be developed as follows:

If we define,

$C_{A,i}$ = concentration of A in phase i, g/cc

q_i = flow rate of phase i, cc/s

$r_{A,i}$ = homogeneous rate of appearence of A, per unit reactor volume, g/cc-s

V = reactor volume

f_i = fraction of reactor volume occupied by phase i

then a material balance over a differential reactor volume dV yields:

$$\frac{q_i}{f_i} \frac{dC_{A,i}}{dV} = r_{A,i} + \frac{\dot{M}_{A,i}}{f_i} \qquad (1)$$

Eq.(1) is valid for each phase i; however, the major difficulty is that f_i is generally unknown and must be determined from fluid mechanics considerations of multiphase flow. As noted above, calculations based on literature correlations indicate that $f_1 = f_2 = 0.5$ would obtain in the SRC reactor at the Wilsonville pilot plant.

As an example, eq. (1) may be applied to the hydrogenation reaction in the SRC process. In this case, if we let i = 1,2 represent the gas and liquid phases respectively, then we obtain, since $r_{A,1} = 0$ and $r_{A,2} = -kC_{A,2}$ (reference 3)

$$\frac{q_1}{1-f_2} \frac{dC_{A,1}}{dV} = \frac{-\dot{M}_{A,2}}{1-f_2} \tag{2}$$

$$\frac{q_2}{f_2} \frac{dC_{A,2}}{dV} = -kC_{A,2} + \frac{\dot{M}_{A,2}}{f_2} \tag{3}$$

In general, the mass transfer rate is

$$\dot{M}_{A,2} = k_1a \ (C_{A,1} - C_{A,2}) \tag{4}$$

where k_1a = transfer coefficient per unit volume, s^{-1}. For the liquefaction of coal, (species B), $r_{B,2} = -kC_BC_A^2$, (reference 4), and eq. (1) becomes:

$$\frac{q_2}{f_2} \frac{dC_B}{dV} = -kC_BC_A^2 \tag{5}$$

In principle, eqs. (2) - (5) may be solved simultaneously to yield the rates of coal conversion and hydrogenation in the SRC tubular continuous reactors. It is important to point out that while the rate functions $r_{A,2}$ and $r_{B,2}$ were obtained in batch autoclave experiments (see references 3 and 4) by virtue of the model developed herein they may be applied immediately to continuous tubular reactors.

Planned Work: The calculations begun here will be pushed further during the next quarter as part of a continuing effort to obtain more accurate modelling for the SRC process. Such models will aid greatly in the design and interpretation of the continuous reactor experiments as well as the pilot plant results and the future design and scale up to commercial plants.

2.C. Catalysis by Coal Mineral Matter

Objective: The objective of this subtask is to seek beneficial methods of utilizing coal mineral matter in the SRC and related processes.

Progress: As a result of work performed earlier in this laboratory (5), it was determined that certain coal minerals, particularly, those containing iron, evidenced a definite effect upon hydrogenation and hydrodesulfurization (HDS) of coal liquids. To pursue this further, a considerable amount of experimental work was performed during this quarter. The effects of adding iron in varying concentrations, and of H_2S partial pressure upon the HDS rate of coal liquids was investigated. In addition, kinetic rate expressions for the HDS of Kentucky 9/14 coal under SRC process conditions were determined. The complete evaluation and details of this work are reported in the manuscript "Hydrodesulfurization in the Solvent Refined Coal Process" contained in the appendix of this report.

Planned Work: The experiments to determine the feasibility of utilizing iron and/or coal minerals as a regenerable and/or inexpensive catalyst for HDS will be continued in the next quarter. To date, only coal liquids (without coal itself) have been employed. The next series of experiments will employ vehicle/coal mixtures and will investigate the feasibility of adding iron as an H_2S scavenger to the SRC dissolver stage to promote HDS. The selectivity of this agent with regard to hydrogenation versus HDS will also be determined.

Task 3: Development and Application of High Pressure Liquid Chromatography (HPLC) to Coal Liquids Analysis and Reaction Kinetics Studies

Objective: The objective of this task is to develop HPLC methodology for characterizing SRC process streams and to apply the resulting techniques to investigate reaction mechanisms and kinetics in coal liquefaction operations.

3.A. Development of HPLC Methodology

Objective: The objective of this subtask is to develop a satisfactory HPLC technique for the analysis and investigation of coal liquids and SRC products.

Progress: During this quarter, experiments to determine the solubility (g/ml) of five types of SRC furnished by Southern Services, are in progress. The types of SRC being used are given in Table 1. As can be seen from Table 1, the SRC's being studied are from various feed coals and are produced under conditions of varying degrees of conversion and hydrogen consumption. The solubility determination involves slurrying the SRC product with various solvents such as tetrahydrofuran, acetonitrile, dioxane, pyridine, acetone, etc., to produce a saturated solution at room temperature. Then, by centrifuging the solids and evaporating a 10 ml aliquot of the clarified solution the solubility is determined by weighing the dried residue.

For a satisfactory HPLC procedure, it is important to know two quantities: (1) the solubility of the material under study and (2) what fraction of the material is not soluble. Since SRC is not a pure compound, but a mixture of large organic molecules, it is necessary to determine what classes of compounds are not soluble in the solvents to be used

Table 1

SRC Types* Used in Solubility Studies

Type Coal	Total Pressure (psi)	Reaction Temperature	H_2 Consumption (MAF Coal)	Solvent/Coal Ratio	% Conversion (MAF Coal)
Ill. #6 Burning Star Mine	1700	824°F	3.5%	2/1	91.1
Amax (Wyodak)	2400	855°F	3.6%	4/1	78.7
Ill. #6 Monterrey Mine (10-14-75)	2400	855°F	2.8%	3/1	94.9
Pitt. #8	1700	855°F	2.5%	2/1	92.8%
W. Kentucky 9/14	1700	821°F	2.6%	3/1	-----

*All SRC's meet specifications for sulfur and ash.

in HPLC and gel permeation chromatography.

Planned Work: The solubility determinations will be continued next quarter in order to find a satisfactory solvent for HPLC analysis of SRC product. After this, the effect of several process variables, including conversion, feed coal and hydrogen consumption, on molecular size distributions in the SRC products will be determined. The purpose of this study is to correlate hydrogen consumption and molecular size in the SRC product in order to provide a method for SRC quality control.

3.B. Characterization of Coal Liquefaction Products

Objective: The objective of this task is to develop hardware and software packages for the on-line qualitative and quantitative analysis of coal liquids.

Progress: With respect to the HPLC analytical method, a software package has been developed on the IBM 370 and is now waiting for memory expansion in the PDP-11/40 for implimentation. The logic behind this package is essentially as follows. In order to obtain accurate areas for the chromatogram produced by HPLC, it is necessary to remove the effects of overlapping peaks. This effort requires the use of a digital computer to deconvolute the chromatograms. There is a large body of literature suggesting ways to accomplish this task.

Various authors have presented model functions (Gaussian, skewed Gaussian, etc.) to describe one chromatographic peak. If an adequate functional representation of the chromatographic peak may be found, then the deconvolution scheme requires the simultaneous determination of a set of parameters to best fit the data.

Our work has shown that the liquid chromotographic peaks may be adequately described by a Gaussian function, which for one peak is given by the following equation:

$$Y(t) = Yo \text{ EXP } (-4 \ln (2) \{\frac{t-to}{w}\}^2) \tag{1}$$

where $Y(t)$ = peak height

Yo = maximum height

t = elution time

t_0 = the centroid

w = full width at half height

Figure 1 presents graphically this relationship.

For a generalized chromatogram which may be represented by the sum of Gaussian peaks, the height at any time may be represented by the following equation:

$$Y(t) = \sum_{i=1}^{N} Y_{o(i)} \text{ EXP } (-4 \ln (2) \{\frac{t-toi}{w_i}\}^2) \tag{2}$$

where N = number of peaks

The area of a given Gaussian peak is given by the expression:

$$\text{Area} = 1/2 \left(\frac{\pi}{\ln 2}\right)^{\frac{1}{2}} Y_o w \tag{3}$$

The software developed at this time will correct the chromatogram for base line offset and linear drift, deconvolute and integrate overlapped or fused peaks and output the appropriate parameters describing each resolved peak. Table 2 gives a comparison between the areas for single peaks obtained with a planimeter and by computer intergration. Table 2 also shows the same comparison for a section of fused peaks (see Figure 2) (with total area obtained with a planimeter) compared to the sum of the areas obtained by computer deconvolution and integration. In each case, the compu-

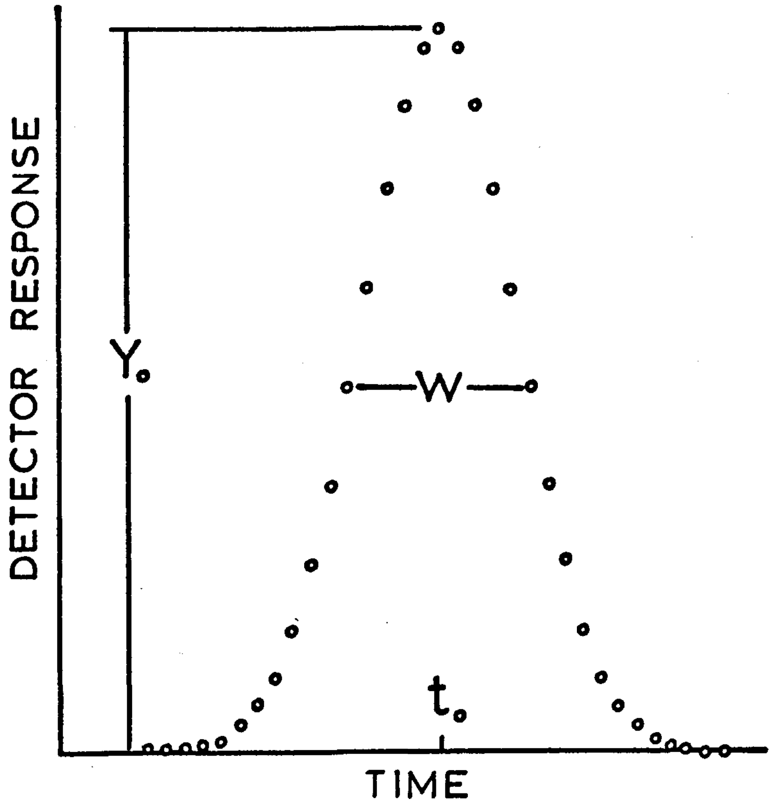


FIGURE 1

Table 2

Comparison of Computer and Planimeter Integration

Technique	A (in^2)	B (in^2)
Computer	2.08	6.16
Planimeter	2.00	6.20

A. Average of five Chromatographic peaks

B. Comparison of sum of deconvoluted areas by computer to total area of fused peaks by planimeter

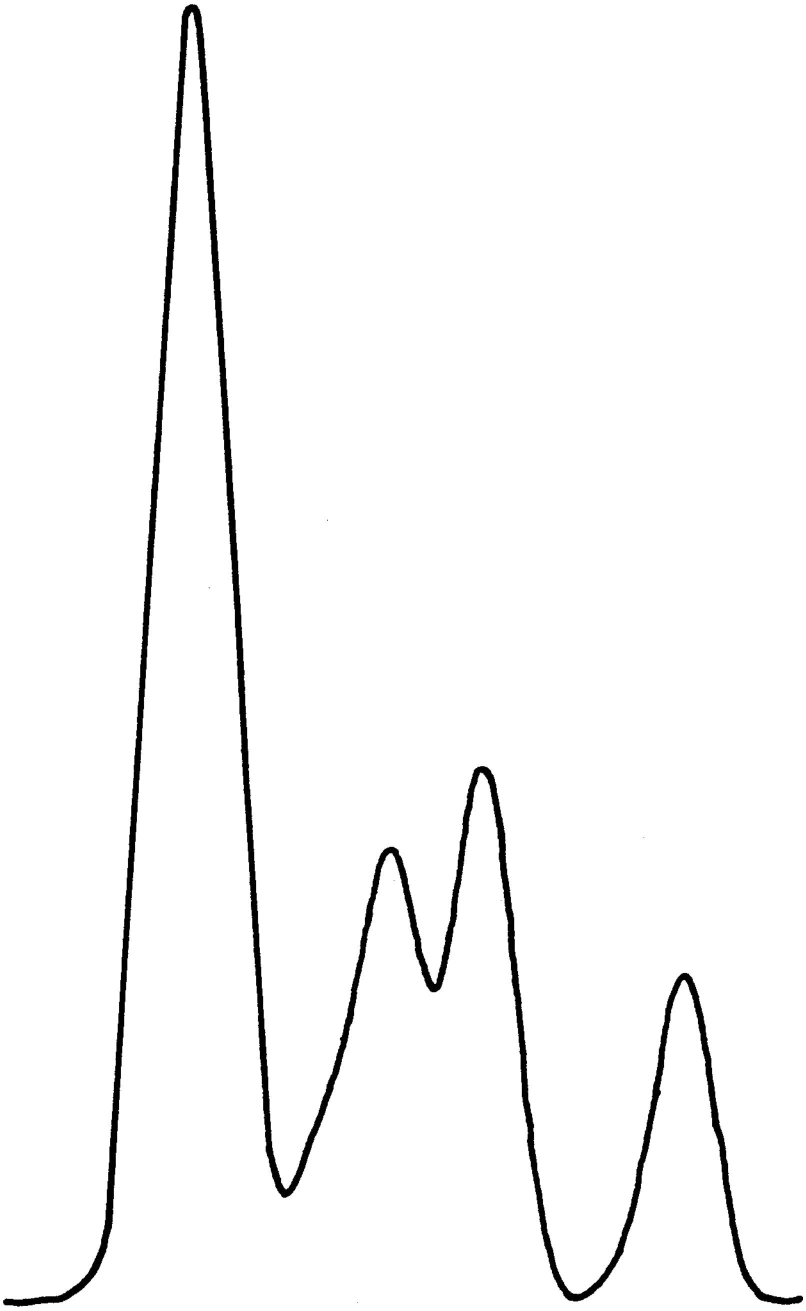


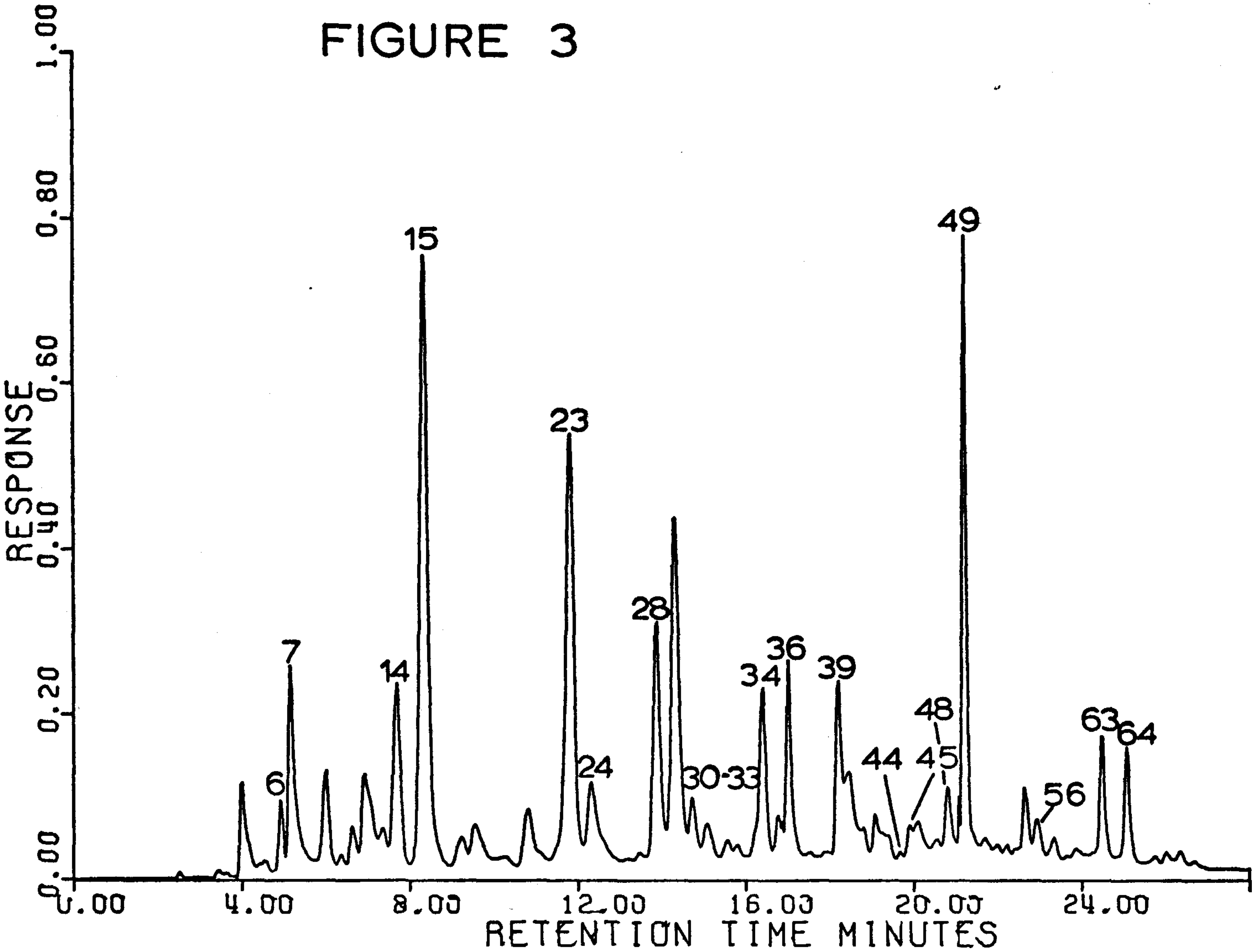
FIGURE 2. FUSED PEAKS

terized deconvolution method yields an accurate value for peak area. After the peak areas are determined, the concentration of each component in the coal liquid may be calcuated by using an appropriate response factor.

In addition to the computerized HPLC, we have also begun the development of a gas chromatography method using a PDP 11/40 computer with an industrial control subsystem. The PDP 11/40 accepts low level, differential signals, amplifies and filters them, and stores the data on the mass storage system. The data is outputed, key punched and run through a spectral processing routine written for the project. The spectral processing routine performs the necessary smoothing and differentiation of the data, and locates significant peaks and shoulders for a complex chromatogram. Figure 3 shows a chromatogram of SRC recycle solvent, with the numbers indicating peaks found by the peakfind program. Table 3 shows compounds presently identified in this chromatogram.

The spectral processing program has a routine to integrate the peaks in the chromatogram. This routine performs a simultaneous, nonlinear regression fit of Gaussian functions, one for each peak or shoulder found by the peak location routine, to the entire gas chromatographic spectrum. The deconvolution routine uses Marquardt's algorithm, which is more stable than the Gauss-Newton methods used by other programs. The routine outputs the final peak parameters, which are: (1) maximum amplitude (2) full width at half height (3) retention time (4) corrected peak area. As in the HPLC method, the concentration may be found from the peak area for each component.

FIGURE 3



RESPONSE
0.00
0.20
0.40
0.60
0.80
1.00
0.00
4.00
8.00
12.00
16.00
20.00
24.00
RETENTION TIME MINUTES
6
7
14
15
23
24
28
30-33
34
36
39
44
45
48
49
56
63
64

Table 3

Compounds Identified in SRC Recycle Solvent

Peak No.	
6	Para-Cresol
7	Ortho, meta-Cresols
14	Tetralin
15	Napthalene
23	2-methyl Naphthalene
24	1-methyl Napthalene
28	Biphenyl
30-33	Isomers of dimethyl Napthalene
34	Acenapthene
36	Dibenzofuran
39	Fluorene
44	9,10 Dihydroanthracene
45	9,10 Dihydrophenanthrene
48	Dibenzothiophene
49	Phenanthrene
56	2-methyl Carbazole
63	Fluoranthene
64	Pyrene

Planned Work: The identification of additional compounds in SRC recycle solvents and other coal liquids will be continued. Additional response factors will be obtained to further quantitate the chromatographic results. Attempts will be made to use digital standard shape functions to describe non-Gaussian chromatographic peaks.

3.C. Application: Reaction Kinetics and Process Variables Studies

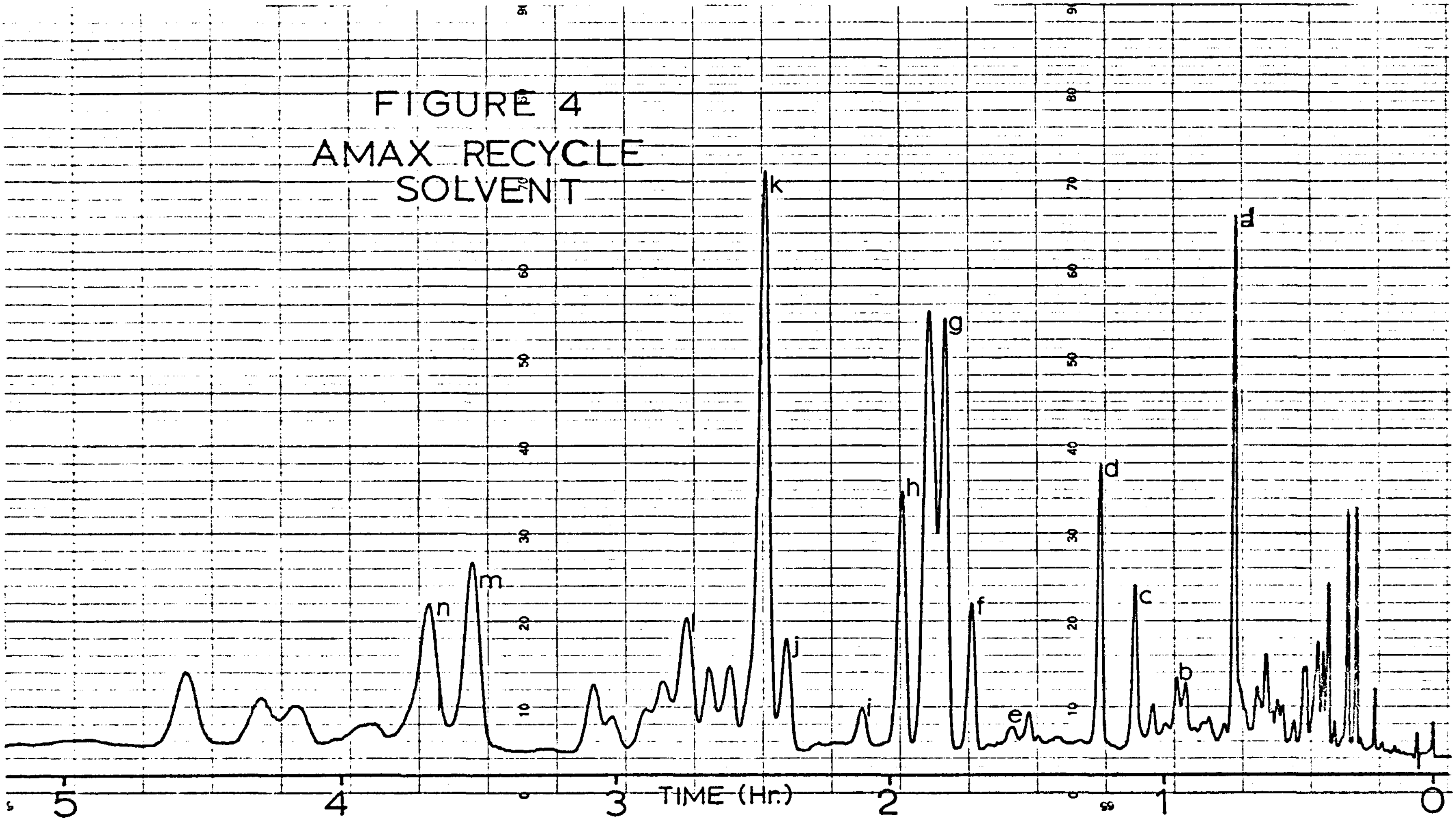
Objective: The objective of this subtask is to apply the analytical methods developed in 3.A. and 3.B. to obtain information concerning reaction kinetics and effects of process variables on specific fractions and compounds present during coal liquefaction.

Progress: Experiments to determine the effect of one process variable, namely feed coal on the composition of the recycle solvent are underway and results on eleven compounds are presented in Table 4. Figures 4-6 show the actual chromatograms for three of the recycle solvents. It is evident from the chromatograms and Table 4 that changes in feed coal do create changes in the recycle solvent, as is shown particularly in the case of naphthalene and 2-methylnaphthalene. These two compounds are interesting since they are involved in the naphthalene-tetralin hydrogen donor system. The concentration of another compound of interest, dibenzothiophene, is not significantly changed in the recycle stream by varying feed coal. The same is true for several of the compounds in Table 4. However, the chromatograms shown in Figures 4-6 do indicate that certain unidentified (as yet) compounds, between 0 and 1 hours and between 4 and 5 hours, are changing in concentration both with respect to the start-up solvent and with varying feed coal. The compounds that elute in the first half hour are polar compounds with low molecular weight. Some of these compounds have recently been tenatively identified as cresols, phenol and indols.

Key To Compounds Identified in Figures 4-6

a	benzofuran (internal standard)
b	naphthonitriles
c	carbazole
d	naphthalene
e	2-methylcarbazole
f	1-methylnaphthalene
g	2-methylnapthalene
h	acenapthene
i	fluorene
j	dibenzothiophene
k	phenanthrene
l	anthracene
m	fluoranthene
n	pyrene

FIGURE 4
AMAX RECYCLE
SOLVENT



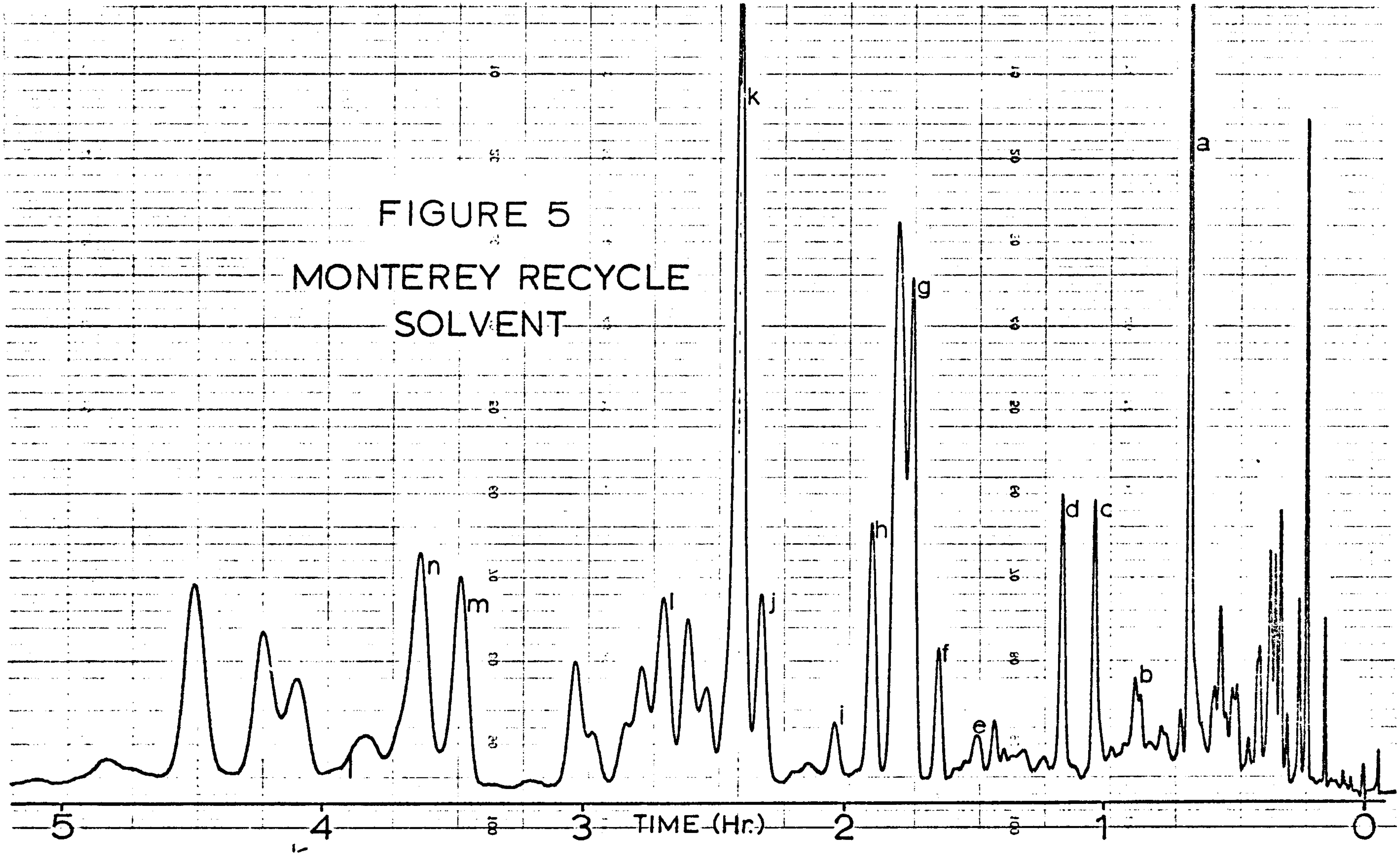


FIGURE 5

MONTEREY RECYCLE SOLVENT

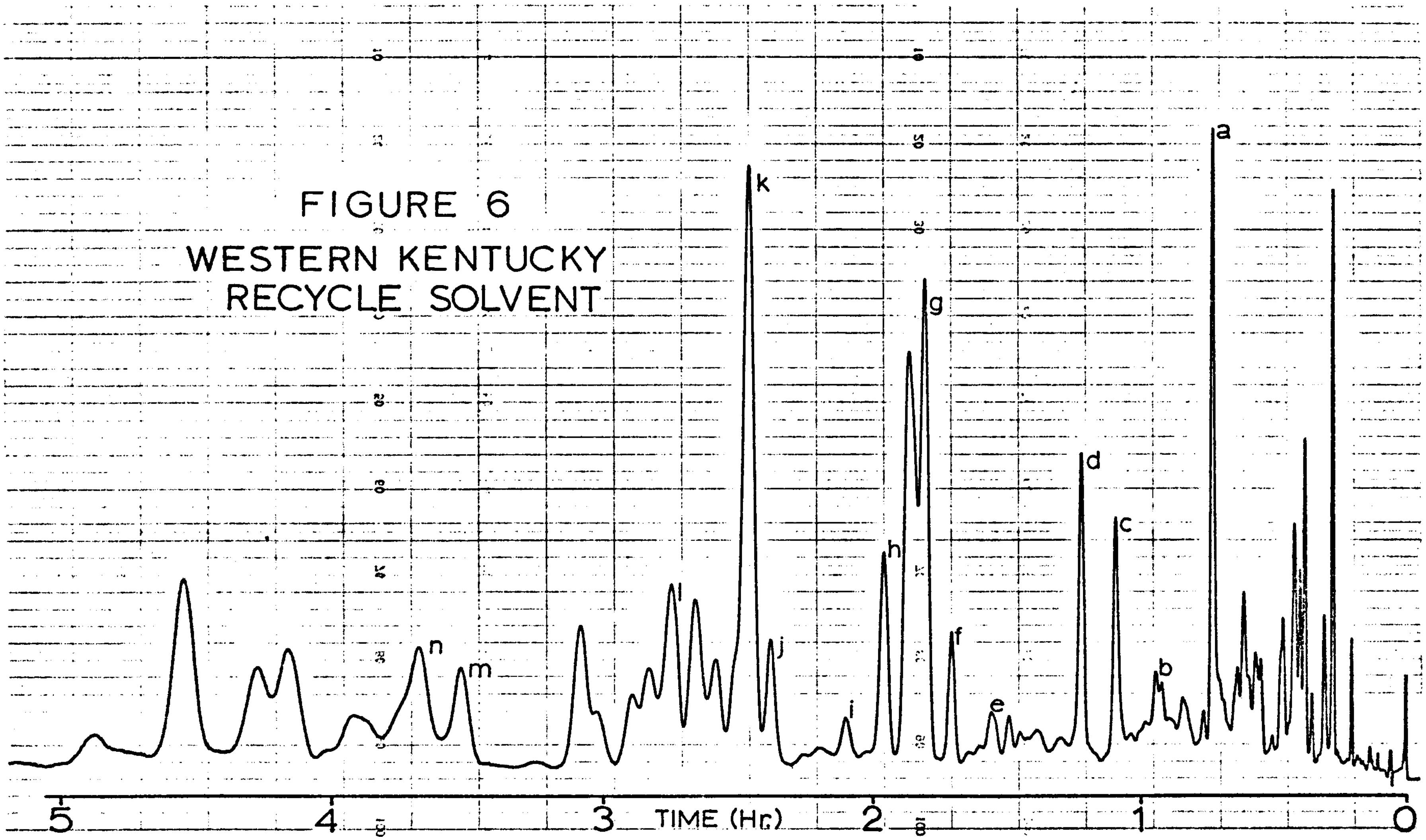


FIGURE 6
WESTERN KENTUCKY RECYCLE SOLVENT

Table 4

HPLC Analysis of Recycle Solvents

	Weight %					
Compound	A	B	C	D	E	F
naphthenitriles	0.611	0.731	0.072	0.137	0.095	0.080
carbazole	0.423	0.266	0.421	0.403	0.412	0.384
naphthalene	8.92	5.48	9.29	10.47	6.38	9.03
2-methylcarbazole	0.106	0.032	0.087	0.083	0.903	0.133
1-methylnaphthalene	5.23	1.83	2.00	3.23	1.93	2.24
2-methlnaphthalene	8.00	6.05	9.86	12.41	8.38	7.54
acenaphthene	6.28	1.18	1.00	1.38	1.00	1.03
fluorene	5.22	1.91	2.45	2.24	2.72	2.49
dibenzothiophene	1.27	0.344	0.529	0.426	0.570	0.526
phenanthrene	12.40	4.28	7.04	6.92	6.36	6.48
anthracene	1.86	1.30	1.58	1.14	1.30	1.29
TOTAL	50.32	23.40	34.33	38.84	30.05	31.22

A. Start-up solvent (allied Chemical 2Δ-CB Cresote Oil)
B. Western Kentucky recycle solvent
C. Pittsburg seam recycle solvent
D. Amax recycle solvent
E. Monterrey (10-75) recycle solvent
F. Monterrey (8-75) recycle solvent

These compounds are interesting as they are very good solvents for SRC products; in fact, some of the highest yields obtained in our autoclave studies were accomplished using an "artificial" solvent that contained cresol isomers as its major constituents. The start-up solvent contains little or no cresol and it appears that this may be one factor causing the lower coal conversions obtained with creosote oil as compared to that with a steady state recycle solvent.

Planned Work: In the next research period, work will be continued toward the positive identification of the "cresols" and the performance of quantitative HPLC analysis on these compounds. Also planned in the next period of research are studies on the reaction products obtained using various amounts of coal minerals, particularly iron, to catalyze desulfurization of SRC recycle solvents.

CONCLUSIONS

1. Under the same conditions, the dissolution behavior of Kentucky coal is significantly different from that of Wyodak coal.
2. The particle size distribution during dissolution is different for Kentucky and Wyodak coals as determined by the Coulter counter.
3. Agitation is important in promoting particle break-up prior to and during dissolution.
4. The rate of coal liquefaction is dependent upon hydrogen donor content of the solvent.
5. The Coulter counter provides a viable technique for coal particle size analysis in the SRC process.
6. Coal conversion may be modeled with homogeneous reaction rate expressions, second order in dissolved hydrogen concentration and first-order in undissolved coal concentration.
7. The continuous SRC reactor is subject to considerable axial dispersion in the liquid phase and has a large gas phase holdup.
8. Coal minerals containing iron promote hydrodesulfurization while H_2S partial pressures retard the same.
9. High pressure liquid chromatography and gas chromatography indicate significant differences in steady state recycle solvents from the Wilsonville SRC pilot plant.

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APPENDIX

REACTION MECHANISMS AND COAL CONVERSION KINETICS IN THE SOLVENT REFINING OF COAL

J. A. Guin

A. R. Tarrer

W. S. Pitts

Coal Conversion Laboratory
Department of Chemical Engineering
Auburn University
Auburn, Alabama

Presented at the ACS Southeastern Regional Meeting,
Gatlinburg, Tennessee, October 27-29, 1976

Mechanism of Solvent Refining

The mechanism of the solvent refining of coal is incompletely understood at this time; however, it is believed to proceed roughly along the path depicted in Figure 1. In step (1), as coal is heated to approximately 400°C, a pyrolytic deploymerization reaction occurs whereby free radicals are created. These free radicals may be terminated to yield smaller, stable products, or they may recombine to form larger, more refractory products. It is thought that the radicals are largely stabilized by the abstraction of hydrogen atoms donated from polynuclear hydroaromatic compounds present in the donor solvent via step (2). In addition, some of the radicals may be terminated by cleavage of diatomic hydrogen molecules as depicted by step (3), although this is believed to be a minor pathway for radical stabilization (1). Finally, some radicals, particularly in the initial stages of depolymerization, may be stabilized by autogenous transfer of hydrogen (2). Since the majority of radicals are stabilized through the abstraction of donor solvent hydrogen via path (2), it is felt that the primary role of hydrogen gas in the process is the replenishment of the donor solvent by step (4). This step has been confirmed to be catalyzed by the action of certain minerals, indigenous to coal (3). It is also possible that the coal minerals act to a lesser degree in promoting step (3). However, at this time it is thought that the primary role of coal mineral matter, in a catalytic sense, is to accelerate the rehydrogenation of the donor solvent. Of course, there is some overlap here since the solvent is inevitably derived from the coal itself and the dividing line between SRC and the recycle solvent is somewhat arbitrary in that it depends upon process conditions, rather than precise chemical compositions.

Coal Conversion Kinetics

The actual dissolution of coal appears to occur very rapidly (1,2,4) under the proper conditions. However, from the standpoint of the SRC process, it is also necessary to achieve the required amount of desulfurization and to generate enough solvent of the proper quality to maintain a balanced continuing process. These latter two requirements may dictate longer dissolver residence times than would be predicated solely by the requirement of coal dissolution. Considering only the dissolution reaction at this time, considerable previous work has been performed in efforts to develop kinetic expressions for the rate of coal liquefaction. Several models have been proposed which suggest a series decomposition of coal into various products. Lienberg and Potgieter (6) proposed a scheme for uncatalyzed dissolution of coal in tetralin. Hill, et al, (7) also studied the uncatalyzed dissolution of coal in tetralin. They proposed a series type reaction scheme, where the products from one reaction form the reactants for the next. Wiser (8) stated that,during the thermal decomposition of coal, free radicals were generated from the rupture of the covalent bonds in the coal structure. He noted that the free radicals thus formed are highly reactive and seek stabilization. This method of decomposition is in agreement with the mechanism illustrated earlier in Figure 1. A model employing two fractions of coal, with varying degrees of reactivity, has been proposed by Curran, et al. (15). A model of this type is used to interpret some batch autoclave experiments performed during this work. It has been noted by Hill, et al. (7) that coal has a porous structure. Spitzer and Ulicky, using small angle X-ray scattering and methanol absorption determined the specific surfaces of several coals (9). For an Illinois #6 coal, the specific surface was determined to be 175 m^2/g. By assuming a particle density of 1.3 $grams/cm^3$ it may easily be shown that the external surface for spherical particles 325 mesh and 35 mesh is $0.11 m^2/gram$ and $0.009\ m^2/gram$ respectively. It is obvious, therefore, that more of the free surface and hence reactive sites of the coal particles are in the interior. However, in spite of this it has been reported by several investigators (2,5) that the initial coal particle size has little effect on the rate of dissolution, and thus, homogeneous reaction rate expressions have been used in modeling coal conversion kinetics. The presence of mass transfer effects has not been adequately demonstrated at this time.

In this work, it is suggested that perhaps the most critical period of the liquefaction phase is during the thermal rupture of the bonds in the coal particle (step (1) in Figure 1). When the coal bonds rupture it is important to have a high concentration of dissolved hydrogen and hydrogen donating species in the interior of the coal particle in order to stabilize the free radicals generated. In other words, the particle size or solvent/coal ratio is not critical but, rather, the hydrogen donor concentration in the pores of the coal particle. This idea is partially supported by Neavel (2) who shows negligible influence of particle size less than 2-3 mm (5 mesh) on liquefaction of coal in tetralin.

To investigate the rate of coal liquefaction, batch autoclave experiments were conducted in this work. The experimental conditions are reported in Table 1. The coal conversion was found to depend upon the hydrogen partial pressure which decreases with time in the batch autoclave. Therefore, it was necessary to incorporate a term accounting for this in the kinetic rate expression. The dissolved hydrogen concentration was found to follow first order kinetics given by: (see reference 10)

$$\frac{C_H}{C_{HO}} = \exp\{-\alpha k_L t\} \qquad (1)$$

The rate of coal conversion (cresol solubles) was found to be adequately modeled by two parallel reactions incorporating two different coal species each with different rates of dissolution. The rate expression for the disappearence of species i was determined to be:

$$r_i = k_i\ C_i\ C_H^{\ 2} \qquad i = 1,2 \qquad (2)$$

with

$$k_i = k_{io} \exp \left[- \frac{\Delta E_i}{RT} \right] \qquad i = 1,2 \qquad (3)$$

The ratio of the two coal species at time zero was $C_{20}/C_{10} = 0.77$ and the parameters for equation (3) are given in Table 2. Using this model the conversion is given by solution of the batch material balance (with equations (1) and (2)):

$$\frac{dC_i}{dt} = -r_i \qquad i = 1,2 \qquad (4)$$

The conversion is defined as:

$$\text{Conversion} = 100 \left[1 - \frac{C_1 + C_2}{C_{10} + C_{20}} \right] \qquad (5)$$

In equations (2) - (5) the following notation is used:

$C_{1,2}$	Concentration coal specie, grams/cc
k_1	Third order rate constant, $cc^2/grams^2$-min
k_2	Third order rate constant, $cc^2/grams^2$-min
k_{10}	Arrhenius pre-exponential factor, $cc^2/grams^2$-min
k_{20}	Arrhenius pre-exponential factor, $cc^2/grams^2$-min
ΔE_1	Activation energy, Kcal
ΔE_2	Activation energy, Kcal
T	Absolute reaction temperature, ^oK
C_H	Dissolved hydrogen, grams/cc
t	Time, minutes

The experimental conversion data are compared with the expression in equation (2) as shown in Figures 2, 3, and 4. The fit is satisfactory, except at 435^{o}C (Figure 4) where the actual conversion is below the predicted valve. This is thought to be caused by coke formation - - note that the solvent, creosote oil, is not a good hydrogen donor. This coke formation would probably not occur with a steady state recycle solvent containing a sufficient amount of hydrogen donor species. Experiments are now in progress to study the effect of hydrogen donor concentration on coal conversion (yield) in a quantitative manner.

Conclusion

Available evidence indicates that the mechanism of SRC production involves the pyrolytic generation of coal free radicals, which are terminated by hydrogen abstraction from donor solvent species. Coal mineral matter can act to increase the rates of hydrogenation and desulfurization of the solvent species, and it is possible that this property may be used to advantage in future process flowsheets.

The kinetics of coal conversion are complex and depend upon temperature, hydrogen pressure, solvent and coal type, etc., as illustrated by the data presented herein. For kinetic rate expressions of the type presented herein, mixing in the reactor would decrease the extent of coal conversion. Examination of literature correlations indicates that the currently used SRC dissolvers operate essentially in well-mixed states, which would reduce coal conversion when compared to plug-flow behavior. Thus, the reactor geometry should be considered a significant variable in the design of SRC plants.

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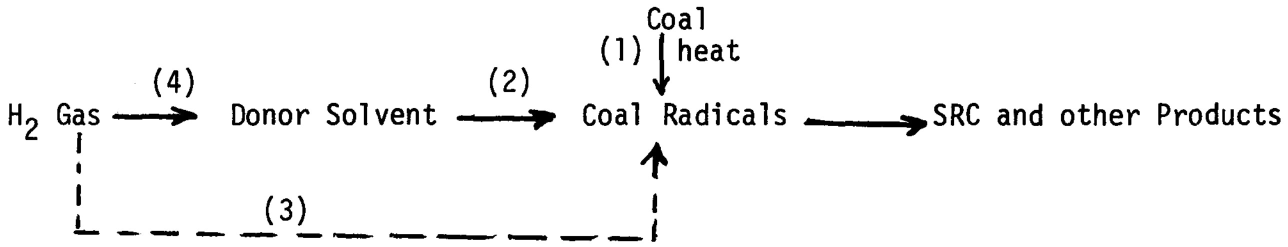

Figure 1. Mechanism of Solvent Refining

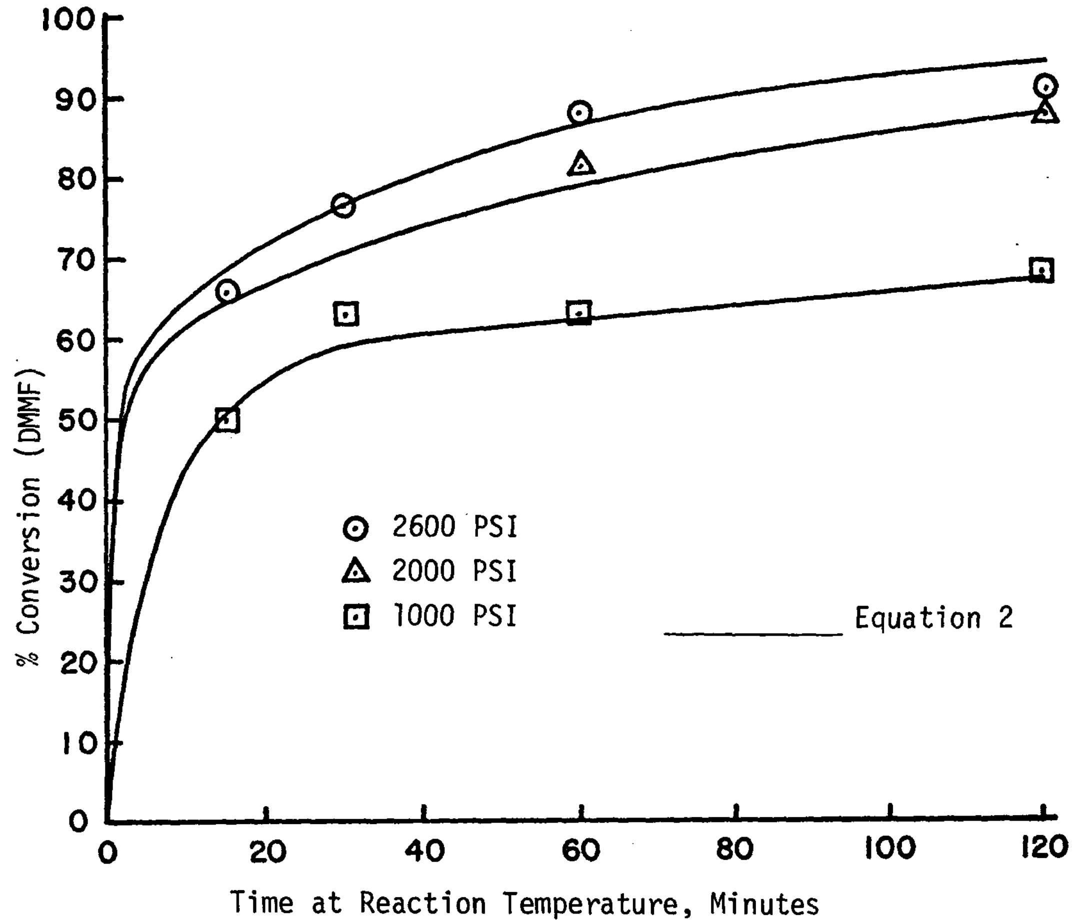

Figure 2. Actual and Predicted Conversion at 385°C.

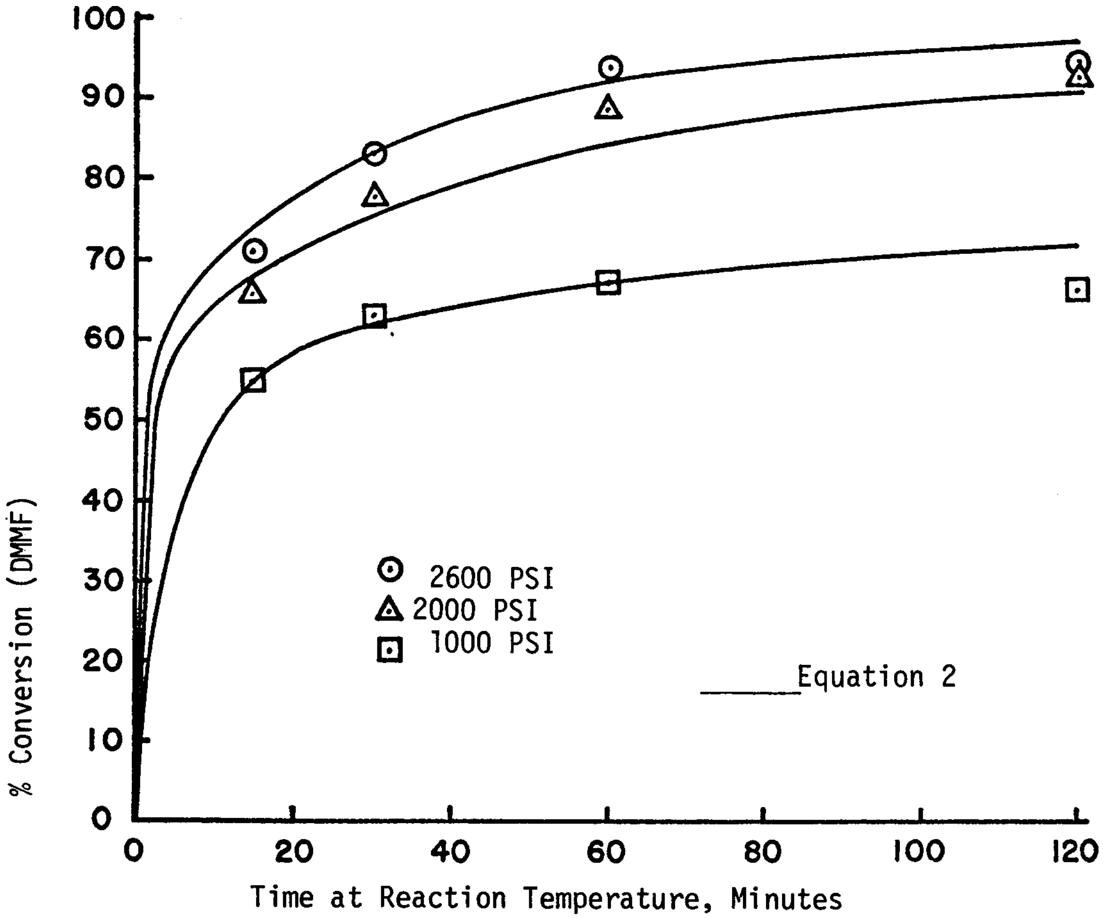

Figure 3. Actual and Predicted Conversion at 410^{o}C.

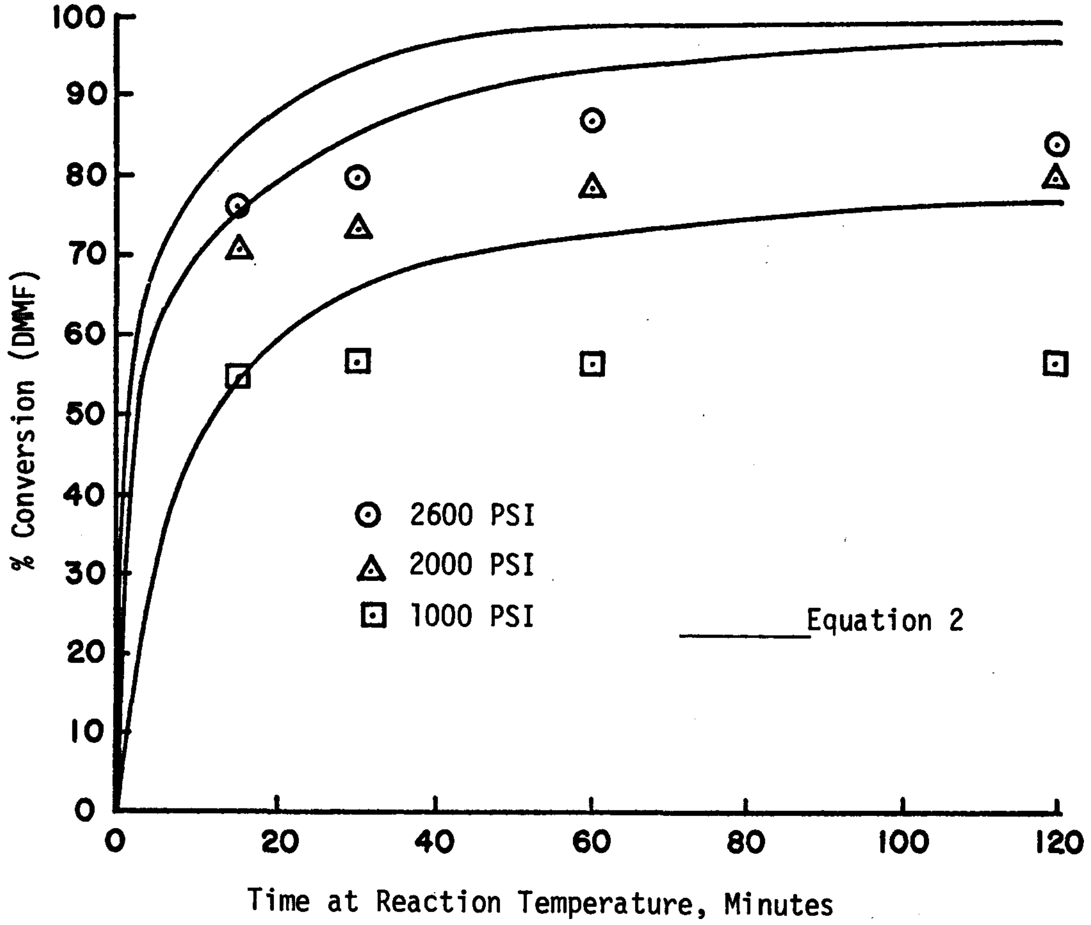

Figure 4. Actual and Predicted Conversion at 435°C.

HYDRODESULFURIZATION IN THE SOLVENT REFINED COAL PROCESS

W. S. Pitts
A. R. Tarrer
J. A. Guin
J. W. Prather

Coal Conversion Laboratory
Auburn University
Auburn, AL 36830

The Solvent Refined Coal (SRC) process is currently recognized as one of the more promising processes for producing an environmentally acceptable boiler fuel from coal. In the SRC process, coal is liquefied to allow removal of entrained mineral matter by physical separation methods and reacted with hydrogen to remove chemically part of its organic sulfur. Liquefaction of coal has been shown to occur almost instantaneously upon reaching reaction temperatures while in the presence of a hydrogen-donor solvent, the overall rate limiting step in liquefaction being rehydrogenation of process solvent - which may be performed separately in the recycle stream - to replenish hydrogen-donor species (1,2). Based on data collected in this laboratory hydrodesulfurization (HDS) of coal, on the other hand, appears to be a much slower reaction. As a result, the kinetics of HDS will be a primary, if not the controlling factor in the design and operation of the dissolver/reactor in the SRC process.

In the present work, an experimental evaluation is made of the feasibility for accelerating HDS of coal by simply varying reaction conditions and utilizing coal mineral matter and/or other cheap regenerable catalysts. The rate data reported were all obtained in a batch system; and, except for one series of experiments, only one coal type, a bituminous Kentucky No. 9/14, was used. Experimental methods and materials are given in (2), except as noted herein. A reaction model was developed that gives an excellent fit to the experimental data. The model, as well as other results of the comparative studies performed, is intended to assist in predicting and interpreting results from pilot studies of the SRC process, such as those at Wilsonville, Alabama, and Tacoma, Washington. The model provides also a useful design tool; but, for a reaction system as complex as the one dealt with here, it would be presumptuous to suggest that it represents the true mechanism.

In a previously reported catalyst screening study (5), several minerals indigenous to coal were shown to have a catalytic effect on the HDS of creosote oil. Of particular interest was the observation that in the presence of reduced metallic iron the HDS rate of the oil was significantly higher than that resulting when no mineral was present; whereas, in the presence of pyrite the HDS rate was about the same as it was when no mineral was present. These observations were surprising in that both reduced iron and pyrite are converted into the sulfide form (pyrrhotite) within the first fifteen to twenty minutes of reaction. Based on these observations, to further examine the practicality of coal mineral catalysis, a series of experiments was performed to ascertain whether the acceleration of the HDS rate in the presence of iron was predominantly thermodynamic or catalytic in nature. It is possible that iron, by removing H_2S, promotes HDS by Le Chatelier's principle, or simply prevents the H_2S from reducing the activity of catalytic sulfides by preferential adsorption.

Basic Nature of Reactions

The influent coal/oil slurry to the reactor/dissolver in the SRC process includes a wide variety of sulfur-containing compounds; thiols, disulfides, sulfides, thiolethers, y-thiopyrone, thiophenes, dibenzothiophenes, and other heterocyclic sulfur compounds. In general, thiols, disulfides, sulfides, thiolethers, and y-thiopyrone are very reactive - undergoing hydrogenolysis at an appreciable rate, forming H_2S and hydrogenated compounds, without the aid of a catalyst; whereas, heterocyclic sulfur compounds are much less reactive - requiring a catalyst to achieve an acceptable HDS rate. As a result of the large difference in reactivity of these two groups of sulfur-containing compounds and to simplify analysis, the HDS reactions involving individual compounds in each of these two groups sometimes are lumped together; and HDS of a coal/oil slurry is often treated as if there were only two reactive compounds (3,4).

In addition to HDS reactions, under reaction conditions used in the SRC process, hydrocracking (i.e., breaking of C-C bonds) and hydrogenation reactions also occur. It is by means of these reactions - particularly cracking reactions - that coal solids are converted into lower molecular weight components that are soluble in SRC process solvent, allowing removal of entrained mineral matter by subsequent physical separation methods. These reactions take on importance, other than liquefaction of coal solids, by consuming hydrogen in the process without removing sulfur. Only that amount of hydrogenation, or cracking, required to liquefy coal solids and allow mineral matter removal is desired. Any excess hydrogenation beyond this amount, such as in the formation of C_1 - C_4 gases, etc., results in inefficient use of hydrogen, thus higher operating costs. This should be avoided as much as possible. Actually SRC product contains a slightly lower hydrogen/carbon ratio (H/C = 0.75) than the feed coal itself (H/C = 0.8). Furthermore, the stoichiometric amount of hydrogen required solely for removal of an acceptable amount of sulfur as H_2S in the SRC process is an order-of-magnitude less than the total amount of hydrogen currently consumed (two weight per cent of MAF coal feed) at the Wilsonville, Alabama, and the Tacoma, Washington, SRC pilot plants. Excess hydrogenation therefore accounts for most of the hydrogen consumed in producing solvent refined coal.

The rate of noncatalytic (except for mineral matter) HDS, unlike that of hydrogenation, appears to be relatively insensitive to hydrogen concentration, in the form of either dissolved molecular hydrogen or readily transferable hydrogen such as that attached to donor species (e.g., tetralin) contained in the process solvent. Variation, for example, in initial hydrogen partial pressure from 1000 to 2600 psig at reaction temperature had no significant effect on the final organic sulfur content of a coal/creosote-oil reaction mixture, even after two hours of reaction (Table 1). Also, as shown in Table 2, the reduction in total sulfur content of the coal was essentially the same after fifteen minutes of reaction when slurried with creosote oil - which contained only trace amounts of tetralin and other known hydrogen-donor species - as when slurried with pre-hydrogenated creosote oil - which, like the SRC recycle oil used, contained significant amounts of tetralin and 9,10 dihydrophenanthrene. The rate of liquefaction, on the other hand, was significantly higher when the coal was extracted in prehydrogenated creosote oil. When reacted in an inert nitrogen atmosphere, the cresol-soluble yield was almost twice that obtained when the coal was extracted with untreated oil. The high sensitivity of the rate of liquefaction, as opposed to the relative insensitivity of HDS to hydrogen concentration is further evidenced in that the cresol-soluble yield was significantly higher when the coal was reacted in an initial 2000 psi hydrogen atmosphere, both when slurried with creosote oil and also when slurried with pre-hydrogenated creosote oil. Also, solvent-to-coal ratio had no significant effect on HDS rate relative to that of liquefaction (Table 3).

The rate limiting step in liquefaction has been shown to be the reaction of dissolved molecular hydrogen with the donor solvent, with the transfer of hydrogen from the donor solvent to coal solids occurring rapidly (1,2). In fact, when extracted in a highly active hydrogen donor solvent such as hydrogenated creosote oil, coal solids have been observed to liquefy almost instantaneously upon reaching reaction temperature (1). Thus, the observed sensitivity of the rate of liquefaction to hydrogen concentration should be expected. Furthermore, as long as solvent quality (i.e., a sufficiently high hydrogen-donor concentration) is maintained - which can be done independently by hydrogenating the recycled process solvent as is done in the Exxon process - with liquefaction occurring almost instantly, HDS should be the controlling factor in the design and operation of the dissolver/reactor. HDS kinetics thus take on a special importance for the commercialization and development of the SRC process.

Coal Mineral Catalysis

A limited experimental evaluation of process advantages and disadvantages of coal mineral catalysis was presented in an earlier work (5). As part of this evaluation, twelve different coal minerals and, also, actual SRC mineral residue as well as coal ash were individually screened to rate their catalytic activity on the HDS rate and hydrogenation of creosote oil relative to that of a commercial Co-Mo-Al catalyst. Some results of this earlier work are given in Table 4 and in Figures 1 and 2. Reduced iron, reduced pyrite (presumably pyrrhotite), and pyrite had decreasing effects on sulfur removal during hydrogenation/hydrodesulfurization of creosote oil at 425°C, with reduced iron being second only to Co-Mo-Al in catalytic activity for HDS and with pyrite, despite its pronounced effect on hydrogenation, having essentially no apparent catalytic activity for HDS. The relatively insignificant effect of pyrite on HDS rate was further evidenced in that the rate of organic sulfur removal from coal slurried in creosote oil remained essentially the same even after about seventy-five per cent of its pyritic content had been removed physically by magnetic separation prior to reaction (Figure 3). Reduced iron, on the other hand, was found to have a significant effect on HDS reactions when present in only trace amounts (Table 5).

The stable form of iron in the presence of hydrogen and hydrogen sulfide in the temperature range of 400 to 500°C is pyrrhotite (6,7). As shown in Figure 4, pyrite is reduced to the sulfide (presumably pyrrhotite) within about fifteen minutes of reaction at 425°C. Rapid reduction of pyrite coal minerals has also been observed to occur in the dissolver/reactor at the Wilsonville SRC pilot plant (8). H_2S product from the reduction of pyrite is thus generated in the early stages of HDS. H_2S is known to inhibit catalytic HDS of petroleum feedstocks; thus, since some of the same sulfur-containing components in petroleum feedstocks exist also in coal/oil slurries, H_2S may inhibit HDS of coal/oil slurries, or possibly react with previously desulfurized components. Therefore, since reduced iron acts as an H_2S scavenger, instead of an H_2S producer as does pyrite, one possible reason for the differences in catalytic activities of reduced iron, reduced pyrite, and pyrite could be the different amounts of H_2S present during HDS as is shown in Table 4. In fact, the H_2S partial pressure was increased by a magnitude of two to three by the reduction of pyrite; whereas no traceable amount of H_2S product was present during the reduced iron run. Also, when different weight percentages of iron were charged with creosote oil (Table 5), no H_2S product was detected until less than one per cent by weight of iron was present. Interestingly enough, when iron was present in higher weight percentages (2.4 to 20%), the amount of sulfur removed during reaction was only slightly different, and when present in lower percentages (1.0 to 0.5%), it decreased in proportion to the amount of iron present, with trace amounts of iron being as effective as 0.5 weight percent. The retarding effect of H_2S on HDS is further evidenced in that when H_2S was added prior to reaction the amount of sulfur removed was less during hydrogenation/HDS of both a bituminous Kentucky No. 9/14 mixture coal and a sub-bituminous (Wyodak) coal (Table 10).

When iron gauze was used to scrub out any H_2S product formed during hydrodesulfurization of creosote oil, while being mounted in the top of the reactor above the oil, the amount of sulfur removal was about 20% higher than that obtained without any scavenger agents present; that is, the final sulfur content of the oil was 0.39% as opposed to 0.50%, a decrease equivalent to that obtained when one weight percent of iron was present. Apparently then, H_2S does have a retarding effect on HDS as might be expected from thermodynamics.

When five weight percent iron and a sufficient amount of H_2S (to prevent its complete removal by reaction) were present during HDS of creosote oil, the amount of sulfur removal was only the same as that when either a trace amount or a half weight percent of iron was present (Table 5). Apparently H_2S retards the effectiveness of iron sulfide as a catalyst, with trace amounts of iron sulfide having about the same catalytic effect on HDS rates as larger amounts when an appreciable H_2S atmosphere exists. Since H_2S does have a thermodynamic effect on the HDS reactions; however, the severity of its catalytic inhibition effect is not completely defined.

In summary then, reduced iron appears to favor HDS by scavenging H_2S product, preventing any reverse reactions and by catalyzing HDS reactions, Unfortunately, as shown in Table 6, reduced iron, like most HDS catalysts, also accelerates hydrogenation; as a result its use as a catalytic agent in the SRC process could contribute to excess hydrogenation. Because of its potential as an inexpensive HDS catalyst, however, further experiments are now in progress to better evaluate its role in accelerating HDS reactions and its selectivity for HDS versus hydrogenation.

Hydrodesulfurization Kinetics in the SRC Process

As shown in Figure 5, the variation of organic sulfur content of a coal/creosote-oil reaction mixture with time follows a path close to that expected for an overdamped second order dependence of rate on organic sulfur content. This kinetic behavior is consistent with the basic nature of HDS reactions as described in the foregoing discussion, in that it can be modelled by considering the reaction mixture to contain only two hypothetical sulfur-containing compounds with significantly different rate constants. The desulfurization reaction of each of the two hypothetical components is assumed to follow first-order kinetics. A test as to whether this assumed kinetic model is representative is the difference in magnitude of the experimental rate constants, for the actual two groups of lumped sulfur components are known to react at two widely differing rates. The large difference in slope of the two lines in Figure 6 indicates that the experimental rate constants are indeed significantly different, attesting that the model is representative.

The high sensitivity of HDS rate to reaction temperature and its low sensitivity to hydrogen concentration suggested that the HDS reactions were chemically controlled and pseudo-homogeneous kinetics were thus used in modeling. Furthermore, since the retarding effect of H_2S and the catalytic effect of pyrite coal minerals apparently either offset each other or exist to such an extent that the effect on HDS rate is insignificant - as a first-hand approximation-no kinetic terms were used to represent the reverse reaction by H_2S product. The rate equation was thus written as:

$$r_{HDS} = -K_1S_1 - K_2S_2 \tag{1}$$

where: S_1, and S_2 are the organic sulfur concentration (g/cc) present in the form of the two hypothetical sulfur-containing components, respectively. For a batch reactor,

$$S = S_{10}e^{-K_1t} + S_{20}e^{-K_2t} \tag{2}$$

The adjustable parameters S_{10}, S_{20}, K_1 and K_2 were determined empirically, using a nonlinear minimum sum-of-the-squares numerical search routine. The Arrhenius relationship was assumed, and rate data for three different reaction temperatures were used in determining empirical values for the four adjustable parameters. A list of these values is given in Table 7; and a comparison between predicted HDS paths and rate data is made in Figure 5, showing good agreement. Also, the Arrhenius plots of the empirical rate coefficients are given in Figure 6. The rate coefficients for the two hypothetical components differ by two orders of magnitude (Table 8), in consistency with the large difference in slopes of the two straight lines in Figure 6. In addition, the high activation energy (Table 8) for the reactive sulfur-containing component provides further evidence that the desulfurization reactions are chemically, rather than mass transfer controlled. Note that there is no catalyst present, except for the indigenous coal mineral matter. Finally, as shown in Table 9, the energies and enthalpies of activation are indicative of chemical rate processes, rather than transport processes. The high activation energy and low entropy of activation for the fast reaction are indicative of a homogeneous reaction; the lower values for the slow reaction indicate a possible catalytic effect, perhaps due to coal mineral matter. Here again, however, since the exact reaction mechanism is unknown, one must exercise caution when attaching significance to these numerical values.

Conclusions

Hydrodesulfurization reactions occur, under reaction conditions used in the SRC process, at a rate that is practically independent of hydrogen concentration. Reduced iron has a catalytic affect on HDS reactions; in fact, it exhibits a significant memory effect. Because of additional H_2S product, pyrite has only a slight catalytic effect on HDS reactions. The retardation of HDS reactions by H_2S product is due to catalytic inhibition as well as thermodynamic effects. HDS reactions can be modeled as two first-order reactions occurring in parallel, with two widely different rate constants.

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Table 1

Wt%
TOTAL AND ORGANIC SULFUR IN REACTION MIXTURE

Reaction Temp. °C.	Reaction Time Min.	2600 PSI		2000 PSI		1000 PSI		Average	
		Total	Organic	Total	Organic	Total	Organic	Total	Organic
385	15	.95	.82	.94	.81	.95	.82	.95	.82
410	15	.88	.75	.89	.76	.91	.78	.89	.76
435	15	.81	.68	.82	.69	.84	.71	.82	.69
385	30	.89	.76	.90	.77	.89	.76	.89	.76
410	30	.81	.68	.83	.70	.86	.73	.83	.70
435	30	.78	.65	.79	.66	.80	.67	.79	.66
385	60	.83	.70	.87	.74	.89	.76	.86	.73
410	60	.81	.68	.75	.62	.81	.68	.79	.66
435	60	.73	.60	.74	.61	.73	.60	.73	.60
385	120	.81	.68	.87	.74	.89	.76	.86	.73
410	120	.74	.61	.71	.58	.71	.58	.72	.59
435	120	.65	.52	.66	.53	.69	.56	.67	.54

Table 2. Effect on Gaseous Hydrogen and Solvent Type on Liquefaction and Hydrodesulfurization of Coal

Solvent Type	Atmosphere (atm)	Conversion (Based on Cresol Solubles) %	Total Sulfur in Reaction Mixture	Total Sulfur in Solvent (%)	Total Sulfur in Coal (%)
Creosote Oil	2000 psi N_2	42.1	.90 ± .02	.5	2.0
Hydrogenated Creosote Oil	2000 psi N_2	83.1	.49 ± .03	trace	2.0
Recycle Oil (Sample No. 16171)	2000 psi N_2	78.9	.73 ± .01	.26	2.1
Creosote Oil	2000 psi H_2	61.0	.91 ± .05	.5	2.1
Hydrogenated Creosote Oil	2000 psi H_2	90.7	.51 ± .03	trace	2.0
Recycle Oil (sample No. 16171)	2000 psi H_2	85.8	.75 ± .02	.26	2.2

NOTE: Reaction Time = 15 min.
Solvent-to-Coal Ratio = 3/1
Reaction Temperature = 410°C

Table 3

Effect of Solvent/Coal Ratio on Hydrodesulfurization and Liquefaction

Solvent-to-Coal Ratio	Temperature (°C)	Conversion Based on Cresol Solubles	Residual Organic Sulfur
1.5/1	410	84.5	1.45
2/1	410	85.3	1.39
3/1	410	90.7	1.55
3/1	385	80.4	1.68
4/1	385	83.6	1.81

Operating Conditions: 2,000 rpm
2,000 psig H_2

Reaction Time = 15 min.

Initial Organic Sulfur = 1.63

Table 4

CATALYST SCREENING RUNS:
LIQUID % SULFUR, TOTAL PRESSURE, AND FINAL GAS COMPOSITION

MINERAL	% S	TOTAL PRESSURE (10^{-3} PSI)	PARTIAL PRESSURES (PSI)				
			H_2 (10^{-3})	H_2S	CO_2	CH_4	C_2-C_5
NONE	0.52	2.40	2.13	10.	2.5	64.	18.
NONE	0.46	2.42	2.23	7.1	2.0	62.	24.
MUSCOVITE (-80)	0.39	2.18	1.94	8.5	1.0	51.	20.
PYRITE (-80, + 150)	0.41	1.99	1.54	230.	1.1	99.	36.
IRON (-325)	0.27	1.98	1.75	<1.	12.	16.	20.
REDUCED PYRITE	0.36	1.96	1.85	17.	0.4	61.	18.
COAL ASH	0.23	1.92	1.72	<1.	1.4	57.	15.3
SIDERITE	0.34	1.81	1.61	<1.	67.	93.	29.
SRC SOLIDS (-325)	0.32	1.73	1.48	13.	24.	85.	30.
PYRITE (-325)	0.55	1.63	1.22	196.	7.3	133.	71.
Co-Mo-AL (-80, + 150)	0.02	1.12	0.92	<1.	1.9	128.	74.
Co-Mo-AL (-325)	0.02	1.02	0.73	1.7	1.3	138.	79.

Table 5. Effect of Iron Concentration On Hydrodesulfurization of Creosote Oil

Iron Concentration (weight percent)	Final H_2S Partial Pressure (Psi)	Residual Sulfur (percent)
20.	0.	.34
20.	0.	.34
13.	0.	.35
13.	0.	.36
13.	0.	.35
4.7	0.	.35
2.4	0.	.38
0.99	8.	.40
0.49	66.	.43
trace (memory effect)	63.	.42
trace (memory effect)	--	.45
0	36.	.50
0	67.	.50

Reaction Conditions:

Temperature = 425°C
H_2 Pressure = 3000 psig @ 425°C
Agitation Rate = 1000 rpm
Initial Sulfur Concentration = 0.64 percent
Reaction Time = 2 hours

Table 6: Comparison of Hydrogenation and Hydrodesulfurization of Creosote Oil in the Presence of Iron Catalyst

Wt. % Fe	$(H/H_o)_{AVG}$	$(S_F/S_o)_{AVG}$
0	0.80	0.78
0.5	0.71	0.68
1.0	0.74	0.62
2.4	0.74	0.58
4.7	----	0.55
13.0	0.69	0.56
20.0	0.64	0.52

Reaction Conditions:

Temperature = 425°C
Initial Hydrogen Pressure = 3000 psi @ 425°C
Stirring Speed = 1000 rpm
Reaction Time = 2 hours
H = Hydrogen Partial Pressure
S = Sulfur Concentration
o = refers to initial condition

Table 7

Hydrodesulfurization Model Parameters

S_{10}	1.53×10^{-3} g/cc
S_{20}	6.51×10^{-3} g/cc
$K_1(385^oC)$	1.69×10^{-2} min^{-1}
$K_1(410^oC)$	5.30×10^{-2} min^{-1}
$K_1(435^oC)$	15.32×10^{-2} min^{-1}
$K_2(385^oC)$	8.15×10^{-4} min^{-1}
$K_2(410^oC)$	13.89×10^{-4} min^{-1}
$K_2(435^oC)$	22.74×10^{-4} min^{-1}

Table 8

Arrhenius Constants

$\ell n\ K_{10}$	27.11	min^{-1}
$\ell n\ K_{20}$	7.417	min^{-1}
ΔE_1	40.78	kcal
ΔE_2	18.99	kcal

Table 9

Comparison of Energies, Enthalpies, and Entropies of Activation of Hydrodesulfurization with Data for Hydrodesulfurization of Coal Tar over WS_2 Catalyst.*

	HDS Model			
	Reaction 1	Reaction 2	Coal Tar*	
ΔE	40.7	18.9	11	kcal/mole
ΔH	39.2	15.8	9	kcal/mole
ΔS	-16.8	-58.2	-50	E.U.

*S. A. Quader, W. H. Wiser, G. R. Hill

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Table 10: Effect of H_2S on Rate of Hydrodesulfurization of Kentucky and Wyodak Coals

Atmosphere	Coal Type	Solvent Type	Solvent-to-Coal Ratio	Cresol Soluble Yield (%)	Total % Sulfur		% Sulfur Liquid Fraction	% Sulfur Solid Fraction
					Before	After		
H_2	Wyodak	Recycle	3:1	76.0	0.52	0.41	0.35	1.15
$H_2 + H_2S$	Wyodak	Recycle	3:1	76.8	0.52	0.72	0.62	2.04
H_2	Kentucky 9/14	Recycle	2:1	86.4	1.10	0.80	0.52	2.86
$H_2 + H_2S$	Kentucky 9/14	Recycle	2:1	88.9	1.10	0.98	0.68	3.58

Reaction Conditions: Time = 15 Min.

Temperature = 410°C

Stirrer Speed = 1000 rpm

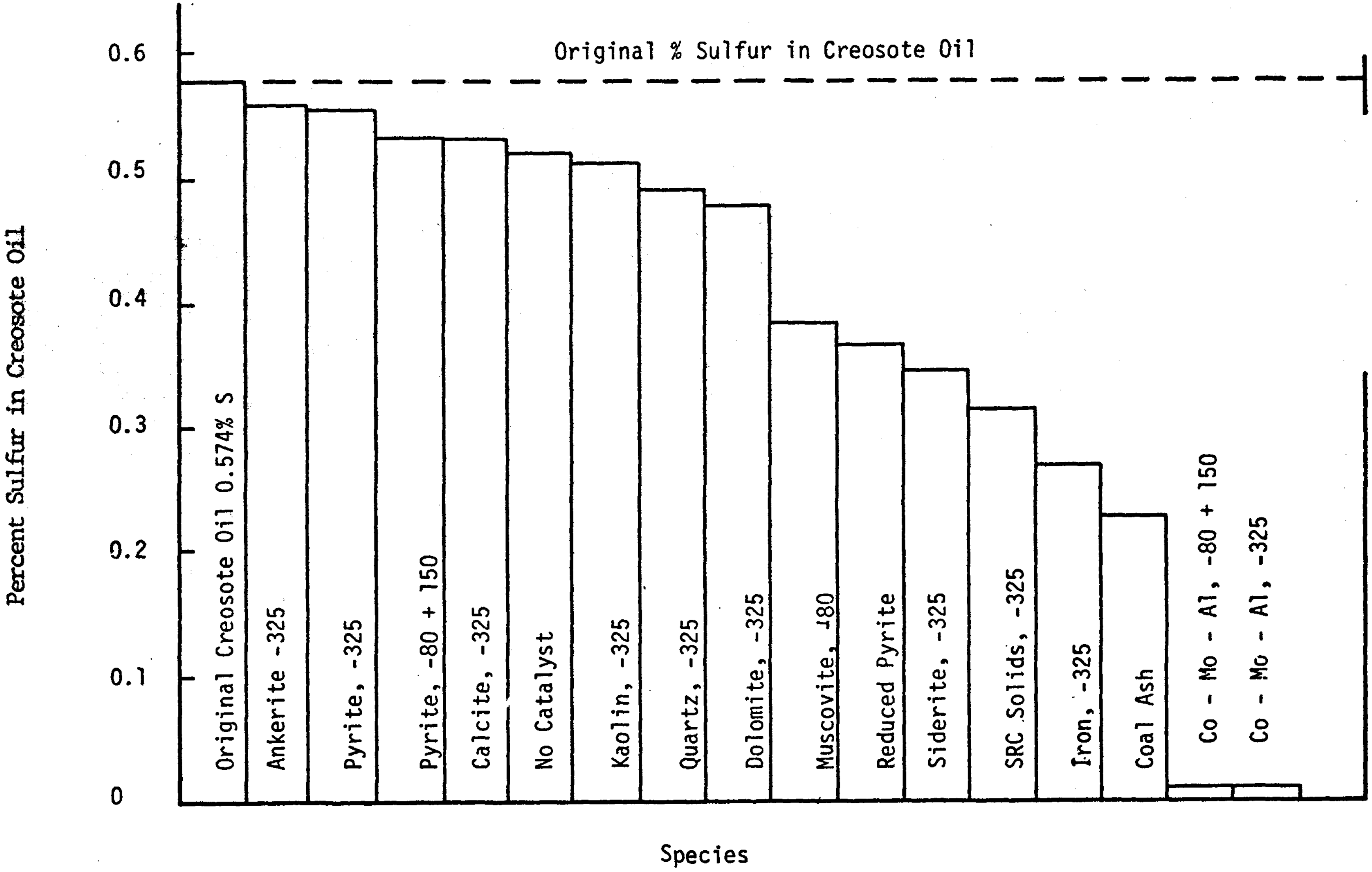


Figure 1. COMPARISON OF DESULFURIZATION ACTIVITY OF CATALYST

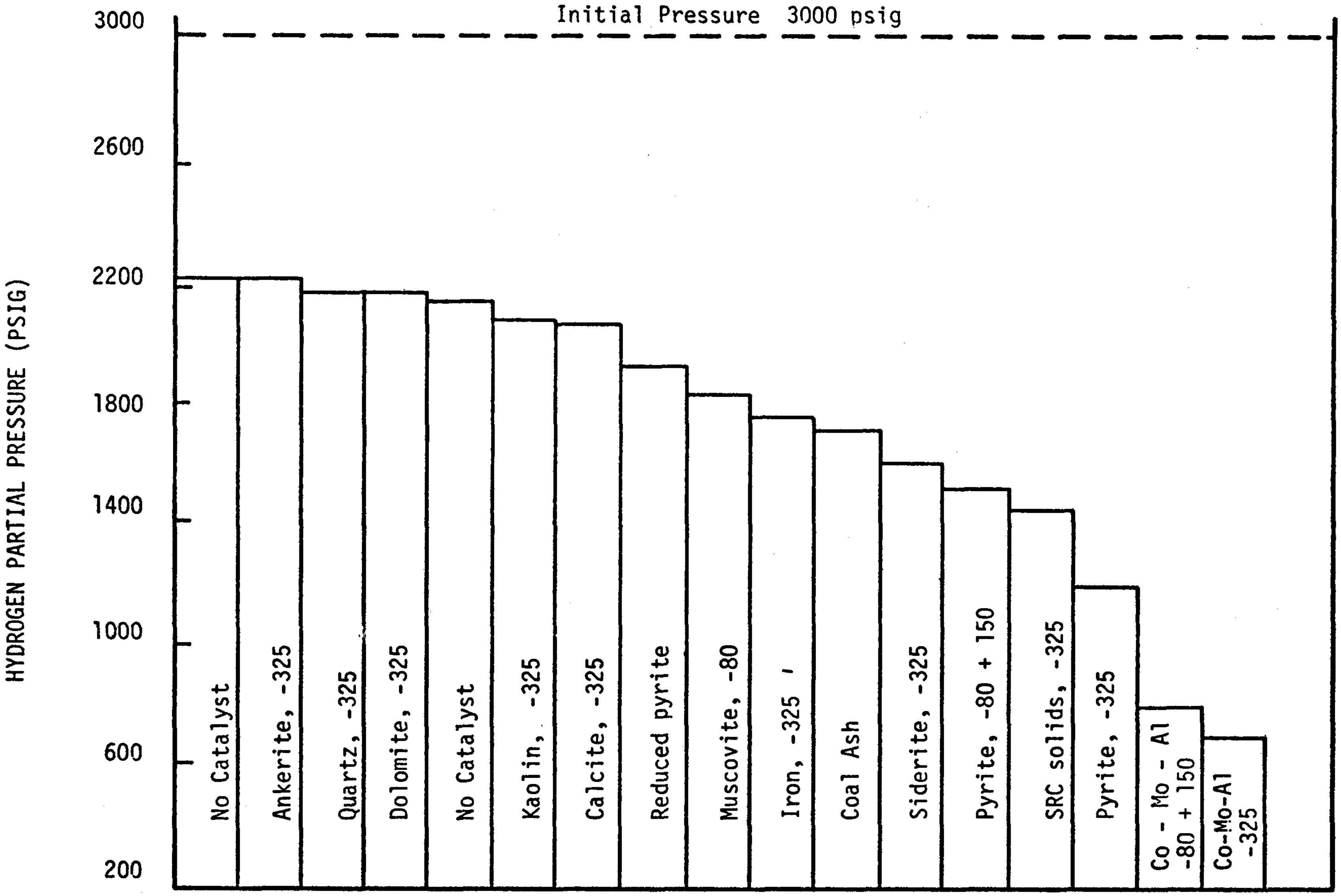
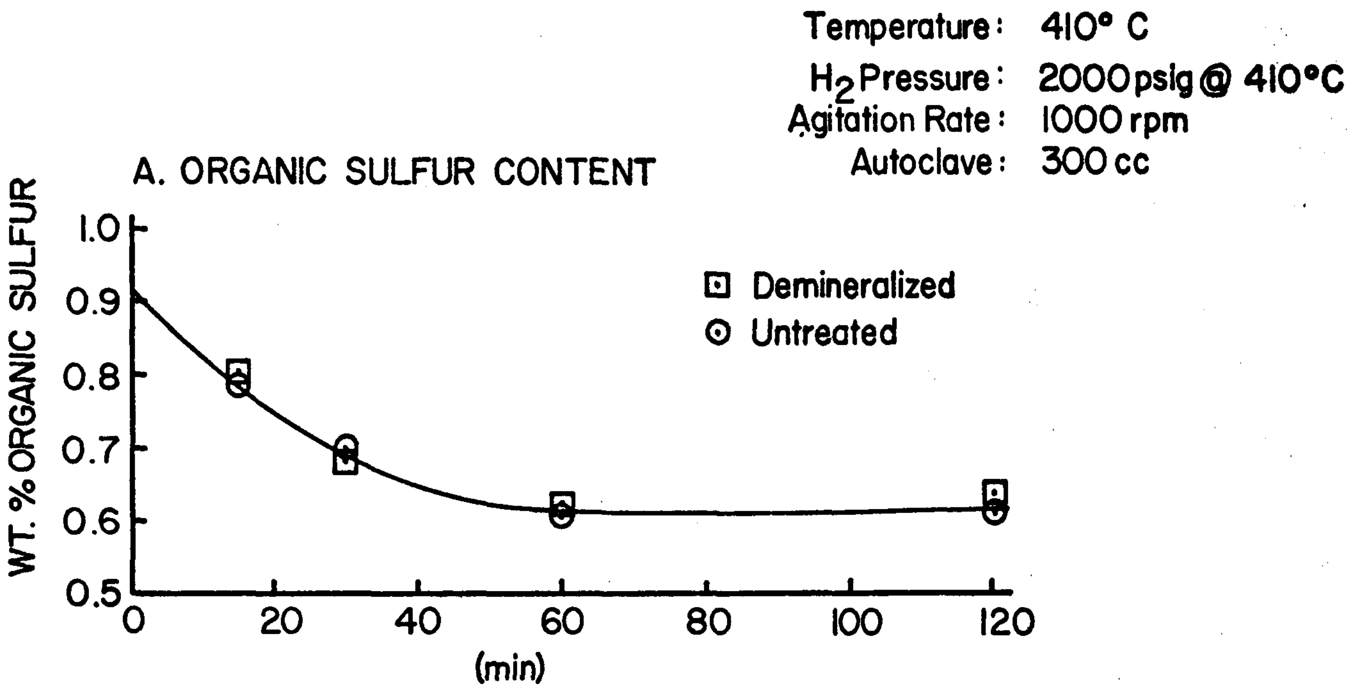
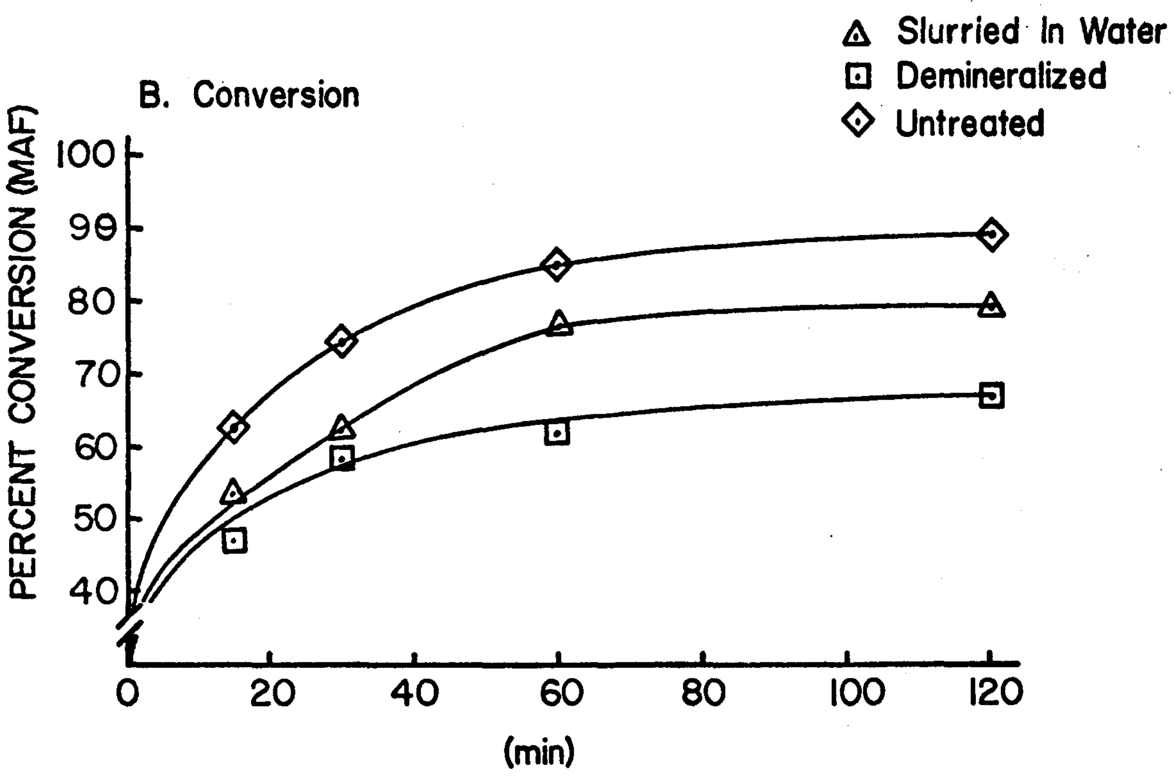


Figure 2. COMPARISON OF HYDROGENATION ACTIVITY OF CATALYST

Figure 3. Effect of Demineralizing Coal Feed and Slurrying Coal Feed with Water on Conversion





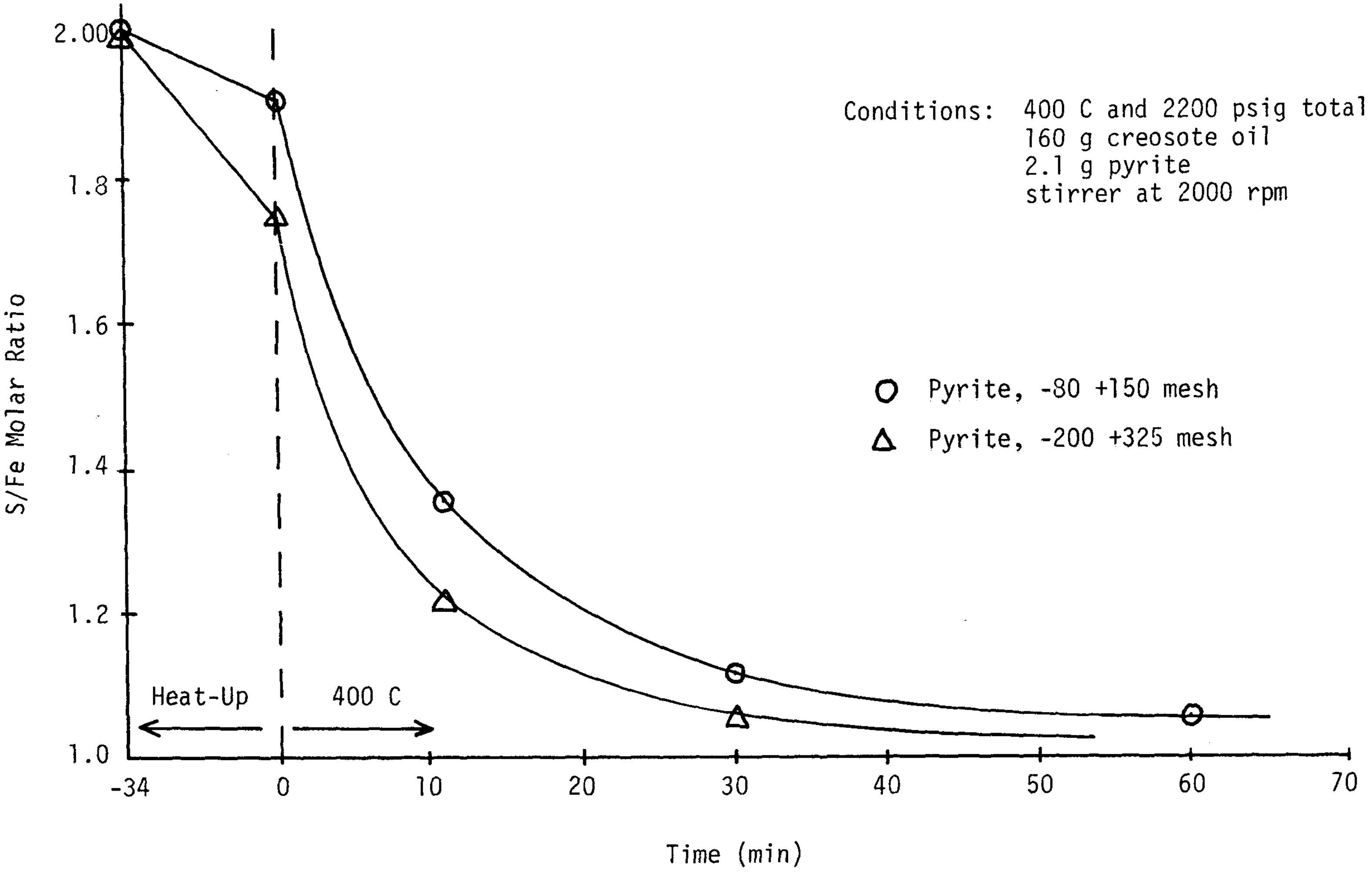


FIG. 4 PYRITE REDUCTION AS A FUNCTION OF TIME

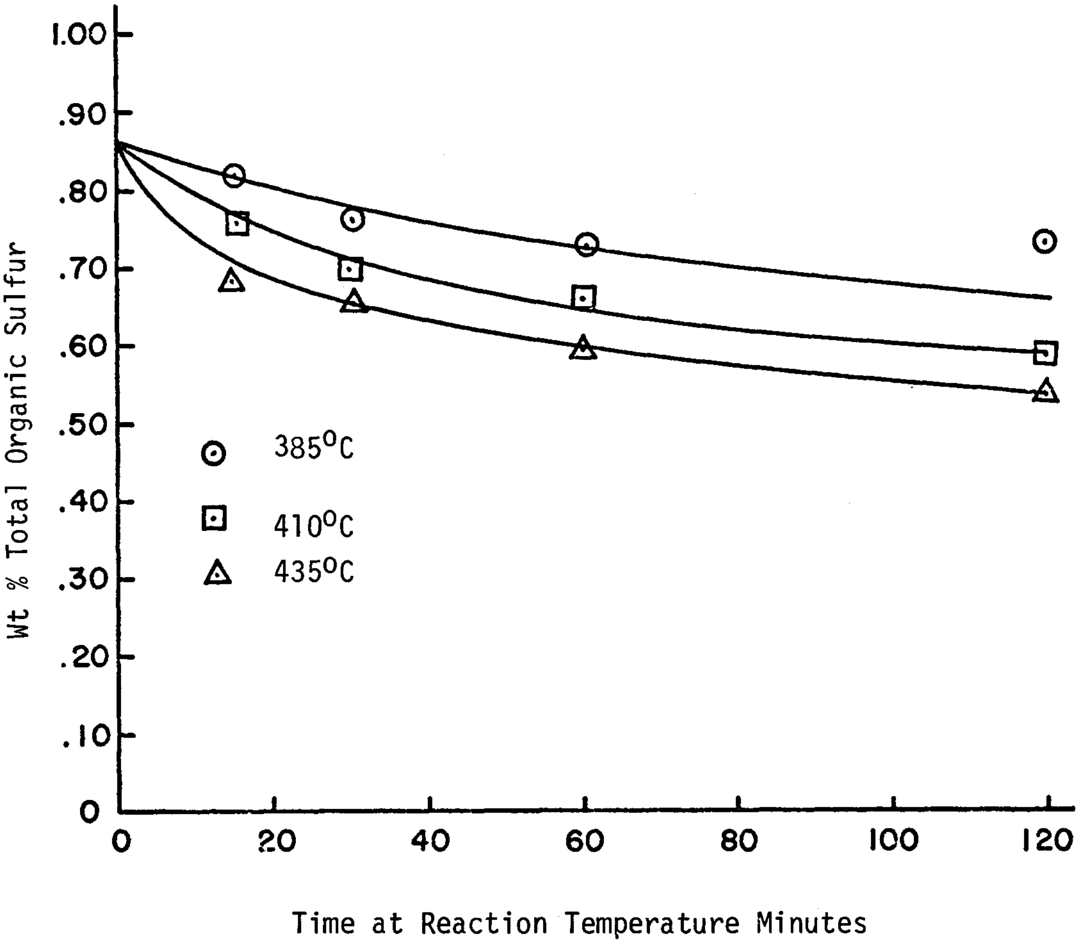


Figure 5. Effect of Reaction Temperature on Organic Sulfur Concentration

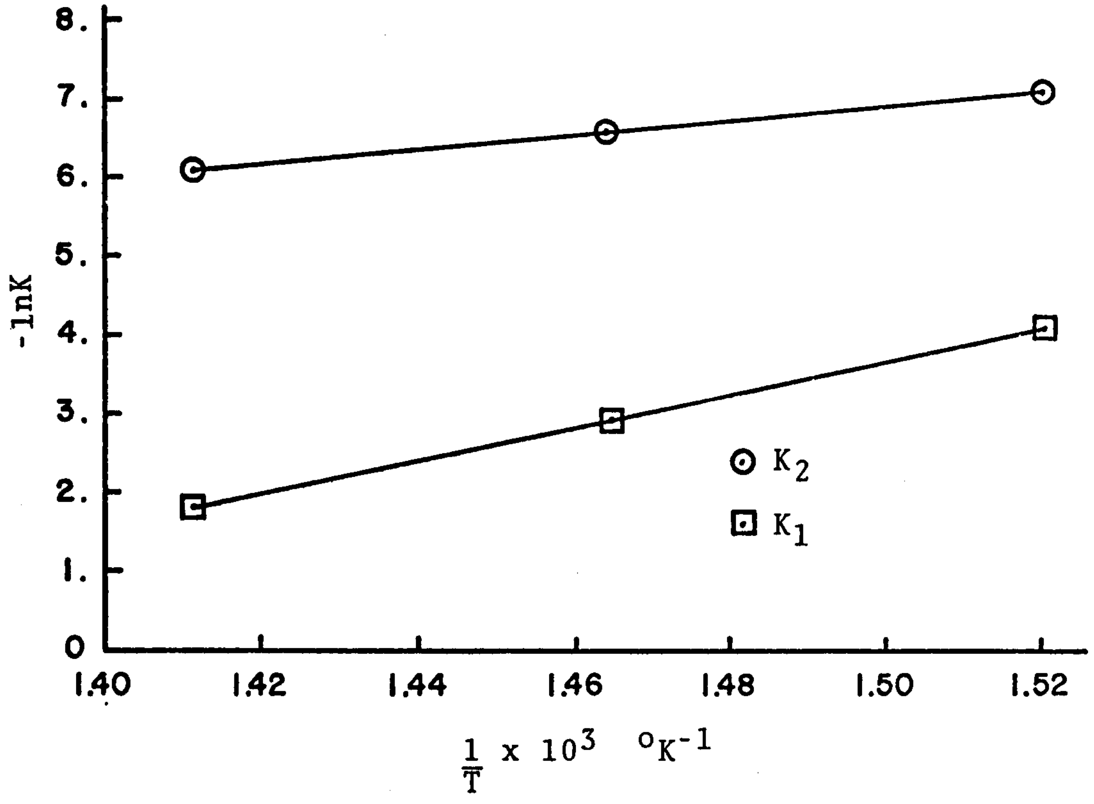


Figure 6. Arrhenius plot for hydrodesulfurization

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