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10/19/79

DR. 177

FE-2454-6
Dist. Category UC-90d

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

MASTER

Quarterly Report for the
Period October - December 1977

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PREPARED FOR THE UNITED STATES DEPARTMENT OF ENERGY

Under Contract No. EX-76-S-01-2454

Available from:

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Price: Printed copy: 8.00
Microfiche: $3.00

ACKNOWLEDGEMENT

The work reported here was made possible by the efforts of the following personnel of the Auburn Coal Conversion Laboratory. Their contributions to this report and to the progress of this work are hereby gratefully acknowledged.

W. C. Neely
J. W. Prather
J. M. Lee
C. W. Curtis
M. H. Lee
H. F. Vanbrackle
S. K. R. Stino
C. Y. Chang
D. Garg
B. M. Adkison
T. E. Smith
D. N. Bush
J. F. Martin
S. D. Miners
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L. C. Davis
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ABSTRACT

This report describes work done in the sixth quarter of a program designed to better understand and improve the Solvent Refined Coal and related liquefaction processes.

This quarter the effect of the initial particle size of a coal on the resulting particle size of the reacted products was determined by Coulter Counter analysis of liquefaction products of Amax and Kentucky coals. Further studies of the effect in coal dissolution with different solvent/coal ratios with four different solvents (tetralin, LRO, creosote oil, naphthalene) were performed using different reaction times. $Fe_2(SO_4)_3$ pretreatment of Kentucky coal showed little effect on the sulfur content of the liquid product and in the liquefaction yield when followed by tetralin liquefaction.

Extensive studies with SRC residue ash and coal ash as possible liquefaction catalysts were done in hydrogenation, hydrodesulfurization, and solvent quality of the coal liquefaction process. In the presence of Co-Mo-Al as catalyst and tetralin as solvent the reactivity of demineralized coal by acid extraction and magnetic separation was found to be almost the same as the untreated coal. Mineral matter present in coal strongly interacted with the LRO solvent, enhancing both the dissolution and hydrogenation reactions, but not with the tetralin solvent. Coal minerals such as Fe, SRC residue ash and pyrite had moderate hydrodesulfurization activity using phenyl sulfide, but not with dibenzothiophene. Mathematical modeling of reaction kinetics in coal liquefaction with tetralin as the solvent was done by the Parameter Estimation Method. Coal dissolution and hydrogen transfer kinetics expressions were obtained based on a second order assumption in the following reaction scheme:

$$\begin{aligned} &\text{Coal + Tetralin} &&\rightleftharpoons &&\text{Preasphaltene + Naphthalene}\\ &\text{Preasphaltene} &&\rightleftharpoons &&\text{Asphaltene}\\ &\text{Asphaltene} &&\rightleftharpoons &&\text{Oil and Gases} \end{aligned}$$

LC, GPC and FTIR were used to characterize and to obtain the molecular weight distribution of coal, SRC and coal-derived products. Flame photometric detectors (sulfur sensitive) were installed and used to identify sulfur-containing compounds. The pattern of GPC molecular weight distribution of the THF soluble portion of coal and SRC was found to be generally broad and very similar regardless of different rank of coal. GPC chromatograms of asphaltene and oil fractions were clearly discernable, but that of preasphaltene was not observed. The arbitrary RI ratio of the GPC chromatogram showed a positive indication of the degradation of coal substances or coal-derived asphaltenes at the higher reaction temperatures, 410°C or 440°C.

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

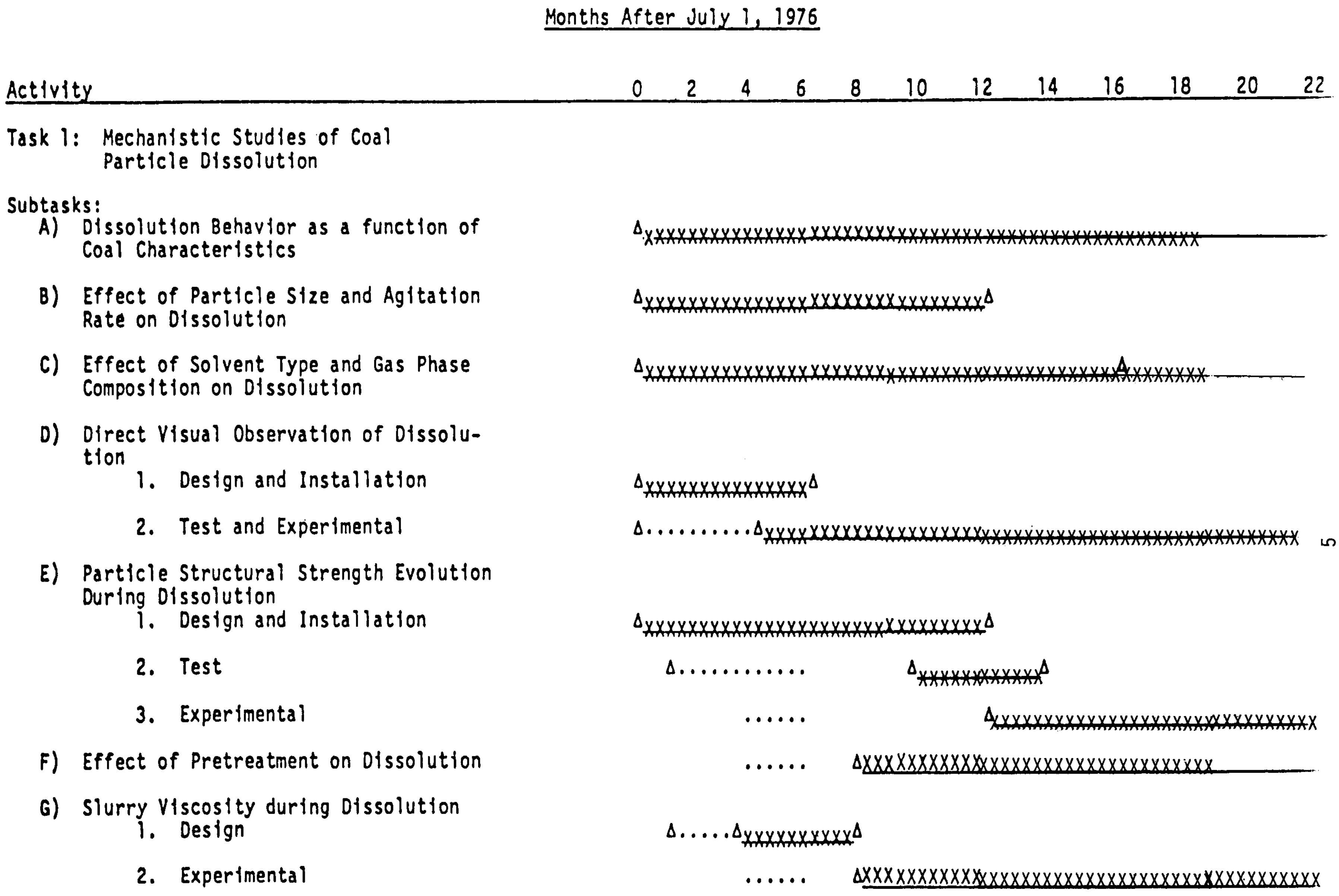


Figure 1. Work Schedule

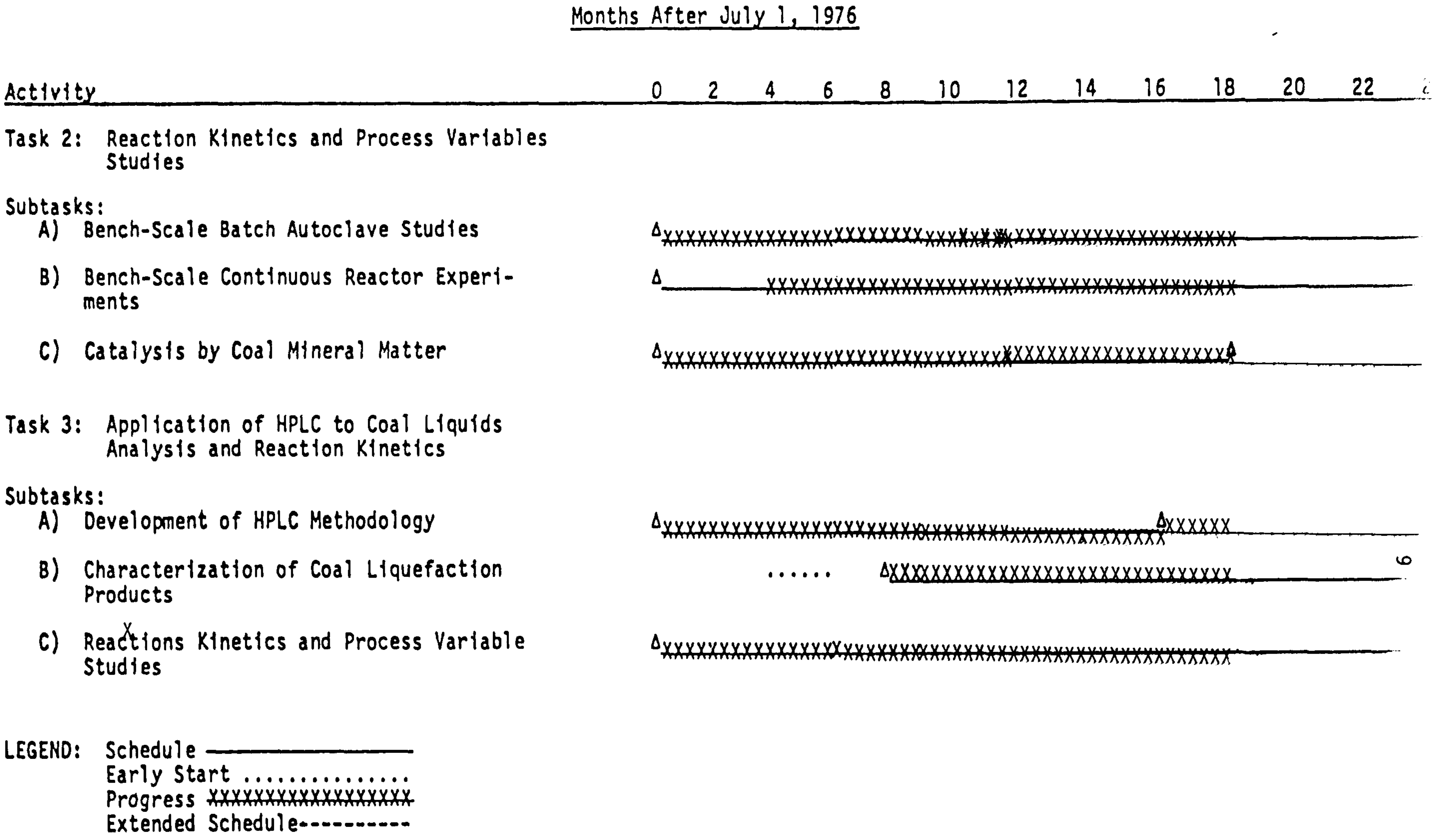


Figure 1 (continued)

TECHNICAL PROGRESS

Task 1. Mechanistic Studies of Coal Particles 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

Initial and mean particle size determination were made via the Coulter Counter Model TA. This data was necessary to determine the changes, if any, of undissolved solids in the particle size distribution of Western Kentucky 9/14 and Amax coals when the initial particle size as well as the final temperature of the autoclave reaction mixtures was varied. The orifices normally used for analyses were 40, 70 and 200 μm.

Reagent grade ammonium thiocyonate (NH_4SCN) and dimethylformamide (DMF) obtained from Mallinckrodt prepared in a 5% solution was the electrolyte used for analysis. Metricel alpha -8 filters with 0.20 μm pore size were used for filtering the electrolyte solution.

Calibration of each orifice was performed using polystyrene calibration standards of 2.02 and 27.0 μm dispersed in isoton.

Autoclave reaction samples were sonicated using a low energy ultrasonic bath, dispersed in the 5% NH_4SCN - DMF electrolyte and again sonicated. The samples were diluted with electrolyte and immediately analyzed. For each sample, 100,000 particles were counted and the particle size distribution was obtained. Extensive filtering with 0.2 μfilters was necessary to maintain the necessary background of the electrolyte.

The Coulter technique measures the particle volume distribution. The smallest particles measured had a diameter of 0.794 μm with an overall diameter range of 0.794 to 80.6 μm. All measurements were taken within the optimum range of the orifice. Particle size distributions were obtained for Amax, Pittsburgh Seam No. 8, and Kentucky 9/14 autoclave reaction mixtures. The particle size distribution measurements for each coal sample can be accurately reproduced within ± 10%. A mean particle size is obtained graphically by plotting the normalized cumulative particle volume percent versus particle diameter and then obtaining the mean particle size at the 50% volume level.

Results and Discussion

The study of the effect of the initial particle size of a coal on the final particle size of the reacted coal shows that the types of coals used are significant to the results. For example, Amax coal, a slow dissolving subbituminous coal, shows radical changes in mean particle size when the initial particle size is varied. When the initial particle size is 4000-5660 μm, the mean particle size is 32.0 μm; however, when the initial particle size is considerably smaller - 44.5 μm, the mean particle size is also considerably smaller - 14.0 μm (see Table 1.A.1). Therefore, Amax coal follows its characteristic dissolution behavior with time: the longer the reaction time, the

Table 1.A.1. Mean Particle Size of Autoclave Reacted Coals with Different Initial Particle Sizes[a]

Initial Particle Size (μm)	Mean Particle Size Amax	Western Kentucky	Pittsburgh
-44.5	14.0	7.0	6.0
40.6 - 105.0		5.2[b] 3.0[c]	
88.9 - 105.0	10.0[d] 40.0	3.25	5.0
4000 - 5660	32.0		

a Conditions are as follows: 3:1 solvent to coal ratio, 15 min. reaction time, 410°C
b reaction mixture at 385°C
c 4:1 solvent:coal ratio at 385°C
d 30 min. reaction time

more the particles dissolve as shown in Figure 1.A.1. The mean particle size in fifteen minutes is 70.0 μm in contrast to 40.0 μm in thirty minutes, when the initial particle size is 88.9-105.0 μm.

In contrast, Western Kentucky 9/14 coal is a fast dissolving bituminous coal. Its rapid and complete dissolution behavior is exemplified by the similarity of the final particle size of the reacted coal when different temperatures and initial particle sizes are used. When an initial particle size of 88.9 - 105.0 μm and a temperature of 410°C is used, the final mean particle size of Western Kentucky autoclave reaction mixture is 3.25 μm (see Figure 1.A.2). When a substantially lower reaction temperature, 385°C and a somewhat smaller particle size is used, the final mean particle size increases slightly to 5.2 μm. If, however, the solvent/coal ratio is changed from 3:1 to 4:1 at 385°C, the final mean particle size decreases to 3.0 μm which is essentially the same as the 410°C final mean particle size. These results are shown in Figure 1.A.3. Western Kentucky coal, therefore, dissolves very rapidly in light recycle oil. The initial particle size and the reaction temperature has very little effect on the final mean particle size.

The effect of initial particle size on Pittsburgh Seam coal another bituminous coal is being currently investigated. Figure 1.A.4 shows the particle size distribution for the Pittsburgh Seam autoclave reaction mixture starting with an initial particle size of 88.9 - 105.0 μm. Future work will include more studies on the effect of initial particle size on Pittsburgh seam and other coal types.

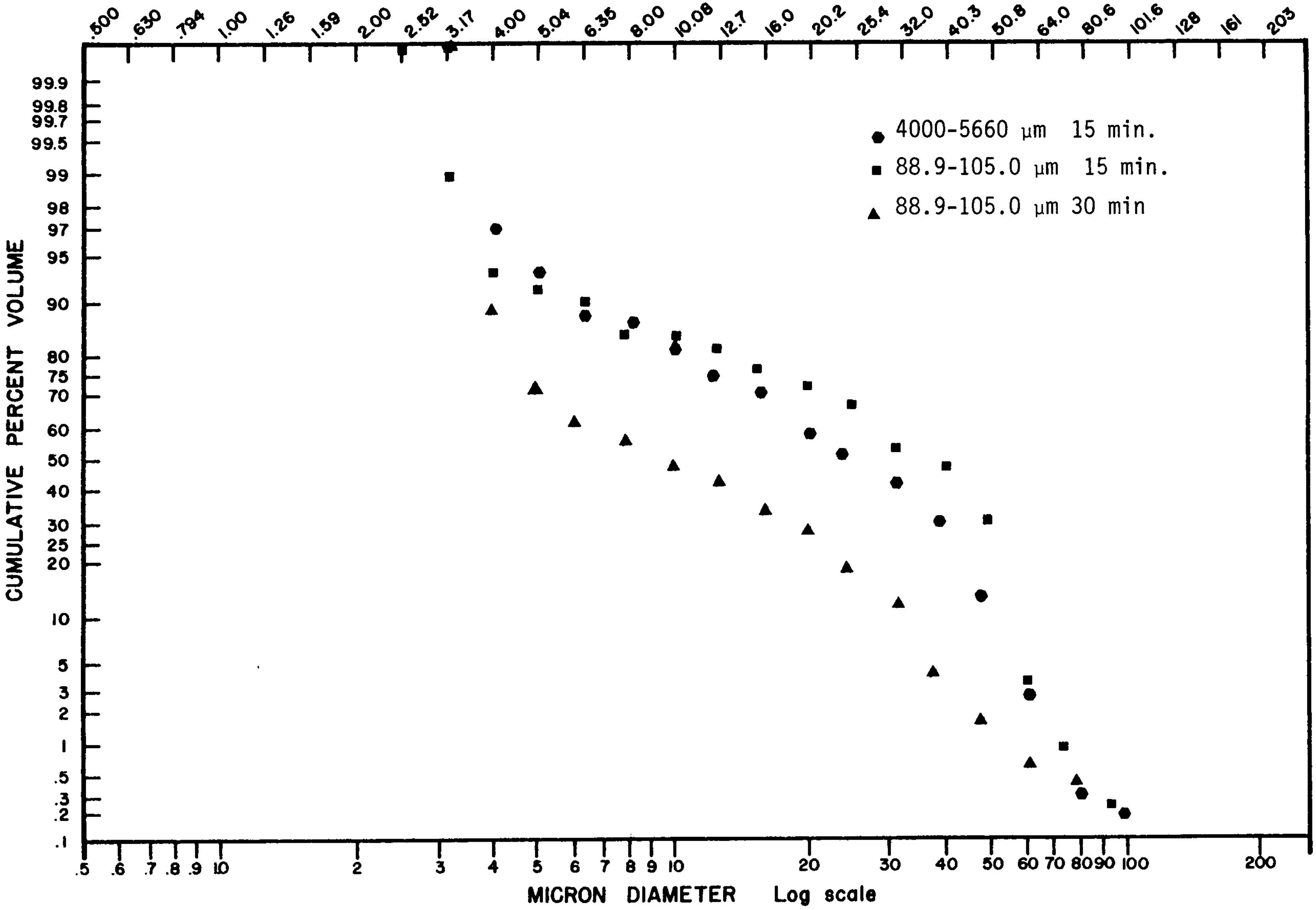


Figure 1.A.1. Particle Size Distributions of Amax Autoclave Reaction Mixtures with Different Initial Particle Sizes

Figure 1.A.2. Particle Size Distribution of Western Kentucky 9/14 Autoclave Reaction Mixtures with Initial Particle Size of 88.9-105.0 µm

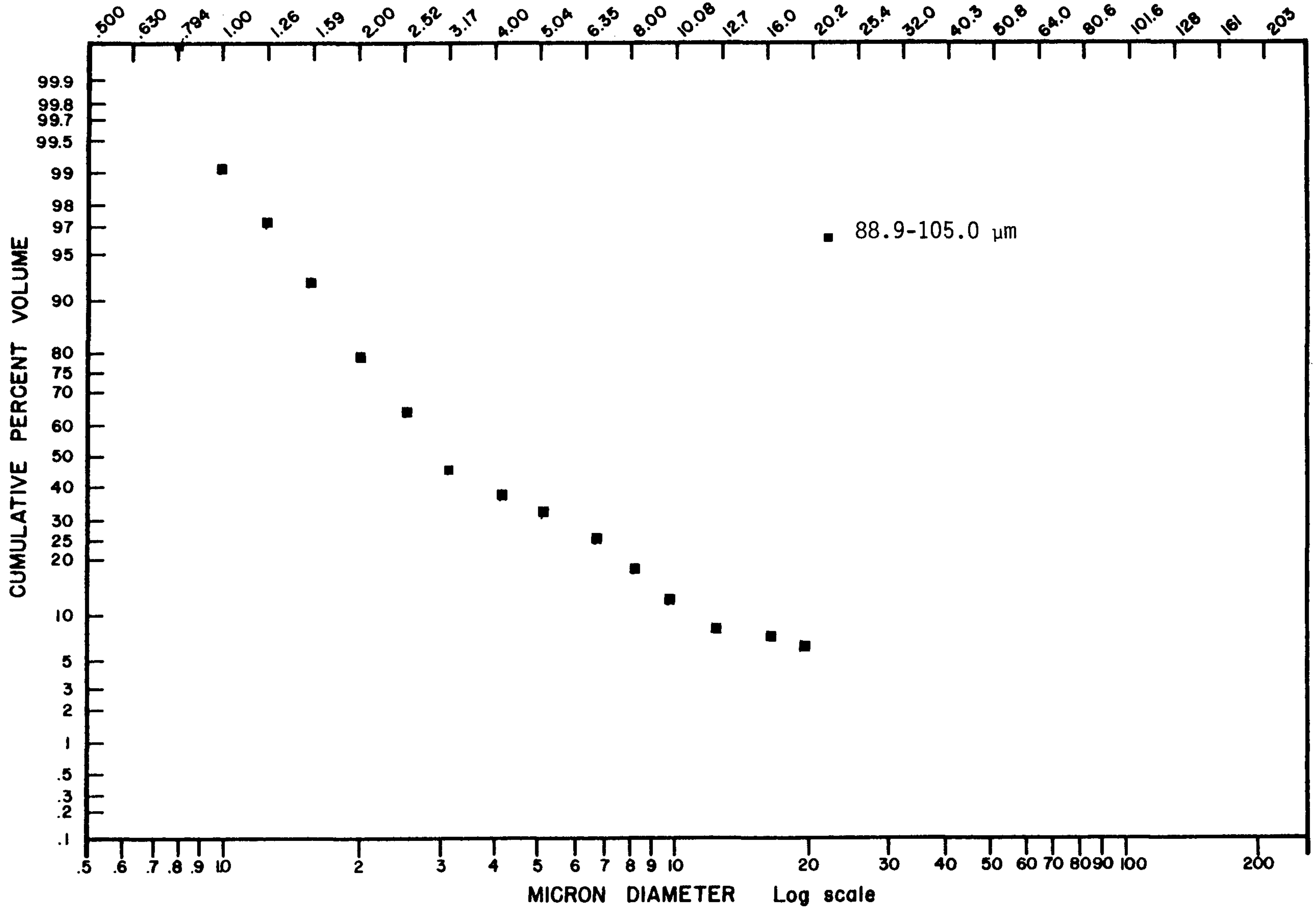


Figure 1.A.3. Particle Size Distributions of Western Kentucky 9/14 Autoclave Reaction Mixtures with Initial Particle Size of 40.6-105.0 μm at 385°C.

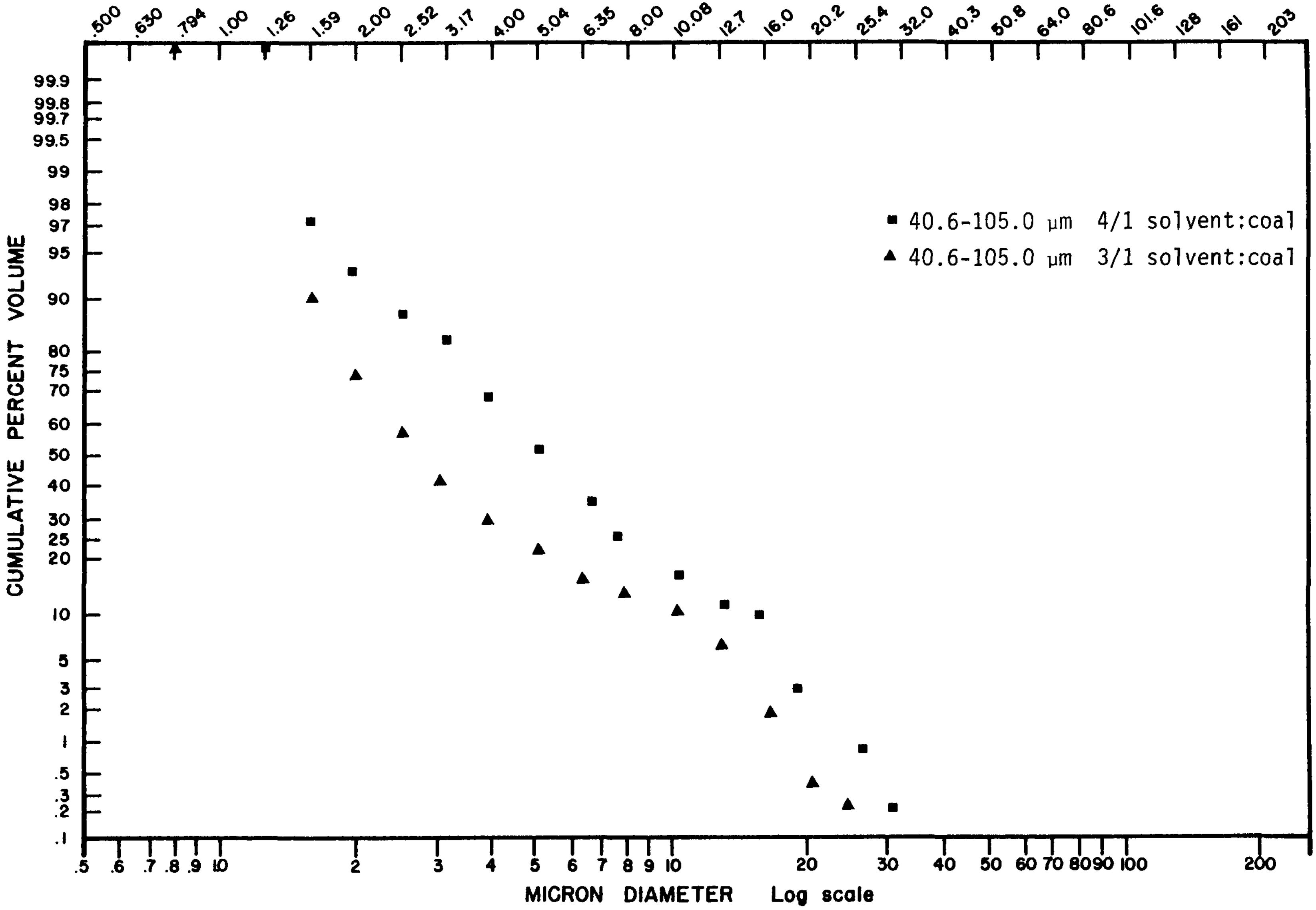
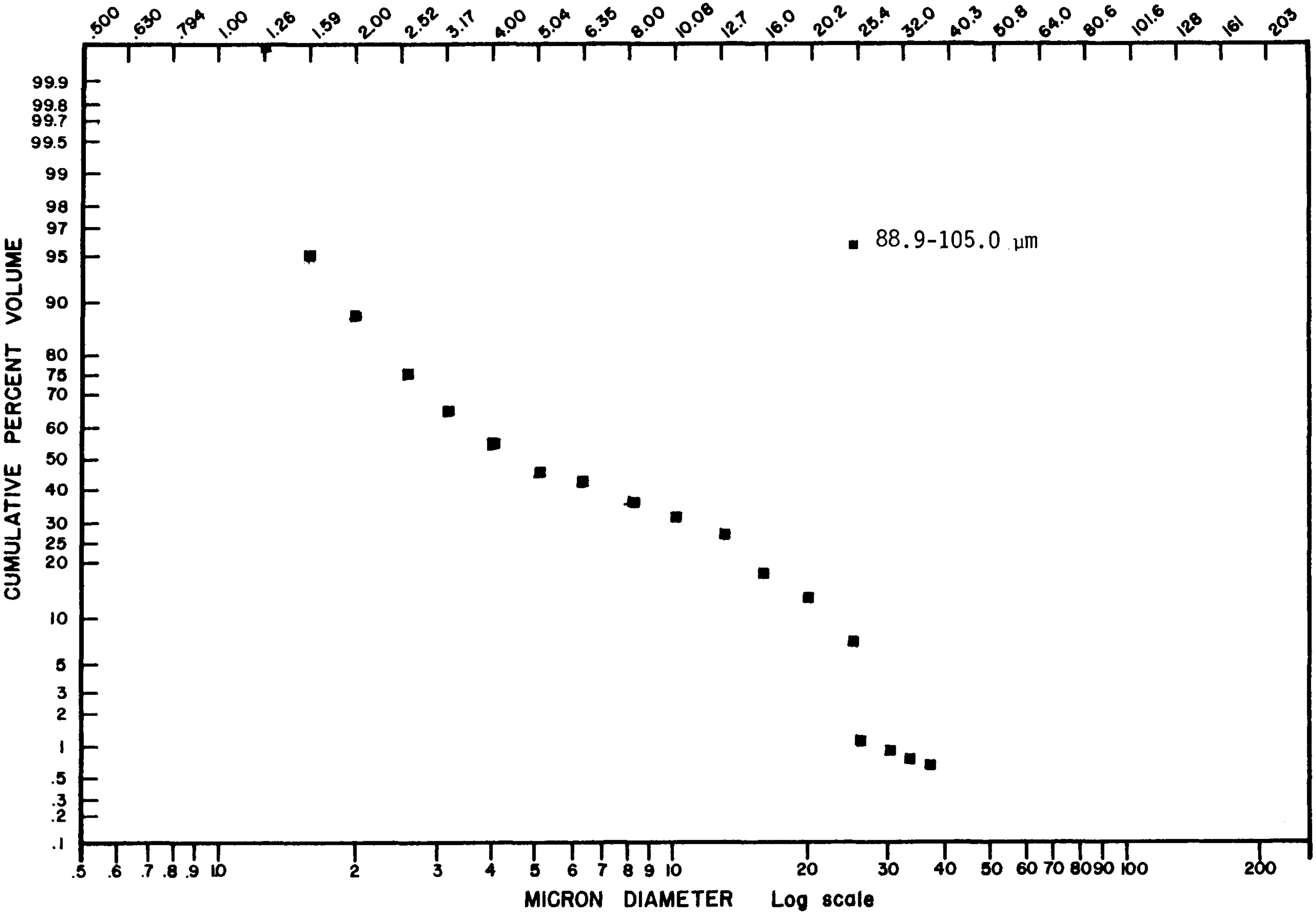


Figure 1.A.4. Particle Size Distribution of Pittsburgh Seam Autoclave Reaction Mixtures with Initial Particles of 88.9 - 105.0 µm



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 several coals 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

During this quarter, four series of experiments were continued in the small tubing bomb reactor to determine the effect of solvent concentration in coal dissolution reaction. Light recycle oil (LRO), tetralin, creosote oil and naphthalene were used for this purpose. The ratio of each solvent to coal was varied from 0 to 10. Kentucky 9/14 mixture coal containing 8.2% ash was used in these experiments. Dissolution yields were calculated based on the ash balance in the initial coal and the cresol insoluble filter cake as shown in the following equation.

$$A = \frac{100\ (M-F)}{M\ (1-F)}$$

where A = yield

M = % ash in the cresol insoluble residue

F = % ash in the original dry coal

In determination of coal dissolution yield, the following procedures were used:

(1) Product slurries were collected from the small tubing bomb and filtered by vacuum to separate the undissolved solids.

(2) The separated solids were then washed with hot cresol and rinsed with THF until the clean filtrate was observed.

(3) The insoluble filter cakes were dried overnight in a vacuum oven at 110^{o}C.

(4) The dried solids were pulverized, redried further in the vacuum oven for one hour and then cooled in a desiccator.

(5) Approximately 3.8 grams of the solids were ashed in the tube furnace for two hours at 910^{o}C and the ash percentage in the solids was obtained.

Results and Discussion

Table 1.C.1 shows the experimental conditions used with four different solvents at various solvent concentrations.

Table 1.C.1. Experimental Conditions for the Solvent Concentration Effect in Coal Dissolution

T = 410^{o}C
solvent + coal = 7.5 grams
solvent/coal ratio = 0 to 10
reaction time = 15 minutes
atmospheric pressure (no hydrogen used)
agitation rate = 600 rpm

The results obtained from these experiments are shown in Figure 1.C.1.

Although a large amount of work has been done in the area of coal dissolution, the mechanisms of coal dissolution have not explained completely. This well reveals the heterogeneous and complicated nature of coal substances and coal dissolution reactions. Several hypothesis and experimental evidences of important reaction steps and for major governing factors in the coal dissolution reactions can be found in the literature (Guin, et al., 1978; Neavel, 1976; Wiser, et al, 1971; Curran, et al., 1967), which have been generally accepted as having occurred in coal dissolution reactions and to affect significantly coal dissolution phenomena. These are briefly summarized in the following:

(1) initial rapid dissolution reaction in the solvent,

(2) thermal cracking of coal substances to produce free radicals,

(3) stabilization of coal-derived free radicals to prevent char formation,

   a) autohydrogen transfer in coal itself,

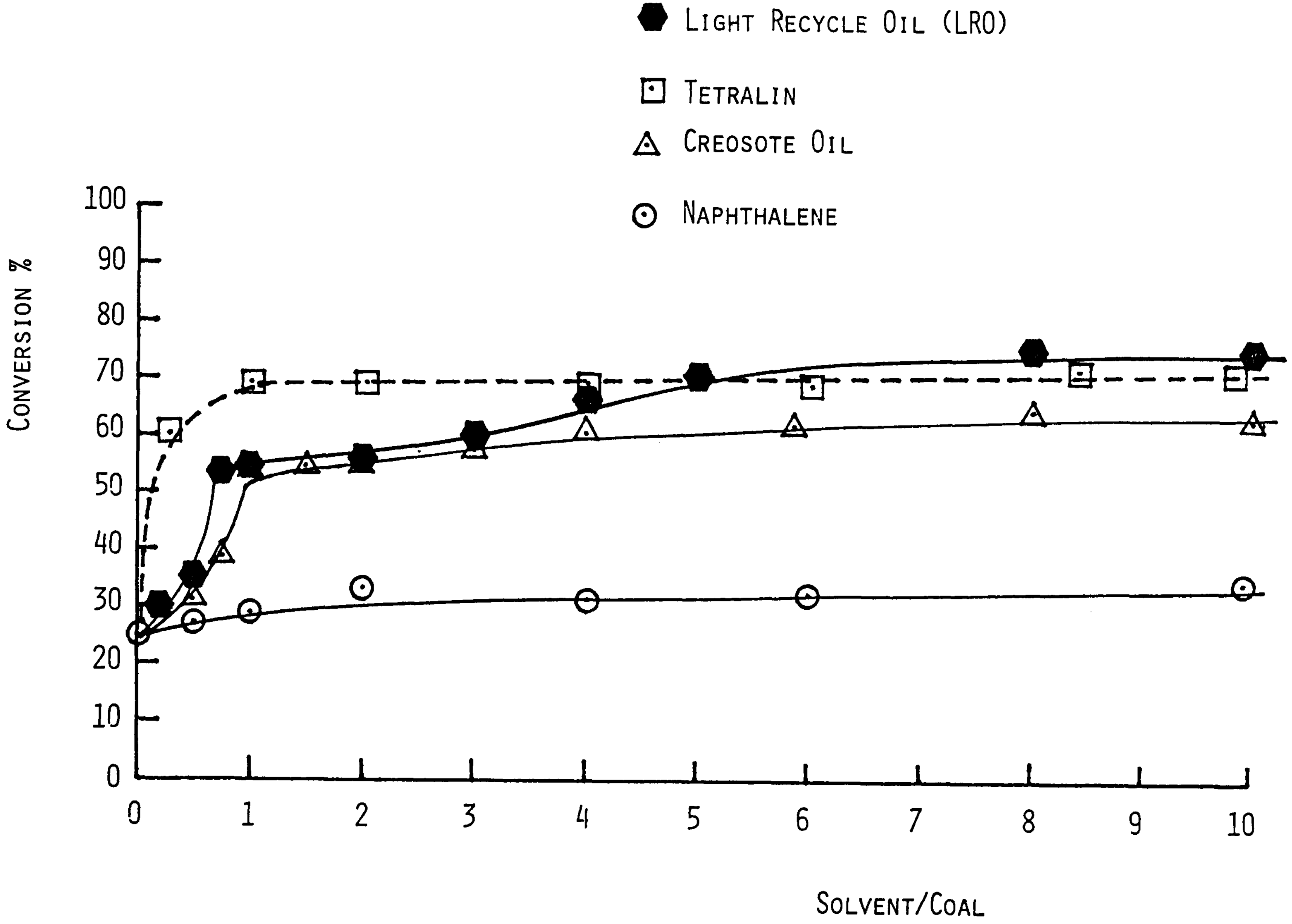
   b) hydrogen transfer from solvent to coal,

(4) physical solvating ability for coal-derived species to prevent char formation.

Different funtionality of solvent-types could affect significantly the above reaction steps (1) and (4), i.e., phenolic types, pyridine types, ether types and aromatic hydrocarbon derivatives. In the previous progress report (Period April-June, 1977), we have shown that the dominant effect in coal dissolution is the presence of the hydrogen donor species, for example, tetralin, by examining mixtures of three different types of solvent, tetralin, cresol and paraffin oil. The initial necessary conditions for effective coal dissolution are thought to be the above reaction steps (2) and (3). Certain reaction temperatures, which are generally above 350^{o}C, are required for efficient thermal cracking of coal substances to produce free radicals and then good hydrogen-donor solvents (for example, tetralin, etc.) are required to stabilize coal-derived free radicals, which prevent polymerization leading to solid char formation. Furthermore, the secondary important aspect in coal dissolution is stabilization of coal-derived products in the solvent, which prevents further polymerization. These could be achieved by the strong physical dissolving power of a good solvent and/or by hydrogen transfer from a good hydrogen-donor solvent.

In Figure 1.C.1 obtained from the present work during this quarter, when tetralin was used as solvent in the coal dissolution reactions, the

Figure 1.C.1. Solvent Concentration Effect in Coal Dissolution with Different Solvents



dissolution yield as cresol-solubles (based on daf coal) rapidly increases up to the solvent/coal ratio = 1. Further increase in the solvent/coal ratio seems insignificant as far as the dissolution yield is concerned. In contrast to tetralin, in the presence of naphthalene as solvent, no detectable change in the dissolution yield has been observed by varying the solvent/coal ratio. The difference between these two solvents, tetralin and naphthalene, shows the importance of the hydrogen-donor ability of solvent in the coal dissolution reactions. Tetralin, a good hydrogen-donor solvent, results in about 40% higher in the dissolution yield than naphthalene, a non-hydrogen-donor solvent. Naphthalene is usually considered as a good hydrogen transfer agent which enhances the above reaction step, (2a), autohydrogen transfer in coal itself. Under our reaction conditions, the enhancement of autohydrogen transfer by the increase of naphthalene concentration has not been observed. This may indicate that the effect by autohydrogen transfer is insignificant in the dissolution yield, compared to the effect by hydrogen transfer from solvent to coal.

In the presence of light recycle oil (LRO) or creosote oil, the dissolution yield again rapidly increases up to the solvent/coal ratio = 1. This rapid increase could be a matter of wetting and accessibility of the solvent to the coal particles. Further increases in the solvent to coal ratio from 1 to 8 result in about 20% enhancement in the dissolution yield with LRO as solvent, and about 10% enhancement with creosote oil as solvent. These phenomena are difficult to explain based solely on the concept of hydrogen transfer (the above reaction step, (3), since only small amounts of hydrogen-donor species such as tetralin, dihydrophenanthrene, etc., are present in LRO and, moreover, only trace amounts are present in creosote oil, compared to those in tetralin solvent. LRO or creosote oil could possess significant physical solvating power for coal-derived species and thus prevent char formation (the above reaction, step (4)). These two factors (hydrogen transfer and physical solvating ability) when combined could still result in relatively high dissolution yield. As solvent concentration increases, the amount of hydrogen-donor species present in the solvent increases along with an enhancement of solvating power for coal-derived species.

To further investigate the effect of the solvent/coal ratio in the presence of tetralin as solvent (Figure 1.C.1), further reaction time studies have been conducted by using two different solvent (tetralin)/coal ratios, 1 and 4. The experimetnal conditions are the same as in Table 1.C.1, except for the reaction time varying from 0 to 60 minutes.

Figure 1.C.2 shows the results of the reaction time studies. There appears to be little difference in the dissolution yield upon changing the solvent/coal ratio from 1 to 4. This confirms the previous results (Figure 1.C.1) that, at the solvent (tetralin)/coal ratio = 1, the concentration of solvent tetralin exists in excess compared to the concentration of coal radicals, and, therefore, further increases in the tetralin concentration do not affect the dissolution yield of coal.

Planned Work

Further reaction time studies will be performed in the presence of LRO or creosote oil as solvent at different concentration levels to discern the effect of hydrogen transfer or physical solubility factors on the dissolution yield. These experiments will provide the basis for the coal dissolution kinetics studies.

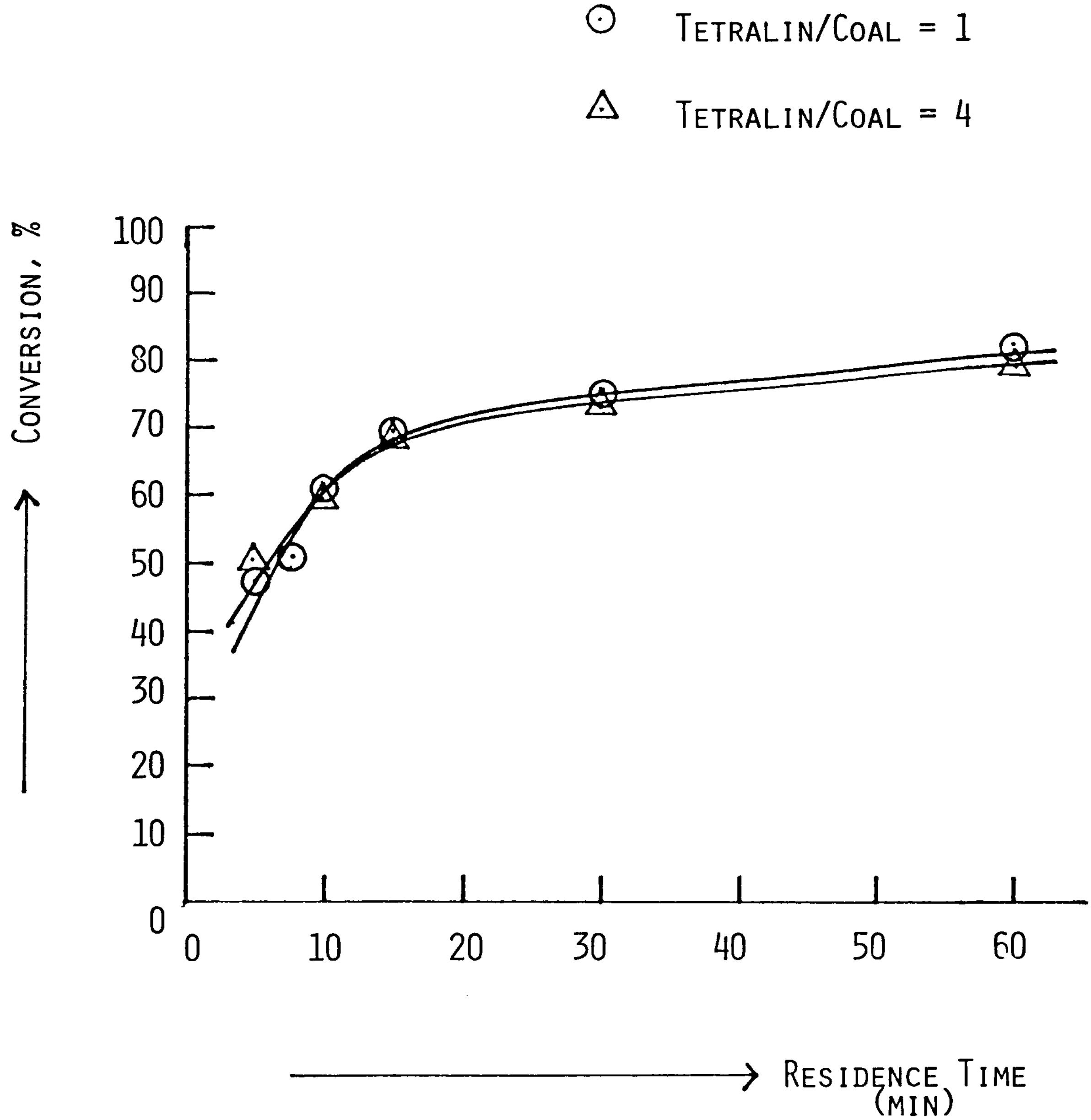


Figure 1.C.2. Time Studies of Coal Dissolution at Different Concentration Levels of Tetralin

1.F. Effects of Chemical Pretreatment on Coal Liquefaction Processes

Objective

The objective of this subtask is to assess the effects of various chemical pretreatments upon processes such as sulfur removal and coal dissolution which occur in the SRC and related coal liquefaction processes.

Progress

During the quarter experiments were performed to investigate the effect of ferric solution pretreatment on the coal liquefaction process. The effect of leaching time and concentration of ferric solution on the sulfur removal and dissolution yield were examined.

Certain coal minerals have been reported to catalyze hydrogenation and/or hydrodesulfurization (HDS) during coal liquefaction by many investigators. An earlier catalyst screening study of Tarrer, et al. (1976) revealed that pyrite appeared to be an ineffective HDS catalyst and resulted in excess hydrogenation. In fact, the presence of pyrite resulted in an increase of sulfur in creosote oil after reaction as compared to that when no catalyst was present. This finding was in agreement with the experiment of present work in which pyrite was added to coal/tetralin slurry before liquefaction. Sulfur content of liquid product increased with the addition of pyrite (Table 1.F.1). A possible back reaction by the H_2S generated during reducing of pyrite was suggested (Tarrer, et al., 1976). The retarding effect of H_2S on HDS was examined by Pitts, et al, (1977) in the study of hydrogenation/HDS of both a bituminous Kentucky No. 9/14 coal and a sub-bituminous Wyodak coal. It was shown that the addition of H_2S prior to reaction decreased the amount of sulfur removal. Further evidence of

Table 1.F.1. Effect of Pyrite on Coal Liquefaction

Liquefaction Conditions:

$T = 415^{o}C$
Tetralin (g)/coal (g) = 2, Time = 30 min, 1000 cpm

Wt. % Pyrite (-200)	% Ash in Coal and Added Pyrite (A')	% Ash in Liquefaction Residue (F)	% Sulfur of Liquid Product	Yield (daf)
0 *	7.5	41.30	.216	88.48
24.80*	19.21 (20.58)	61.96 (61.54)	.373	85.40 (86.97)***
0 **	7.5	28.39	.213	79.55
25.12**	19.32 (20.73)	48.46 (51.23)	.387	74.53 (75.10)

$$\text{Yield} = \frac{F - A'}{F(100-A')} \times 10^{4}$$

% Ash in Coal = 7.5, % Ash corresponding to pyrite = 66.42
* Initial Pressure = 1,200 psig H_2
** Initial Pressure = 1 atm air
*** Numbers in Parentheses are obtained by considering the loss of pyrites during ashing (the loss free basis) and by assuming that FeS_2 is in the form of Fe_7S_8 after liquefaction.

the inhibition of H_2S on catalytic activity was illustrated by comparing the HDS rate of coal-creosote oil-coal ash reaction (Lee, et al., 1977). During the HDS of creosote oil nearly all of the produced H_2S was scrubbed out by the coal ash which thus behaved as an effective HDS agent; whereas in the HDS of coal/creosote oil slurry an excessive amount of H_2S was produced for the coal ash to scrub out which then became ineffective in the HDS reaction. Hence, as far as HDS is concerned, removal of pyrite prior to liquefaction would be advantageous not only by avoiding the production of excessive H_2S but also by reducing the hydrogen consumption.

In the removal of pyrite, an oxidative treatment of coal with aqueous ferric solution was reported by Meyers, et al. (1972)(Figure 1.F.5). Ranges of 84% to 98% of the pyritic sulfur and 40% to 75% of total sulfur were removed depending on the coal characteristics. The Meyers process has been extended to coal liquefaction (Meyers, et al., 1976). Some pyritic sulfur may become sulfate during ferric solution treatment (Hamersma, et al., 1973; Youh, 1977). Nearly all the pyrite and 72% of the total sulfur of a Kentucky No. 9 (Camp) coal and a Meiggs Creek No. 9 (Muskingum) coal were removed in a combination of the two processes for which liquefaction was performed at 425°C, 2000 psig H_2, anthracene oil solvent/coal = 4, residence time = 1 hour. Based on the sulfur content of slurry after reaction, Meyers, et al. (1976) suggested that the filtration step after the liquefaction process be eliminated. This, however, resulted in the need of further removal of ash after combustion but prior to emission into the atmosphere if the product coal so obtained was directly used in a power plant.

In the present work, an experimental evaluation was made of the feasibility for accelerating HDS of coal by varying leaching time and concentration of ferric solution pretreatment. The dissolution yield and HDS of liquid product

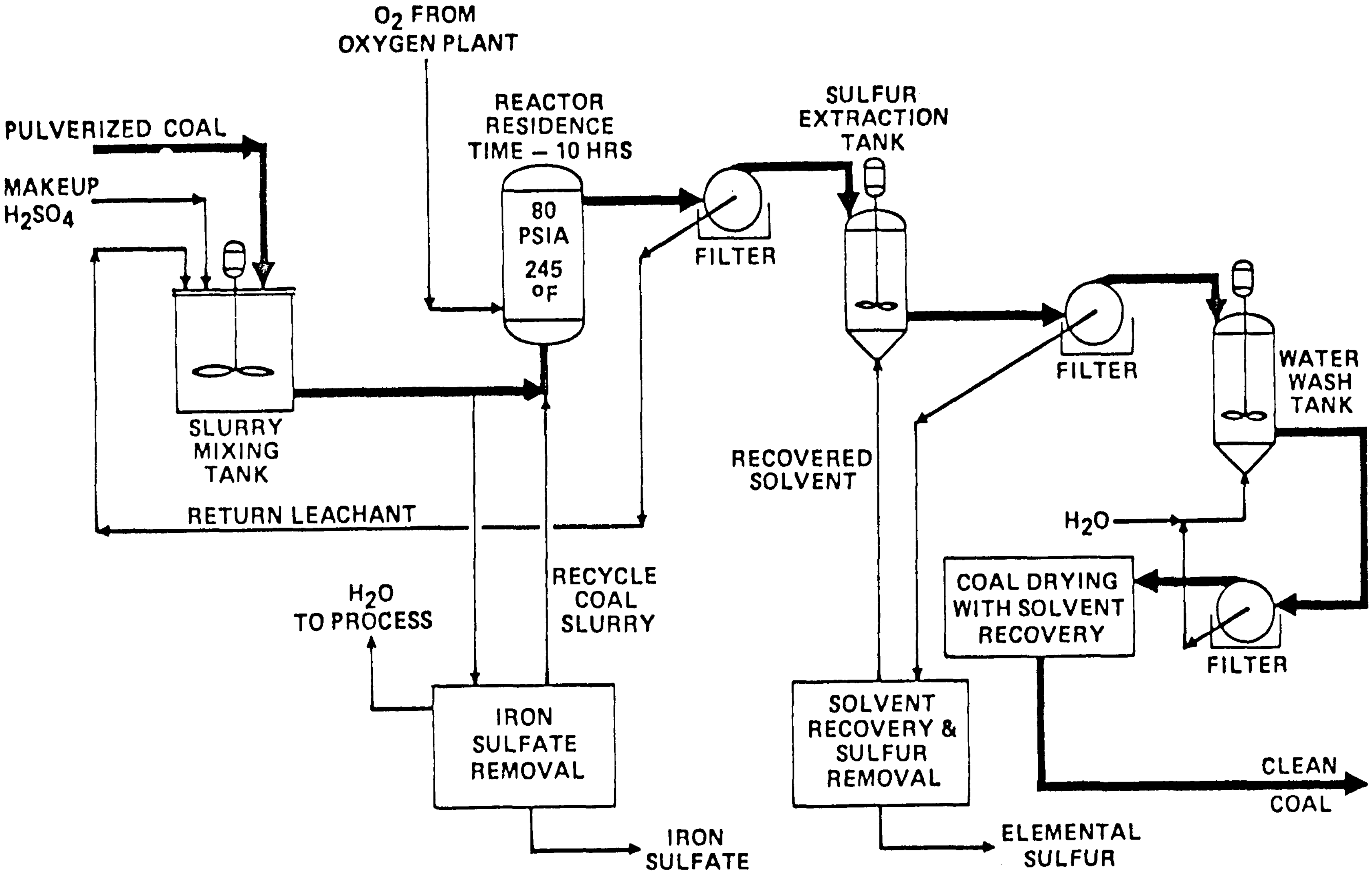


Figure 1.F.5. TRW Meyers Process Flow Diagram

were examined to justify the Meyers process in connection with coal liquefaction.

Experimental

Materials

Ferric sulfate is a reagent grade powder from Matheson Coleman & Bell. The 1M ferric sulfate solution used in this work represents approximately 399.88 gm $Fe_2(SO_4)_3 \cdot xH_2O$ in 1 liter solution. The analytic reagent grade of ferric chloride is from Mallinckrodt. A liter of 1M ferric chloride solution contains approximately 270.3 gm $FeCl_3 \cdot 6H_2O$.

Procedures

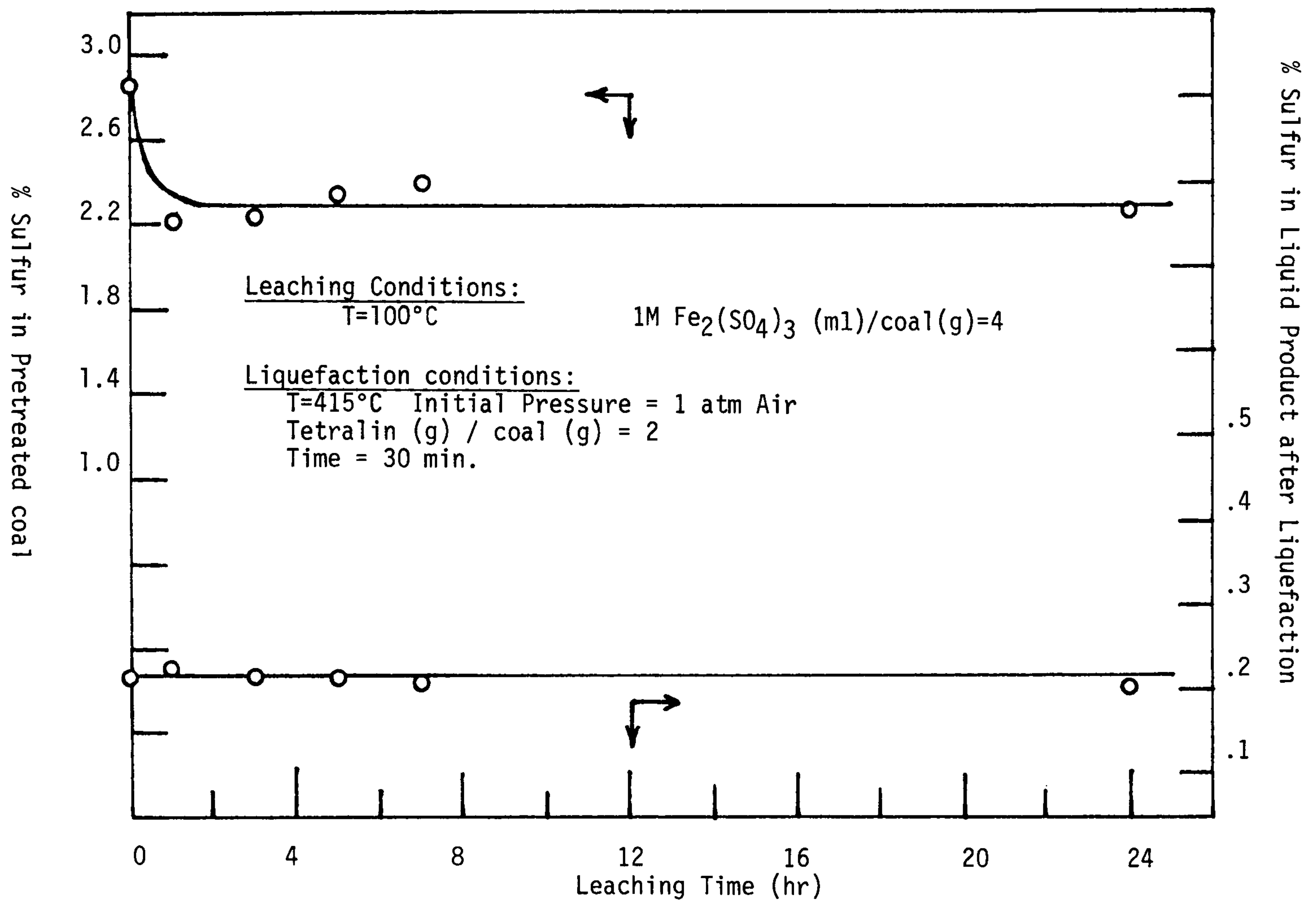
About 10 gm of coal was slurried with 40 ml ferric solution in a 300 ml boiling flask which was then connected to a condenser to maintain the solution in the flask at boiling point (~100°C). After a given leaching time, the aqueous solution was filtered out and the filter cake was washed to remove residual iron salts. The reduced free sulfur in the filter cake was then removed from the coal matrix by toluene extraction, suggested by Meyers, et al., (1972). More than 96% of the coal was recovered. Sulfur analysis was performed to give total, sulfate, and pyritic sulfur contents in the treated coal.

The leached coal which is basically pyrite-free was then followed by liquefaction using a tubing bomb reactor. The dissolution yield and sulfur contents of liquid product and solid residue were obtained.

Results and Discussion

Effect of Ferric Solution Leaching Time

Figure 1.F.1 shows the effect of $Fe_2(SO_4)_3$ leaching time on sulfur content of treated coal and of liquid product after liquefaction. The total sulfur content of coal leached for 24 hours is essentially the same as compared to that of coal leached for 1 hour only. A more detailed analysis for



Leaching Conditions:
T=100°C

1M $Fe_2(SO_4)_3$ (ml)/coal(g)=4

Liquefaction conditions:
T=415°C Initial Pressure = 1 atm Air
Tetralin (g) / coal (g) = 2
Time = 30 min.

Figure 1.F.1. Effect of $Fe_2(SO_4)_3$ Leaching Time on Sulfur Content

different forms of sulfur in the treated coal is presented in Table 1.F.2. It is seen that the pyritic sulfur was reduced from 0.835% to 0.279%. Sulfate sulfur was found to be incompletely removed after washing the leached coal by toluene extraction in our experiments. Examination of sulfur contents of liquid products as shown in Figure 1.F.1 and those of solid residue as shown in Table 1.F.3 revealed that the reducing of pyrite did not significantly affect the HDS in the following liquefaction. In fact, the total sulfur removal for the combined process is practically the same for various leaching time as may be seen in Figure 1.F.2. Since the addition of 25% pyrite into the coal did decrease the HDS in liquefaction as shown in Table 1.F.1 in which the sulfur content of liquid product increased from .22% to .38%, the insignificant HDS effect associated with reducing pyrite in coal may be due to the low pyritic sulfur content (~0.84%) in the Kentucky coal. The retarding effect of H_2S on HDS contributed by the small amount of pyritic sulfur may not be significant. Should the pyritic sulfur content in a coal be significantly higher, the reducing of pyrite would promote the HDS rate in liquefaction as illustrated in Table 1.F.1 and as pointed out by previous research (Tarrer, et al., 1976; Pitts, et al., 1977; Lee, et al., 1977). The dissolution yield as shown in Figure 1.F.2 is nearly the same for various degree of leaching. This indicates that liquefaction is insensitive to the presence of pyrite as may further be seen from Table 1.F.1 in which the addition of 25% pyrite to the coal resulted in only ~5% decrease in yield, which may be considered the same considering the reproducibility of this experiment. This may be as the result of a good hydrogen donor solvent, tetralin, which is considered to be very effective solvent in coal dissolution. Therefore, the catalytic enhancement of coal dissolution by pyrite may not be significant compared to the dissolution by the solvent tetralin alone.

Table 1.F.2. Comparison of Sulfur Reduction and Forms of Sulfur

	Dry Forms of Sulfur (Wt.%) of Leached Coal				% Sulfur of Leached Coal after Liquefaction				
Leaching Time (hr)	Total (1)	Sulfate (2)	Pyritic (3)	Organic (1)-(2)-(3)	Total (1)	Sulfate (2)	Pyritic (3)	Sulfide (4)	Organic (1)-(2)-(3) -(4)
0 *	2.86	.621	.835	1.40	1.75	-	-	-	-
1 *	2.21	.238	.554	1.42	1.28	-	-	-	-
7 *	2.40	.323	.505	1.57	1.13	-	-	-	-
24 *	2.26	.453	.279	1.53	1.28	-	-	-	-
0 *	2.98	.30	.81	1.87	1.35	0	.08	.32	.95
Several hours**	2.26	.28	.02	1.96	.85	0	.01	0	.85

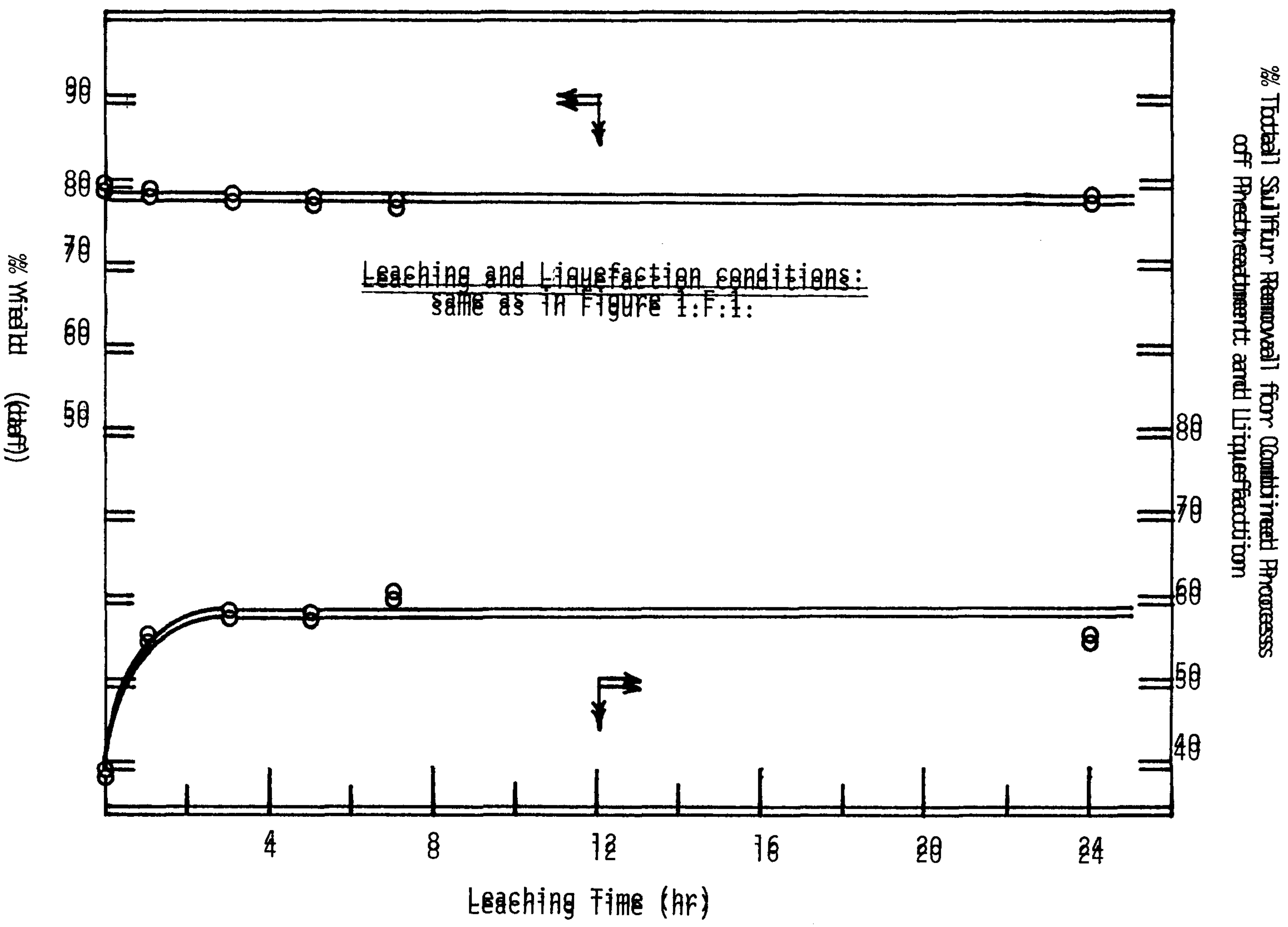
* Leaching and liquefaction conditions are specified in Table 1.F.3. Total sulfur of coal after liquefaction is based on solvent free by assuming that the amount of solvent is the same before and after liquefaction.

** Data of Meyers et al. (1976), leaching conditions were given by Hamersma et al. (1974), Liquefaction Conditions: 425°C, 2000 psig H_2, Residence Time = 1 hr., Anthracene Oil Solvent/Coal = 4.

Table 1.F.3: Effect of $Fe_2(SO_4)_3$ Leaching Time on Coal Liquefaction

Leaching Conditions: T = 100°C, 1M$Fe_2(SO_4)_3$(ml)/coal(gm) = 4
Liquefaction Conditions: T = 415°C; Initial Pressure = 1 atm Air; 1000 rpm
Tetralin (g)/Coal(g) = 2 Time = 30 min.

	Results for Pretreated Coal			Results after Liquefaction for Pretreated Coal					
Leaching Time (hr)	% Ash in Coal (A)	% Sulfur in Coal	% Sulfur Removed by Pretreatment	% Ash in Residual (F)	% Sulfur in Liquid	% Sulfur in Residue	% Sulfur Removed by Liquefaction	Yield (daf)	% Sulfur Removed by Combined Process
0	7.5	2.86	0	28.39	.213	4.4	38.95	79.55	38.95
1	5.43	2.21	22.73	21.46	.225	2.60	42.31	78.99	55.42
3	5.54	2.23	22.03	21.21	.211	2.36	46.46	78.21	58.25
5	5.39	2.34	18.18	20.55	.213	2.36	48.59	77.97	57.94
7	5.21	2.40	16.08	19.48	.207	2.12	52.75	77.28	60.35
24	5.25	2.26	20.98	20.18	.203	2.78	43.32	78.08	55.21



Leaching and Liquefaction conditions: same as in Figure 1.F.1.

Figure 1.F.2. Effect of $Fe_2(SO_4)_3$ Leaching Time on coal Liquefaction

Since only about 67% of the pyritic sulfur was removed (reduced from 0.835% to 0.279%) even after 24 hour leaching, test runs for the reaction between pure pyrite and ferric solution were made to determine the extent of this reaction. As shown in Table 1.F.4 only 34% dissolution after 24 hours was achieved as compared to 99.5% dissolution after 16 hours reported by Meyers, et.al. (1972). In fact, various claims have been made in much earlier work as noted by Meyers, et al. (1972). Those included (1) that ferric salts do not attack pyrite or (2) that the extent of reaction ranges from 50 to 80 percent (Mellor, 1935). Thus, further study is needed to examine the reaction between pyrite and ferric solution.

Effect of Ferric Solution Concentration

The effects of $Fe_2(SO_4)_3$ concentration on sulfur content and total sulfur removal for the combined process are shown in Figure 1.F.3 and 1.F.4. It is seen that both 2M and 0.25M ferric solutions removed practically the same amount of sulfur. Since the dissolution of pyrite is low for 1 hour of leaching time (Table 1.F.4), the pyrite reduction in coal using ferric solutions of various concentrations may not be significantly different. Thus the high concentration of ferric solution does not improve the HDS for a short leaching time. The yield corresponding to 2M solution as shown in Figure 1.F.4 is not much different from that corresponding to 0.25M solution. This may be due to the insensitiveness of liquefaction to the presence of pyrite as was pointed in the previous section. The data of Figures 1.F.1-1.F.2 and 1.F.3-1.F.4 are tabulated in Tables 1.F.3 and 1.F.5, respectively.

Conclusions

1. An addition of pyrite to coal before liquefaction decreases the hydrodesulfurization rate. Thus, a significant removal of FeS_2 prior to liquefaction,

Table 1.F.4. Extent of Pyrite-Ferric Solution Reaction[1]

	% of Pyrite Dissolved in Ferric Solution			
	$Fe_2(SO_4)_3$		$FeCl_3$	
Particle Size of Pyrite *	1 hr Reaction[2]	24 hr Reaction[3]	16 hr Reaction[4]	24 hr Reaction[3]
-34 +48	-	-	-	18.06
80% Min. through 50 mesh	5.14	19.14	-	-
-200	-	22.31	99.5	33.64

* From Matheson Coleman & Bell

[1] Reaction Temperature = 100°C

[2] 1.5 g Pyrite + 25 ml 0.5M Solution,

[3] 1.5 g Pyrite + 50 ml 0.5M Solution

[4] Dissolved in 1M Solution, Data of Meyers, et al., (1972)

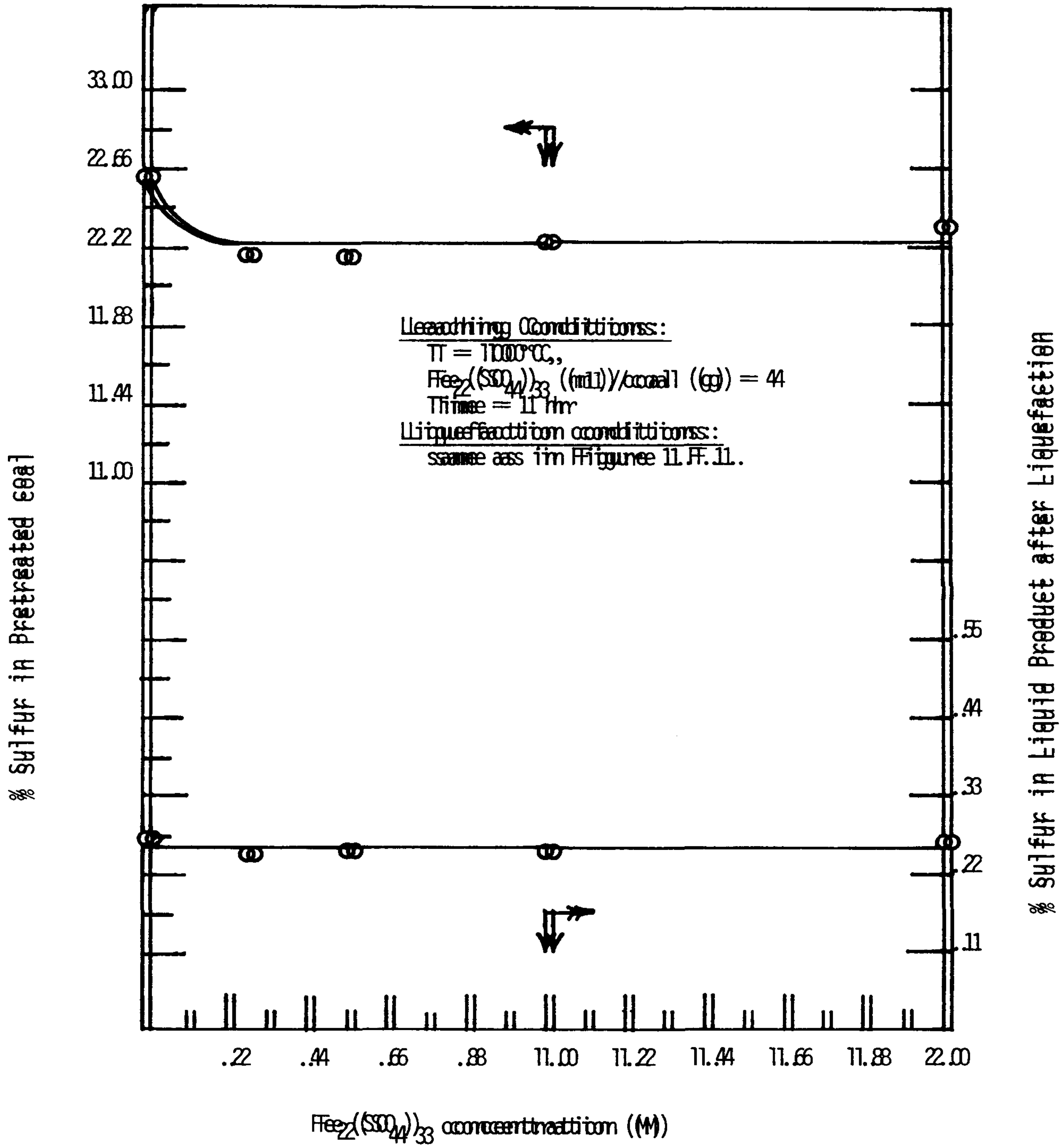


Figure 1.F.3. Effect of $Fe_2(SO_4)_3$ concentration on Sulfur Content

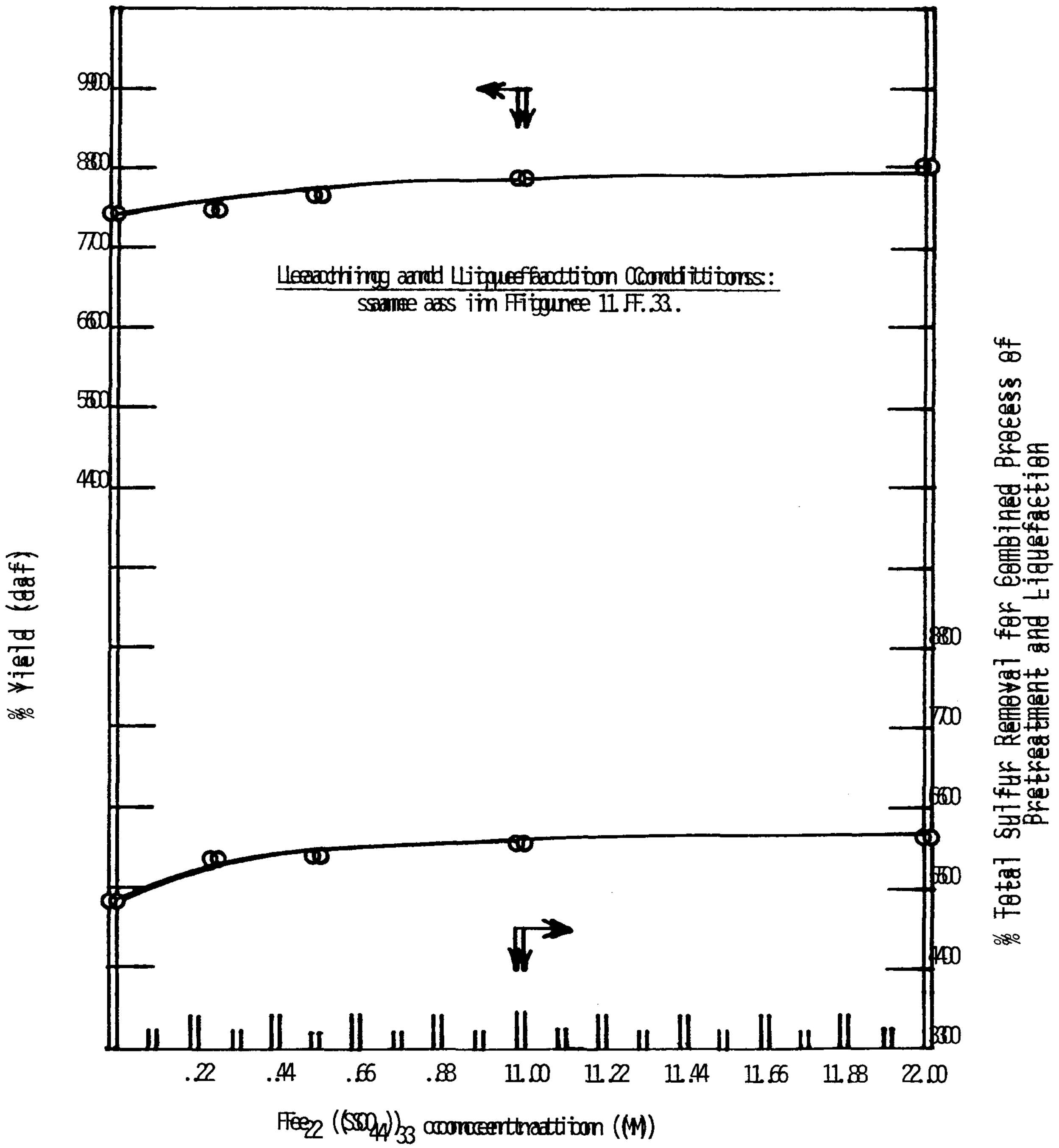


Figure 1.F.4. Effect of $Fe_2(SO_4)_3$ concentration on Coal Liquefaction

Table 1.F.5. Effect of $Fe_2(SO_4)_3$ Concentration on Coal Liquefaction

Leaching Conditions: T = 100°C, $Fe_2(SO_4)_3$ (ml)/coal(gm) = 4
Time = 1 hr.
Liquefaction Conditions: Same as in Table 1.F.3.

	Results for Pretreated Coal			Results after Liquefaction for Pretreated Coal					
$Fe_2(SO_4)_3$ Concentration (M)	% Ash in Coal	% Sulfur in Coal	% Sulfur Removed by Pretreatment	% Ash in Residue	% Sulfur in Liquid	% Sulfur in Residue	% Sulfur Removed by Liquefaction	Yield (daf)	% Sulfur Removed By Combined Process
0 *	6.95	2.56	10.49	22.43	.243	2.68	41.99	74.17	48.08
0.25	6.74	2.16	24.48	22.27	.221	2.41	38.61	74.77	53.64
0.5	6.19	2.15	24.83	21.94	.228	2.47	38.74	76.52	53.95
1	5.43	2.21	22.73	21.46	.225	2.60	42.31	78.99	55.42
2	5.17	2.29	19.93	21.65	.236	2.54	45.11	80.27	56.05

*Leached with Distil Water at T = 25°C

with the result that the H_2S partial pressure is greatly lowered may then avoid the formation of sulfur species by the possible undesired reverse reaction and would give an improved desulfurization for a coal with high pyritic sulfur content.

2. The sulfur content of liquid product after liquefaction is not significantly reduced by ferric solution pretreatment for the Kentucky coal which contains low pyritic sulfur.

3. The dissolution yield is insensitive to the pressence of pyrite.

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. Catalysis by Coal Mineral Matter

Objective

The objectives of this task are as follows:

(1) To identify rate limiting steps in hydrogenation, hydrodesulfurization, and liquefaction reactions in different ranges of the process variable space that are of practical significance in SRC processing.

(2) To evaluate the activity and selectivity of various coal mineral catalysts in the different regions of practical significance in SRC processing.

(3) To identify the characteristics of coal mineral catalysts that prove to be active and selective for hydrogenation, desulfurization, and liquefaction reactions.

(4) To identify processing requirements for preparation and/or regeneration of coal mineral catalysts. This work should establish a basis from which a preliminary evaluation of the technical/economic feasibility of commercial-scale application of coal mineral catalysis can be made.

Progress

It is well known that coal minerals catalyze liquefaction, hydrogenation, and hydrodesulfurization in coal conversion processes. It has been shown earlier (Guin, et al., 1976, 1977, 1978) that coal minerals or other added catalysts are thought to replenish the hydrogen donor solvent in order to maintain the proper level of hydroaromatics and/or are involved directly in hydrogenation and hydrodesulfurization of coal-derived liquids such as asphaltenes or preasphaltenes.

Batch autoclave studies were further performed during this quarter to determine the effect of reaction time and amount of mineral matter added on hydrogen consumption, liquefaction, hydrogenation and hydrodesulfurization. in the solvent refined coal process. Mineral matter (SRC residues, oxidized SRC residue, Kentucky 9/14 coal ash) were evaluated. The selectivity of these mineral catalysts for accelerating hydrodesulfurization (HDS) reactions over hydrogenation reaction was evaluated in terms of the reduction of sulfur content of liquid product and hydrogen consumption. Kentucky coal ash (prepared by oxidizing Kentucky coal) and SRC residue ash (oxidized SRC residue obtained from Wilsonville pilot plant) were found to have an appreciable effect on the rate of sulfur removal.

In our earlier studies (Guin, et al., 1976; 1977; 1978) we determined that the mineral matters like reduced iron, CuO, CaO, etc., help in desulfurization. The desulfurization effect in all these cases seems to be not only catalytic, but also scrubbing. At the present time we could not distinguish these two factors. It would be advantageous in the process to use some materials which are readily available and also cheap. For this reason we have tried SRC residue ash and coal ash as possible catalysts for coal liquefaction process.

Table 2A.1 shows the summary of various minerals studied. We see that SRC residue ash and Kentucky coal ash work very well as far as hydrodesulfurization

Table 2.A.1. Effect of Coal Mineral Catalysts in Liquefaction of Coal

Solvent (LRO)/coal = 2, T = 410°C, 120 min., catalyst = 14.3%, 1000 rpm

			Partial Pressure (psig)							
Catalyst	Initial Pressure ($1x10^{-3}$ psig)	Final Pressure ($1x10^{-3}$ psig)	H_2 (10^{-3})	H_2S	CO_2	CH_4	C_2-C_5	% Sulfur Content of Liquid Products	Hf/Ho*	% Yield**
None	2.04	1.65	1.280	77.6	84.2	246	128	0.41	0.63	85.6
None	2.09	1.70	1.250	50.0	70.0	220	110	0.39	0.64	86.0
None	2.00	1.64	1.229	17.4(?)	72	204	118	0.45	0.62	89.7
SRC solids	2.00	1.47	0.909	58	117	240	146	0.43	0.46	76.5+
SRC solids	2.00	1.56	0.739	35	115	206	125	0.37	0.40	77.0+
Slag (Texaco)										
-200 mesh	2.09	1.51	1.077	46	57	200	130	0.4	0.52	90.1
-325 mesh	1.99	1.52	1.072	68	54	206	120	0.45	0.54	90.5
SRC ash										
coarse	2.10	1.44	0.956	8	70	261	145	0.30	0.46	89.3
coarse	2.14	1.43	0.987	4.5	72	230	137	0.29	0.46	89.8
-250 mesh	2.10	1.37	1.150	0	23(?)	74	123	0.35	0.55(?)	88.8
-250 mesh	2.06	1.36	0.980	1.4	72	200	106	0.25	0.48	86.5
-325 mesh	2.04	1.38	1.007	3.3	60	186	124	0.34	0.49	89.2
-325 mesh	2.12	1.43	1.023	2.5	73	214	117	0.34	0.50	89.3
Ky. Coal Ash	2.10	1.46	1.148	0	49	160	103	0.3	0.55	89.2
Ky. Coal Ash	2.06	1.45	1.096	0	62	188	99	0.32	0.53	89.0

* Hf/Ho: the ratio of the final hydrogen pressure to the original

** Yield = (Ash, final-Ash,initial)/Ash,final(1-Ash,initial)

\+ SRC solids-free basis = 98% yield, actual valve: between 77 and 98%

is concerned, but the hydrogen consumption in the presence of these catalysts is more than in the "no catalyst" run. Slag (supplied by Texaco) doesn't help in dehydrodesulfurization. This may be due to coating of minerals by silica in the form of glass.

The effect of amount of SRC-residue ash added is also important as far as the SRC process is concerned. Table 2.A.2 shows the results with different amounts of added SRC-residue ash. We see that the addition of SRC-residue ash helps in hydrogenation (higher hydrogen consumption), which could also be proved by higher T/N ratio in the case of added SRC-residue ash (T/N ratio 0.33-0.5) than no added catalyst (T/N ratio 0.24). This means that the SRC-residue ash not only maintains the solvent quality but also improves it. We also see that the addition of 1 or 2 g. of SRC-residue ash doesn't help in hydrodesulfurization, but 5g or more of SRC-residue ash helps in hydrodesulfurization as well. Table 2.A.3 also shows the effect of amount of SRC-residue added on total sulfur, SRC sulfur and oil sulfur (The product obtained from autoclave run is filtered to get liquid product and subjected to distillation to recover the light molecular weight substances like oil as top product and SRC solid product as bottom product. Please refer to the details of the separation procedures for the SRC product, attached at the end of this task.). We see that with the addition of 20 g. of SRC residue ash (14.3% of total slurry) the SRC sulfur is reduced by 22 percent over non-catalytic run using the same reaction parameters.

In the earlier work (previous progress report) we evaluated the effect of SRC-residue ash on SRC process. We reported the effect of reaction time on product distribution, liquid sulfur, and yield. During this quarter we performed similar studies with Kentucky coal ash. Table 2.A.4 and Fig. 2.A.1 shows the catalystic effect of Kentucky coal ash on conversion, liquid sulfur and hydrogen consumption. Comparing the results of Kentucky coal ash and that

Table 2.A.2: Effect of SRC Residue Ash Concentration in Liquefaction of Coal

Solvent (LRO)/coal = 2; T = 410°C; 120 min.; 1000 rpm

Catalyst (grams)	Initial Pressure (1x10-3 psig)	Final Pressure (1x10-3 psig)	Partial Pressure (psig)					% Sulfur Content of Liquid Products	Hf/Ho*	% Yield**
			H_2 (10^{-3})	H_2S	CO_2	CH_4	C_2-C_5			
1	2.03	1.52	1.01	22	63	186	104	0.49 (?)	0.53	90.0
	2.06	1.55	1.034	22	66	192	101	0.43	0.54	90.0
2	2.05	1.49	0.971	18	64	187	115	0.46	0.51	91.5
	2.05	1.38	0.853	37	65	183	107	0.47	0.45	91.0
5	2.07	1.31	0.819	12.6	64	173	107	0.45	0.42	91.2
	2.11	1.36	0.870	12	60	185	98	0.45	0.46	91.6
10	1.92	1.34	0.887	13	58	152	85	0.36	0.50(?)	90.8
	2.11	1.46	0.968	7.5	59	188	103	0.34	0.54(?)	91.0
15	2.05	1.33	0.776	5.8	74	226	113	0.34	0.41	91.2
	2.01	1.32	0.821	7	70	170	117	0.35	0.44	91.2
20	2.10	1.44	0.866	7.3	63	236	133	0.30	0.44	89.3
	2.14	1.43	0.894	4	65	208	125	0.29	0.45	90.0

*,** refer to Table 2.A.1.

Table 2.A.3. Effect of SRC Ash Catalyst on Sulfur Content of SRC and Oil Fractions

Solvent (1RO)/coal=2, T=410°C, Pi=2000 psi H_2
120 min., 1000 rpm

Wt.% Catalyst	% Sulfur in Liquids	% Sulfur in SRC	% Sulfur in Oil
0	0.43	0.81	0.21
0	0.44	0.82	0.23
0	0.49	0.77	0.25
7.7	0.35	0.69	0.21
7.7	—	0.7	0.26
13.3	0.32	0.64	0.23

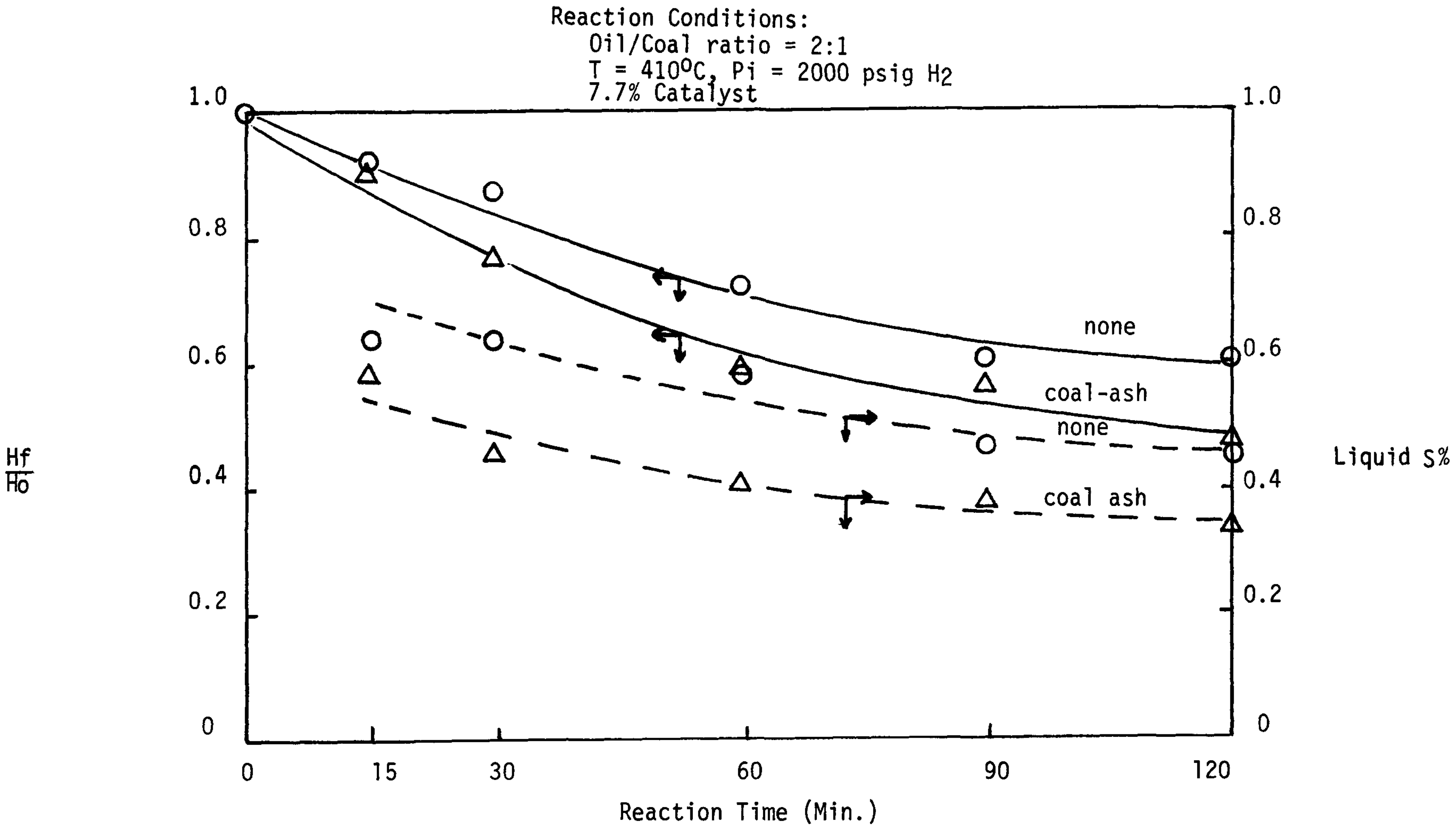
Table 2.A.4. Effect of Kentucky Coal Ash in Liquefaction of Coal

Solvent (LRO)/coal=2, T=410°C, 1000 rpm

				Partial Pressure (psig)						
Catalyst	Reaction Time (min.)	Initial Pressure (1×10^{-3} psig)	Final Pressure (1×10^{-3} psig)	H_2 (10^{-3})	H_2S	CO_2	CH_4	C_2-C_5	% Sulfur Content of Liquid Products	Hf/Ho*	% Yield**
None	15	2.00	1.94	1.713	13	40	26	13	0.64	0.92	79.8
None	30	2.00	1.91	1.632	13	40	56	34	0.64	0.88	84.3
None	60	2.00	1.75	1.360	20	56	109	70	0.46	0.73	87.6
None	90	2.00	1.65	1.136	16 (?)	50	144	79	0.46	0.61	88.8
None	120	2.00	1.64	1.127	16 (?)	66	187	109	0.45	0.61	89.7
Ky. Coal Ash (10 gr)	15	2.03	1.92	1.712	0	40	18	15	0.59	0.90	80.5
Ky. Coal Ash	30	2.03	1.73	1.46	1	46	54	34	0.46	0.77	84.4
Ky. Coal Ash	60	2.04	1.47	1.122	0:1	48	100	65	0.41	0.59	88.7
Ky. Coal Ash	90	2.08	1.52	1.105	1	54	137	88	0.38	0.57	88.2
Ky. Coal Ash	120	2.04	1.45	0.912	1.8	70	210	121	0.34	0.48	88.0

*,** refer to Table 2.A.1.

Figure 2.A.1. Effect of Reaction Time on Hydrogen Partial Pressure (Hf/Ho) and on Sulfur Content of Liquid Products with and without Ky. Coal Ash Present During Reaction



of SRC residue ash (previous progress report) we find that they are almost identical except for lower yield (15 and 30 min. reaction time) in the case of Kentucky coal ash as opposed to SRC-residue ash.

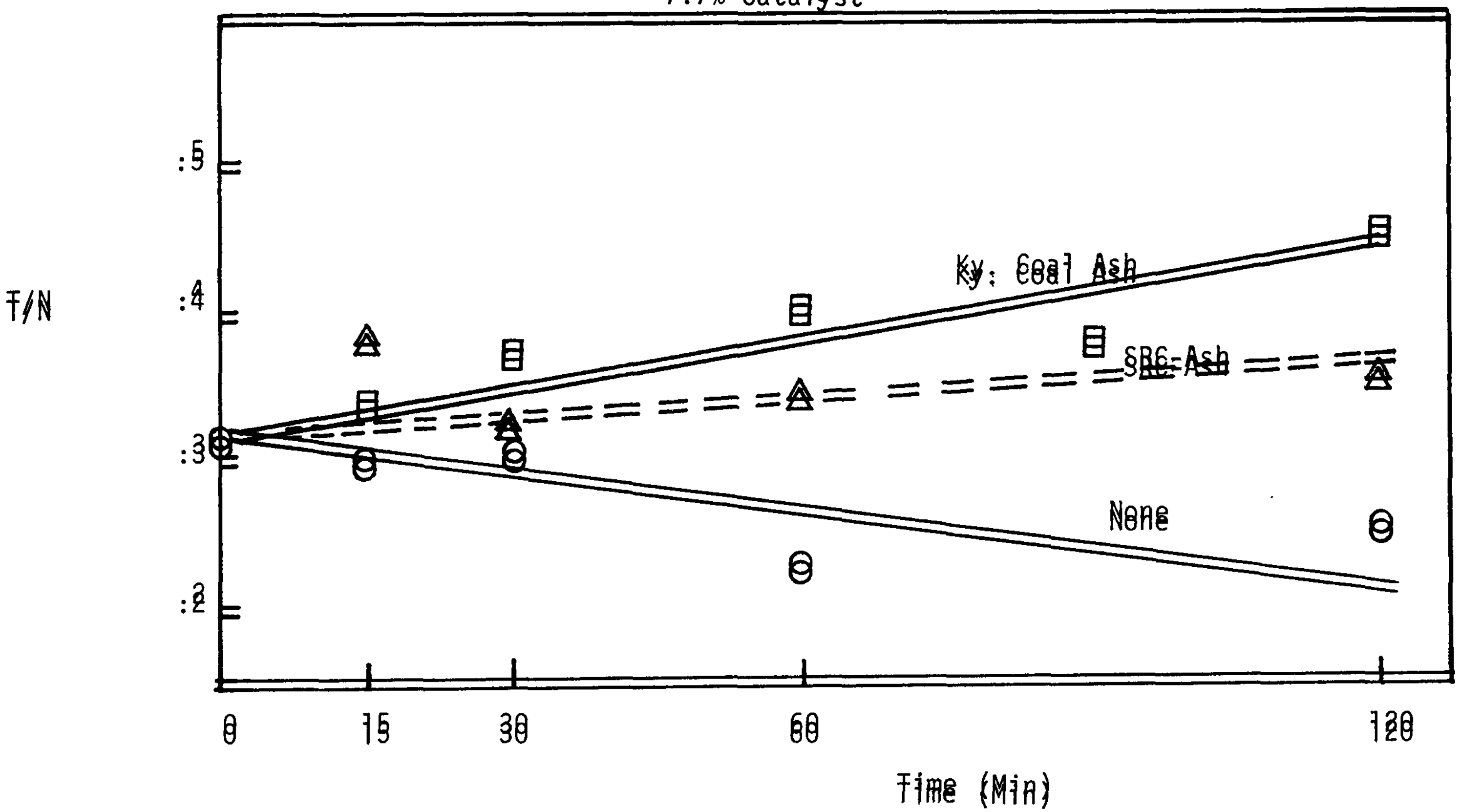
So far we looked at liquid sulfur and yield, but little mention has been made about solvent quality. This is one of the most important characteristics of the use of mineral matter in SRC process. Fig. 2.A.2 shows the variation of T/N (Tetralin/Naphthalene) ratio with reaction time in the presence of no catalyst, SRC residue ash, and Kentucky coal ash. The starting recycle solvent has a T/N ratio of 0.33. In the absence of catalyst the T/N ratio decreases with reaction time. This means that the hydrogen donating capability of the solvent decreases with time. Fig. 2.A.3 shows the process scheme for SRC process with no catalyst. We see that we have to use a rehydrogenator to upgrade the solvent recovered by distillation to improve its T/N ratio to 0.33 consuming additional hydrogen gas. On the other hand in the presence of SRC-residue ash or coal ash the T/N ratio increases with reaction time resulting in better quality solvent than solvent than the starting recycle solvent (i.e. higher hydrogen donating capability). Thus, we do not require additional rehydrogenation. Also, the improved quality of solvent would ultimately result in lower hydrogen consumption in subsequent runs. Fig. 2.A.4 shows the process scheme for the SRC process with SRC-ash catalyst. This way we can conclude that higher hydrogen consumption in the case of coal ash or SRC-residue ash is partly due to hydrogenation of solvent which will be compensated in the following runs, while additional hydrogen will be needed to upgrade the solvent recovered in no catalyst runs.

Earlier studies in this laboratory showed that CaO aids in desulfurization (acts as a scrubber), but doesn't aid in liquefaction. In order to utilize the hydrogenating capability of SRC-residue ash and desulfurization capability of CaO, a mixture of SRC-residue ash and CaO was tried as a catalyst. Table

Figure 2.A.2. Effect of Reaction Time on Tetralin/Naphthalene (TN) Ratio of Liquid Products

Reaction Conditions:

Oil/Coal ratio = 2:1
T = 410C, P_i = 2000 psig H_2
7.7% Catalyst



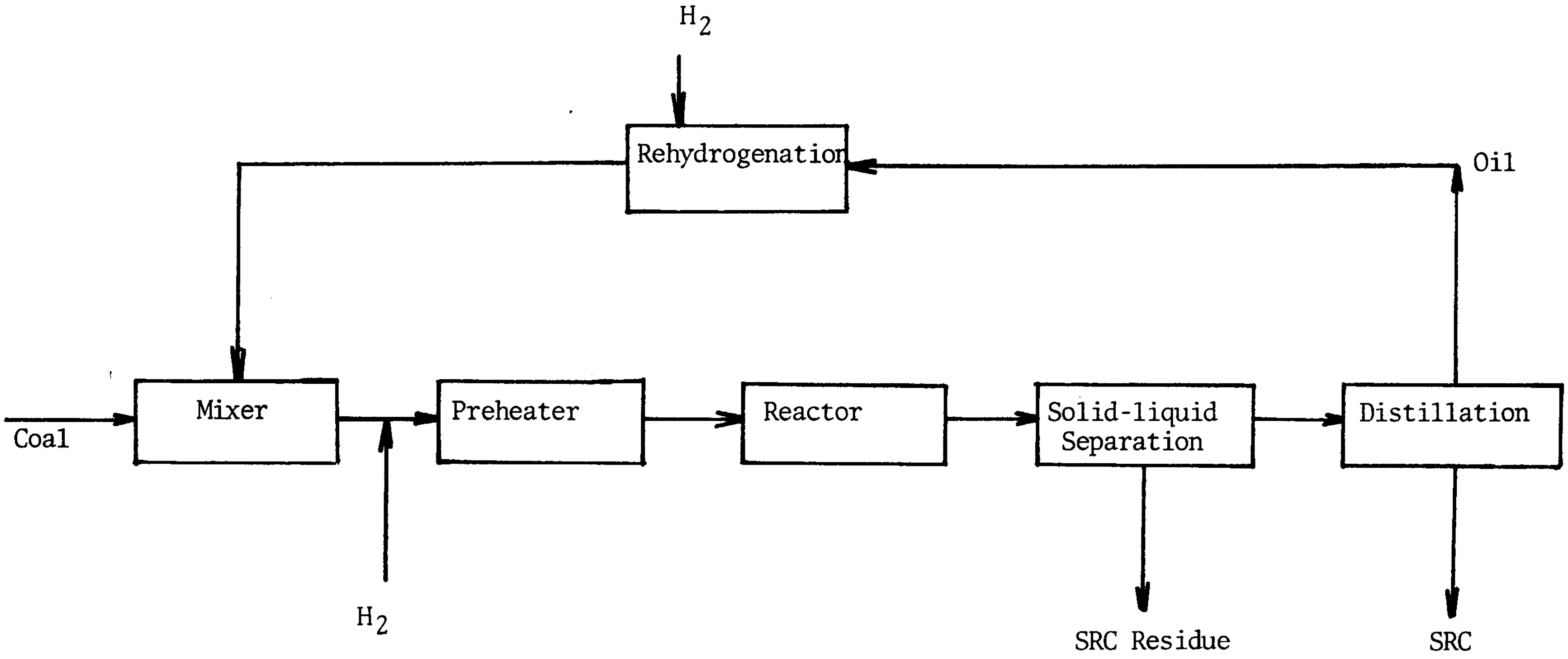


Figure 2.A.3. SRC Process Scheme with No Catalyst

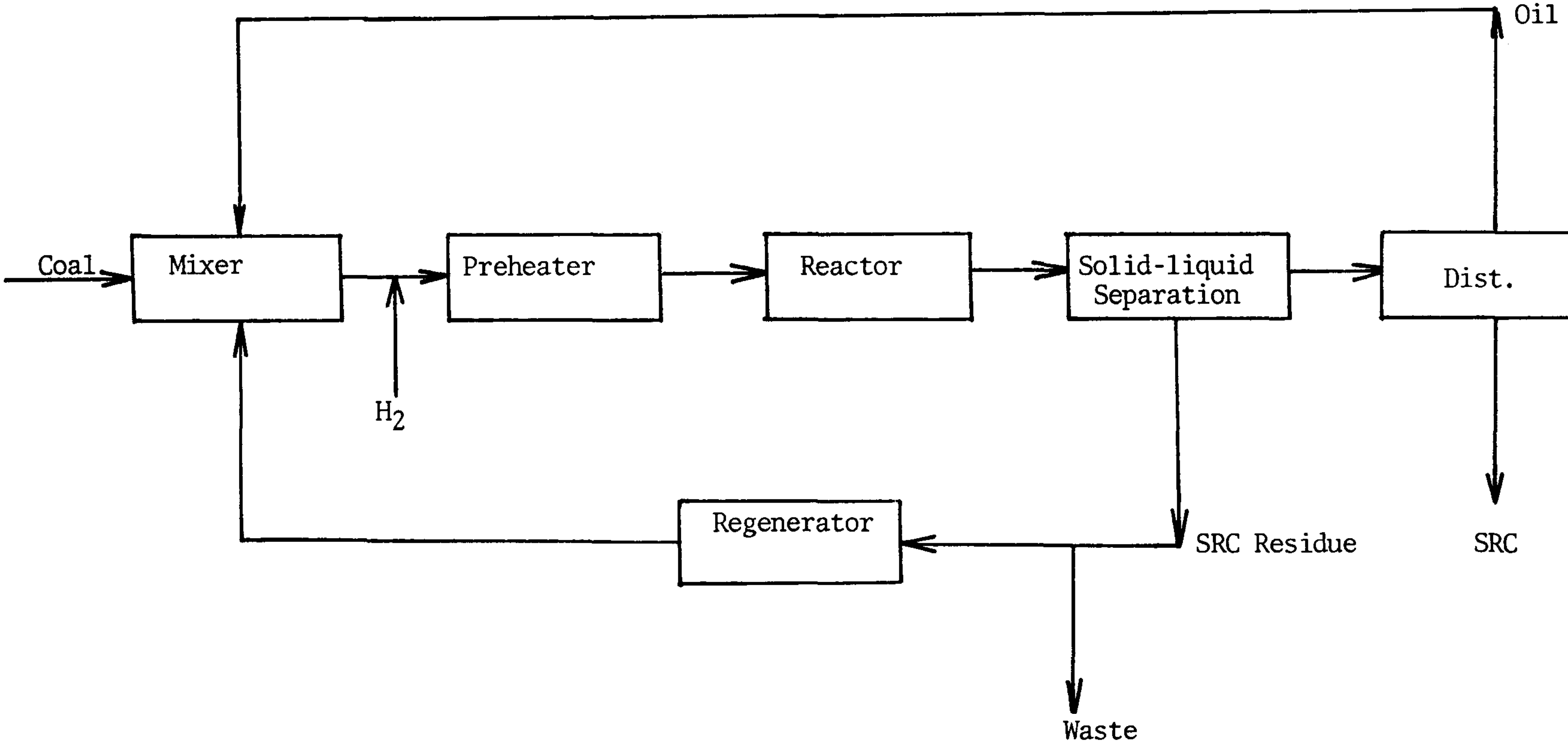


Figure 2.A.4. SRC Process with SRC-Residue Ash As Catalyst

Table 2.A.5: Effect of CaO with SRC Ash in Liquefaction of Coal

Solvent (LRO)/coal=2; T=410°C; 1000 rpm; 120 min.

Catalyst	Initial Pressure (1×10^{-3} psig)	Final Pressure (1×10^{-3} psig)	Partial Pressure(psig) H_2 (10^{-3})	H_2S	CO_2	CH_4	C_2-C_5	% Sulfur Content of Liquid Products	Hf/Ho*	% Yield**
10 gr SRC Ash	1.92	1.34	0.887	13	58	152	85	0.36	0.50	90.8
	2.11	1.46	0.968	7.5	59	188	103	0.34	0.54	91.0
10 gr SRC Ash + 1 gr CaO	2.02	1.41	0.928	13	24	205	105	0.35	0.51	91.1
	2.09	1.45	0.891	11	39	245	129	0.36	0.47	91.9
10 gr SRC Ash + 2 gr CaO	2.00	1.45	1.056	0	3	140	116	0.39	0.58	92.3
	1.87	1.33	0.964	5	2	142	81	0.34	0.58	89.6
	2.00	1.40	1.014	0	0	145	105	0.34	0.56	89.9
10 gr SRC Ash + 3 gr CaO	1.95	1.40	0.967	0	0	183	114	0.34	0.55	81.0

*,** refer to Table 2.A.1.

2.A.5 shows the results obtained with various combinations of SRC-residue ash and CaO. We found that there was no improvement in lowering of liquid sulfur percentage. On the other hand use of 3g CaO or more severely affected the yield and it dropped drastically. Further studies related to negative effect of CaO are needed to explain this phenomenon.

Separation Procedures for SRC Product

The distillation process is used to separate the solvent refined coal (SRC) from the oil portions. This distillation is performed after filtration to remove the catalyst and unreacted coal.

Procedure

Filtration

The operator first filters the hot autoclave mixture through a Büchner funnel fitted with Whatman #50 hardened filter paper. The SRC and and light recycle oil passes through as filtrate and the residue and unreacted coal remains as filter cake. The SRC and light recycle oil are collected in a 125 ml flask (see Fig. 2.A.5). The residue is washed with tetrahydrofuran (THF) until the filtrate is clear. The filter papers are collected in a 400 or 500 ml beaker. The filter papers are changed as needed. After the sample is filtered, the sample vial is washed with a stream of THF washing the solid particles onto the last piece of filter paper. Then the filter paper is added to the beaker.

The filter papers are then removed leaving the residue in the beaker. About 200 ml of hot cresol is added and heated until near boiling. The cresol mixture is then filtered through a Büchner funnel fitted with Whatman #50 hardened filter paper and washed with THF until a clear filtrate is coming through the filter paper. The filter paper is changed as needed always washing

Figure 2.A.5. Filtration Unit

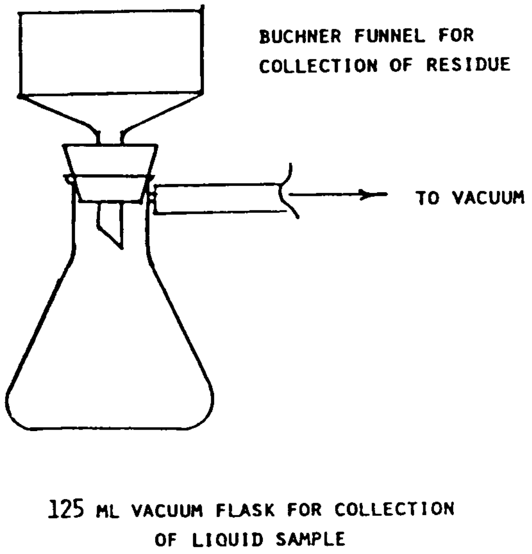
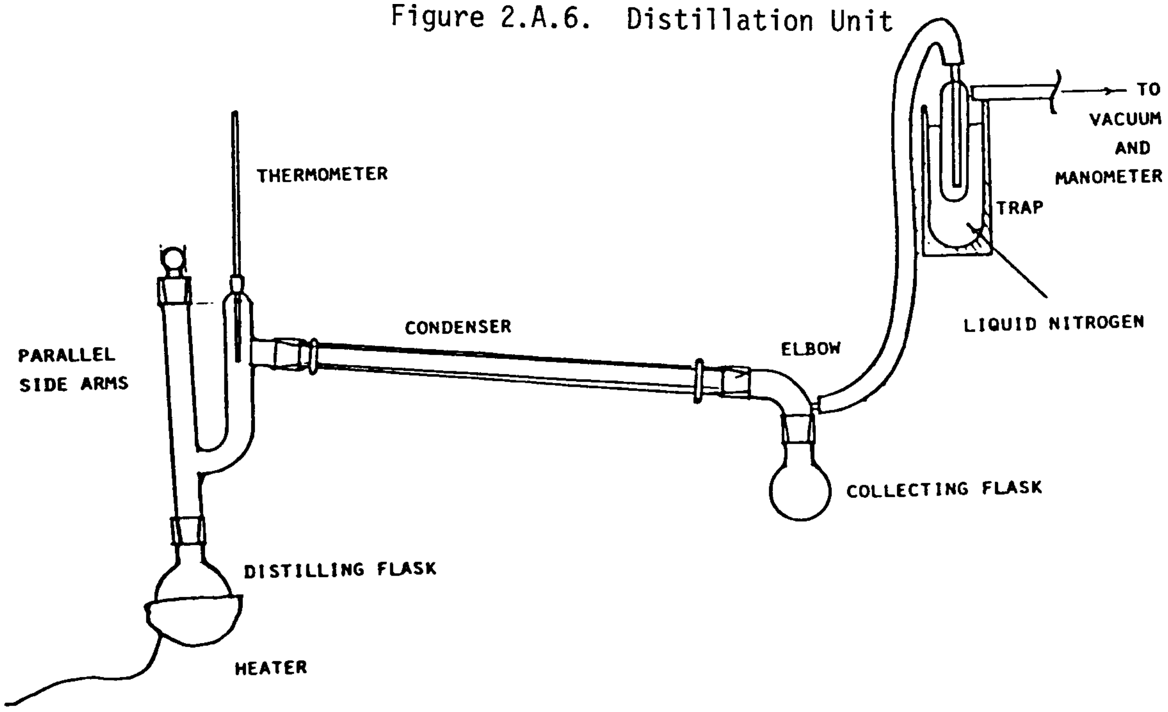


Figure 2.A.6. Distillation Unit



the residue with THF. The next day the sample is placed in a dried and tared combustion boat and placed in an ashing furnace with a flow of oxygen. The temperature is set at about 920°C. The sample is burned for about two hours or to constant weight. The boat is then cooled in a desiccator and weighed, and the ash yield is calculated.

Distillation

At this point the liquid portion of the autoclave sample, collected in the 125 ml flask, is distilled. The sample is first heated to make it less viscous. A small sample (total) is taken and placed in a sample bottle (for sample analysis), and the rest is poured into the distilling flask (see Fig. 2.A.6). Under a vacuum the sample is heated gently at first, then the temperature is raised slowly until the oil distills off freely. When the distillation temperature reaches about 230-260°C under 28 inch Hg vacuum pressure, the heat is turned off. The apparatus is allowed to remain under vacuum for about twenty minutes.

Each part of the apparatus is weighed before and after the distillation. The differences in weights are calculated. A mass balance is calculated: 1) the difference in weight of the parallel side arms is added to the bottom product, and 2) the difference in weight of the elbow, condenser, and thermometer is added to the top product. Then the percent sulfur of the top product, bottom product, and total sample is determined by Leco sulfur analysis.

Reactivity of Demineralized Coals

During this quarter, the reactivity of coals demineralized by acid extraction and magnetic separation has been examined in the small tubing-bomb reactor. The reactivity of demineralized coals has been obtained based on product distributions in terms of oil and gases, asphaltene, preasphaltene and pyridine insolubles. A strong hydrogenation catalyst, Co-Mo-Al, and two different solvents, tetralin and light recycle coil (LRO) have been tested for this purpose.

In Table 2.A.6, when the untreated Kentucky coal was reacted in the tetralin solvent (runs A and B), the presence of Co-Mo-Al as catalyst (run B) seems to significantly enhance the liquefaction yield, that is, about 13% increase in benzene solubles and 14% increase in pyridine solubles. Acid demineralized Kentucky coal (runs C and D) was also found to be reactive in the presence of Co-Mo-Al as catalyst, that is, about 29% increase in benzene solubles and 11% increase in pyridine solubles. In Table 2.A.7, magnetically demineralized Illinois coal shows a similar trend as does the acid demineralized Kentucky coal — about a 24% increase in benzene solubles and a 13% increase in pyridine solubles. These results indicate that the pretreatment of coals by acid extraction or magnetic separation methods does not alter significantly the reactivity of organic material in the coal matrix when reacted in tetralin solvent in the presence of Co-Mo-Al as catalyst. These results could indicate beneficial physical or chemical pretreatments in coal liquefaction in the sense of ash material removal prior to the coal liquefaction reactions.

The results obtained from the studies of solvent effects in coal liquefaction using two different solvents, tetralin and LRO, have been summarized in Tables 2.A.8 and 2.A.9. In Table 2.A.8, runs I and II show the different results in coal dissolution. Apparently, LRO is much better with respect to pyridine solubles, that is, about 19% higher than tetralin. This phenomenon was further observed in runs with Illinois coal (runs V and VI in Table 2.A.9). Generally, tetralin is considered to be a better hydrogen donor solvent than LRO, because of small amount of hydrogen donor species present in LRO. As discussed under Task 1., LRO could behave completely different from tetralin. In the presence of tetralin as solvent the hydrogen transfer reaction may be the major governing factor in coal dissolution, while in the presence of LRO as solvent there may be another strong governing factor, perhaps the strong physical solvation of coal derived-species along with the hydrogen transfer

Table 2.A.6. Reactivity of Acid Demineralized Kentucky Coal

Solvent(tetralin)/coal=2, 410°C
1200 psig H_2, 30 min., ~1000 rpm

Runs	A	B	C	D
demineralization	–	–	Acid	Acid
catalyst (7.7%)	–	Co-Mo-Al	–	Co-Mo-Al
product, %*				
oil + gases	23.3	27.6	17.7	30.8
asphaltene	24.3	33.3	20.3	35.9
benzene insolubles	52.4	39.1	62.0	33.3
preasphaltene	24.8	25.7	29.5	11.8
insolubles	27.6	13.3	32.5	21.5

* mineral matter-free, solvent-free

Table 2.A.7. Reactivity of Magnetically Demineralized Illinois Coal

Solvent (tetralin)/coal = 2, 410^{o}C
1275 psig H_2, 30 min., -1000 cpm

runs	E	F	G
demineralization	-	Magnetic	Magnetic
catalyzt (7.7%)	-	-	Co-Mo-Al
product,%*			
oil + gases	19.6	20.2	38.4
asphaltene	28.5	23.3	29.3
benzene insolubles	51.9	56.6	32.3
preasphaltene	28.5	35.5	24.0
insolubles	23.4	21.1	8.3

* mineral matter-free, solvent-free

Table 2.A.8. Solvent Effect of Kentucky Coal

Solvent/Coal = 2, 410^{o}C
30 min., -1000 cpm

runs	I	II	III	IV
gas, Pi, psig H_2	1210	1275	1200	1275
solvent	tetralin	LRO	tetralin	LRO
catalyst (7.7%)	-	-	Co-Mo-Al	Co-Mo-Al
product,%*				
oil + gases	23.3	19.9	27.6	20.9
asphaltene	24.3	25.1	33.3	34.6
benzene insolubles	52.4	55.0	39.1	44.6
preasphaltene	24.8	46.0	25.7	29.4
insolubles	27.6	9.0	13.3	15.2

*mineral matter-free, solvent-free

Table 2.A.9: Solvent Effect of Illinois Coal

Solvent/Coal = 2, 410°C, 1275 psig H_2
30 minutes, 1000 cpm

runs	V	VI	VII	VIII	IX	X
solvent	tetralin	LRO	tetralin	LRO	tetralin	LRO
demineralization	-	-	Magnetic	Magnetic	Acid	Acid
product,%*						
oil + gases	19.6	13.6	20.2	12.7	24.5	12.2
asphaltene	28.5	35.5	23.3	21.4	24.1	25.7
benzene insolubles	51.9	50.9	56.6	65.9	51.5	62.0
preasphaltenes	28.5	37.9	35.5	38.0	26.6	25.3
insolubles	23.4	13.1	21.1	28.0	24.9	36.7

* mineral matter-free, solvent-free

reaction. Further, more detailed studies to distinguish these two factors are in progress. In the presence of Co-Mo-Al as catalyst two solvents, tetralin and LRO, behave similarly, and enhance benzene solubles about 10 to 13%.

Interesting phenomena have been observed in Table 2.A.9 with respect to the effect of solvent on Illinois coal liquefaction. In the presence of tetralin as solvent (runs V, VII and IX) demineralization of Illinois coal by acid extraction and magnetic separation methods did not significantly affect the product distribution. These indicate well that the presence of mineral matter in coal liquefaction may not be a significant factor when tetralin is used as solvent, because the major governing reaction step is the hydrogen transfer reaction from tetralin to coal-derived free radicals, which by nature is non-catalytic. Contrary to the case with tetralin as solvent, runs with LRO as solvent (VI, VIII and X) show that the presence of mineral matter in coal liquefaction could affect greatly the product distributions, that is, about an 11 to 15% increase in benzene solubles and a 15 to 24% increase in pyridine solubles. These results with LRO as solvent could be explained by the combined effects of hydrogen transfer reaction and physical solvation of coal-derived species. Furthermore, it may be suggested that coal mineral matter may be strongly involved in the catalytic hydrogenation of spent LRO or original LRO solvent. This leads to the higher concentration of hydrogen donor species and consequently the higher yield of coal liquefaction.

Up to now we can observe the difference between two solvents, tetralin and LRO, in the coal liquefaction product distribution, but we can not completely explain the phenomenon. Further studies are necessary to distinguish the governing reaction steps such as hydrogen transfer reaction or physical solvation of coal-derived species. Upon completion of sulfur analysis of each product, the reactivity of demineralized coal by acid extraction or magnetic separation methods in the hydrodesulfurization reaction will be reported in the next progress reports.

Model Compound Studies with Coal Minerals as Catalysts

Further studies in the hydrodesulfurization of model compounds, such as phenyl sulfide and dibenzothiophene, were performed in the small tubing-bomb reactor. Some of oxygen- and nitrogen-continaing model compound studies, such as with benzofuran and benzonitrile have been initiated during this quarter to examine the catalytic activity of coal minerals in hydrodenitrogenation and hydrodeoxygenation reactions.

Hydrodesulfurization of Phenyl Sulfide

Two reaction courses have been reported for the hydrodesulfurization of sulfide compounds (Schuit and Gates, 1973; Weisser and Landa, 1973):

$$\begin{tikzcd} R \cdot S \cdot R' + H_2 \arrow[r] & RSH + R'H \arrow[d, "{[H_2]}"'] \\ & RH + H_2S \end{tikzcd}$$

or

$$R \cdot S \cdot R' + 2H_2 \rightarrow RH + R'H + H_2S$$

As Table 2.A.10 indicates, most of the phenyl sulfide is converted to benzene when hydrogenated in the presence of Co-Mo-Al. The amount of benzene produced is not quantitative because of evaporation of benzene during the handling of samples and therefore the amount of phenyl sulfide converted (first column) is a better measure of the catalytic activity. Any thiophenol production as a reaction intermediate was not apparent as not significant amount of thiophenol was identified in the reaction products. Other mineral catalysts such as Fe, pyrite and SRC residue ash showed 10 to 20% conversion of the phenyl sulfide, while SRC residue and reduced pyrite had essentially no effect. It

Table 2.A.10. Hydrodesulfurization of Phenyl Sulfide in Dodecane

Sample	Catalyst	GC Peak Area Ratio*($X10^3$) Phenyl Sulfide to Dodecane	Benzene to Dodecane
Untreated	---	95.4 ± 3.6	0.0
Treated	none	85.3 ± 4.8	trace
	Co-Mo-Al	0.0	63.8 ± 9.4
	Fe	70.3 ± 3.1	15.8 ± 4.4
	SRC residue	96.7	trace
	SRC residue ash	83.3 ± 4.0	12.9 ± 2.3
	Pyrite	79.5	14.
	Reduced Pyrite	97.	trace

T = 410°C, Pi = 1200 psig H_2, 1000 cpm

10 wt. % phenyl sulfide in dodecane

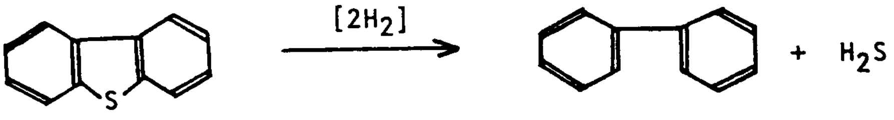
10 wt. % catalyst

* normalized area ratio

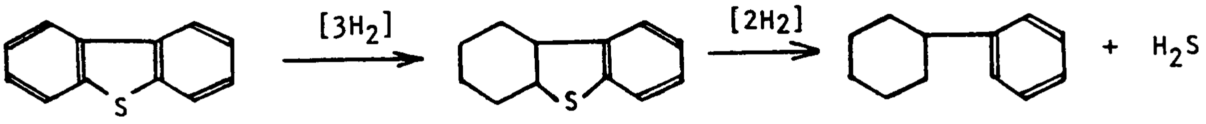
is interesting to note that the activity of representative coal minerals such as Fe, pyrite and SRC residue ash in hydrodesulfurization of phenyl sulfide is significantly lower than in the hydrodesulfurization of benzothiophene or thiophene, in contrast to that of Co-Mo-Al catalyst, which is more active with respect to phenyl sulfide. The activity of Co-Mo-Al in hydrodesulfurization of phenyl sulfide has been reported in the literature as being similar to that in hydrodesulfurization of benzothiphene, which is in agreement with this work (Tables V and VII).

Hydrodesulfurization of Dibenzothiophene

Two reaction courses have been reported for hydrodesulfurization of dibenzothiophene (Schuit and Gates, 1973; Weisser and Landa, 1973)



or



It is generally thought that hydrodesulfurization of dibenzothiophene is more difficult and requires more hydrogen consumption than that of thiophene or benzothiophene.

In Table 2.A.11, as expected, about 30% of the dibenzothiophene was converted when hydrogenated in the presence of Co-Mo-Al. Thus the activity of Co-Mo-Al in hydrodesulfurization of dibenzothiophene is much lower than in the hydrodesulfurization of benzothiophene, phenyl sulfide or thiophene, in agreement with the results reported in the literature. All representative

Table 2.A.11. Hydrodesulfurization of Dibenzothiophene in Dodecane

		GC Peak Area Rato* ($X10^3$)			
			Unknown to Dodecane		
Sample	Catalyst	Dibenzothiophene to Dodecane	#1	#2	Others (5 peaks)
Untreated	---	31.5 ± 1.	0.0	0.0	0.0
Treated	---	32. ± 1.4	0.0	0.0	trace
	Co-Mo-Al	20.5 ± 0.7	3.5±0.7	trace	trace
	Fe	29.8 ± 3.4	0.0	0.0	trace
	SRC residue	31.3 ± 1.2	0.0	0.0	trace
	SRC residue ash	30. ± 2.	0.0	0.0	trace
	Pyrite	27.5 ± 2.1	0.0	0.0	trace
	Reduced Pyrite	30.5 ± 2.9	0.0	0.0	trace

T = 410°C, Pi = 1200 psig H_2, 30 min., 1000 cpm

3 wt. % dibenzothiophene in dodecane

10 wt. % catalyst

* normalized area ratio

coal minerals such as Fe, pyrite, SRC residue, SRC residue ash and reduced pyrite showed only insignificant activity compared to that of the Co-Mo-Al when tested with dibenzothiophene. This may be one reason as to why a significant accumulation of dibenzothiophene has been reported in coal liquefaction streams, particularly in the recycle solvents.

2.B. Bench Scale Continuous Reactor

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. Toward this end, a better process model is being developed for the SRC continuous reactor.

Coal Dissolution and Hydrogen Transfer Kinetics Studies

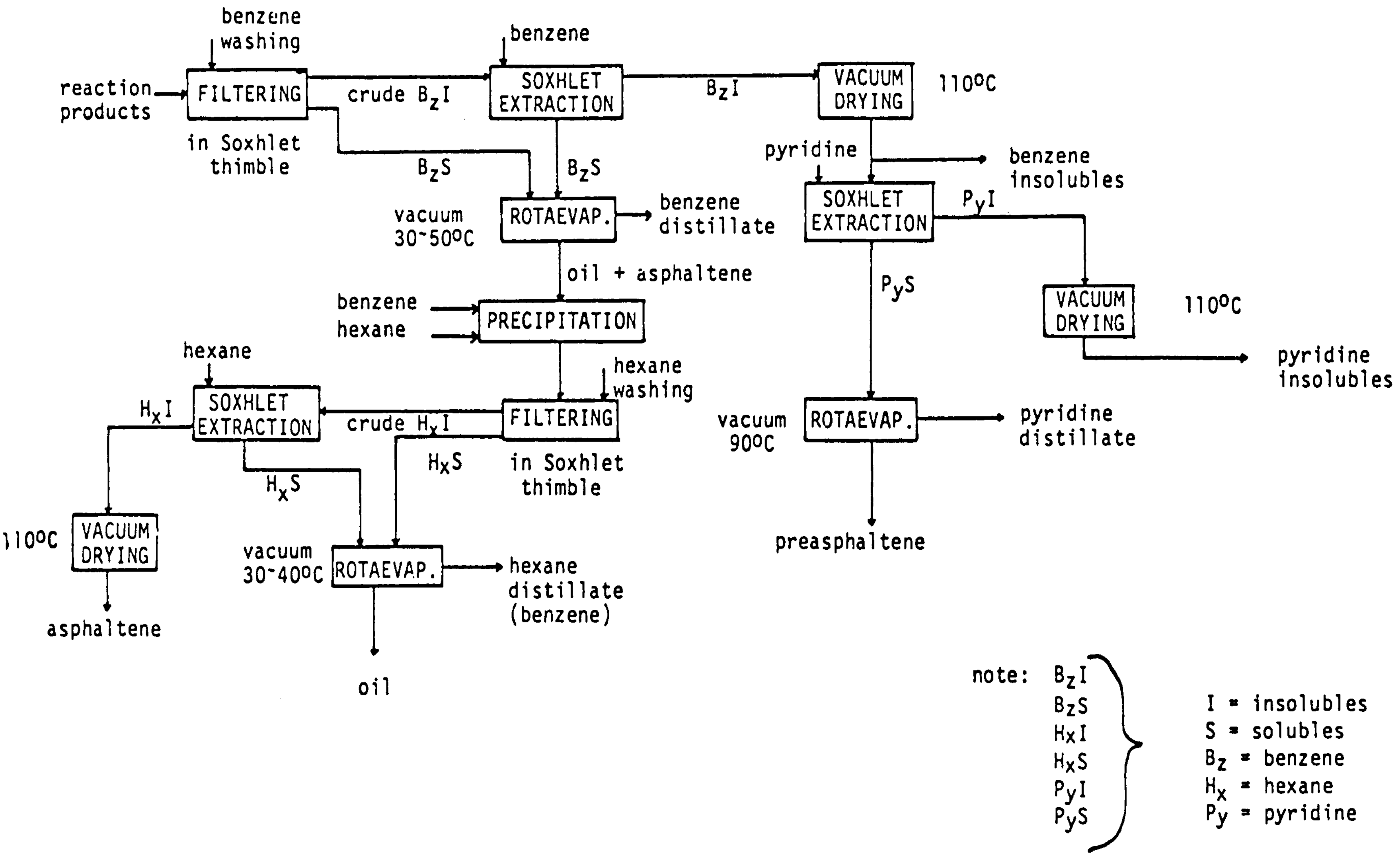
Objective

The objective of this task is to study the coal dissolution and hydrogen transfer kinetics as a function of reaction variables such as reaction temperature and reaction time; and to understand fundamental reaction steps in coal dissolution such as hydrogen transfer and dissolution reactions; and to provide a design basis for the governing reaction kinetics expression for the Solvent Refined Coal process.

Progress

During this quarter extensive kinetics studies of coal dissolution reactions have been performed in the small tubing bomb reactor. Kentucky coal and tetralin as solvent were used for this purpose. Product distribution in terms of oil and gases, asphaltene, preasphaltene and pyridine insolubles was determined by following the conventional solvent extraction scheme as shown in Figure 2.B.1 (refer to the previous progress report, period October-December, 1976). Pentane, benzene (or toluene) and pyridine were used as extraction sol-

Figure 2.B.1. Block Diagram for Separation Procedures



vents. Oil is defined as pentane and benzene soluble; asphaltene as benzene soluble and pentane insoluble; preasphaltene as pyridine soluble and benzene insoluble in the process of the usual atmospheric Soxhlet extraction scheme. The oil fractions were analyzed by G. C. to obtain tetralin conversion to naphthalene, which accounts for the reaction of hydrogen transfer from tetralin to coal-derived free radicals.

As we discussed in Task 1.C., the major reaction step with tetralin as solvent is thought to be hydrogen transfer from solvent tetralin to coal, which results in stabilization of coal-derived free radicals to prevent char formation. The current work has been pursued in further exploration of kinetics of the hydrogen transfer reaction in coal dissolution and of its effect in coal dissolution yield and product distribution. An extensive investigation of several mathematical models with different kinetics expressions has been achieved by computer assistance using the Parameter Estimation method.

Reaction conditions for these experiments are shown in Table 2.B.1.

Table 2.B.1

Reaction Conditions for Kinetic Study

Atmospheric Pressure
Tetralin + Coal = 7.5g
Tetralin : Coal = 1.5:1
Agitation Rate = 600 rpm
Reaction Time = 0 to 60 min.
Reaction Temperature = 350, 380, 410^{o}C

Results and Discussion

At each reaction temperature, 350, 380 and 410^{o}C, the product distributions in terms of oil and gases, asphaltene, preasphaltene and pyridine insolubles were plotted against varying reaction time as shown in Figures 2.B.2, 2.B.3, 2.B.4. The tetralin conversion at different reaction temperatures is also shown in Figure 2.B.5.

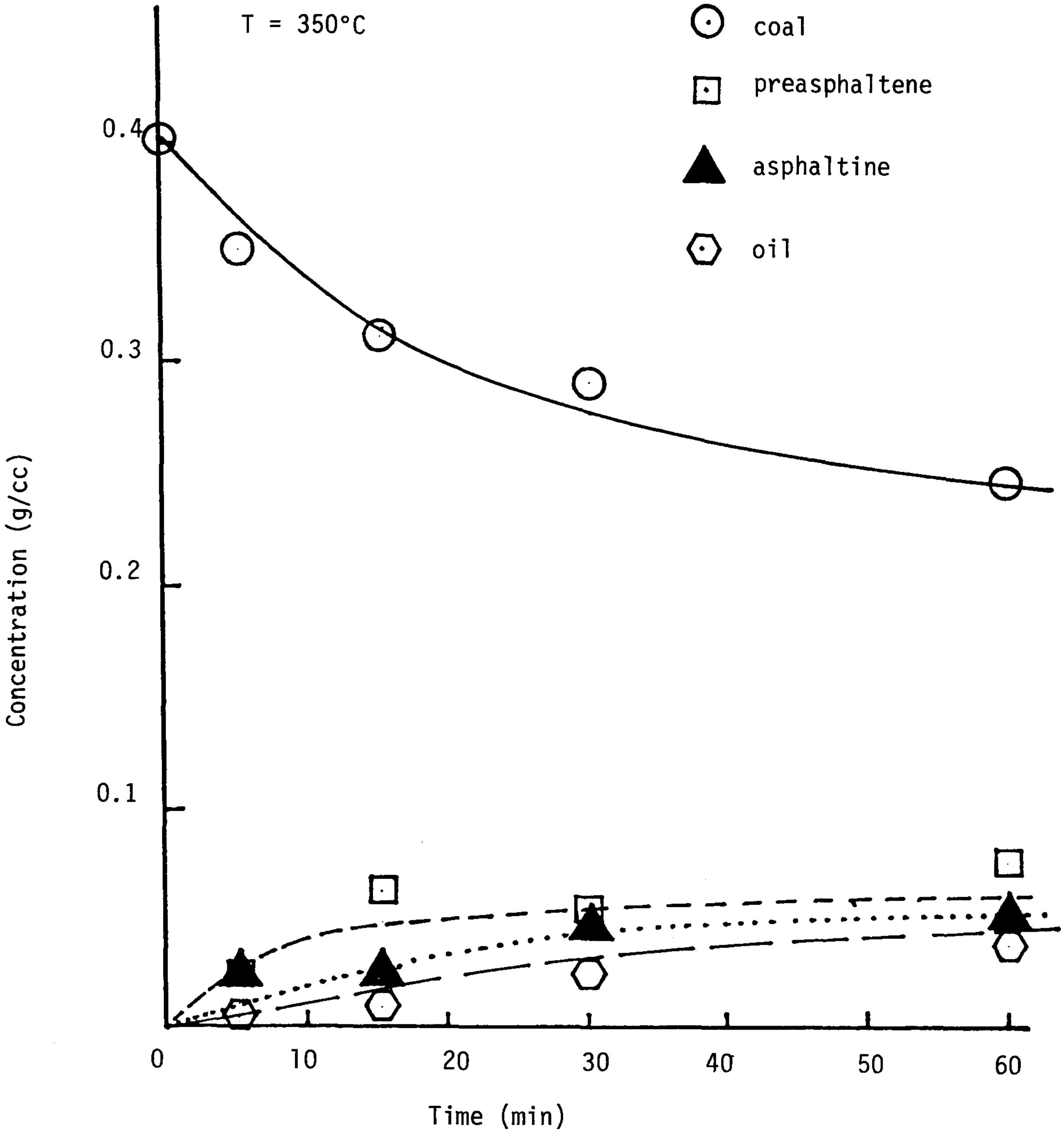


Figure 2.B.2. Product Distribution at 350°C

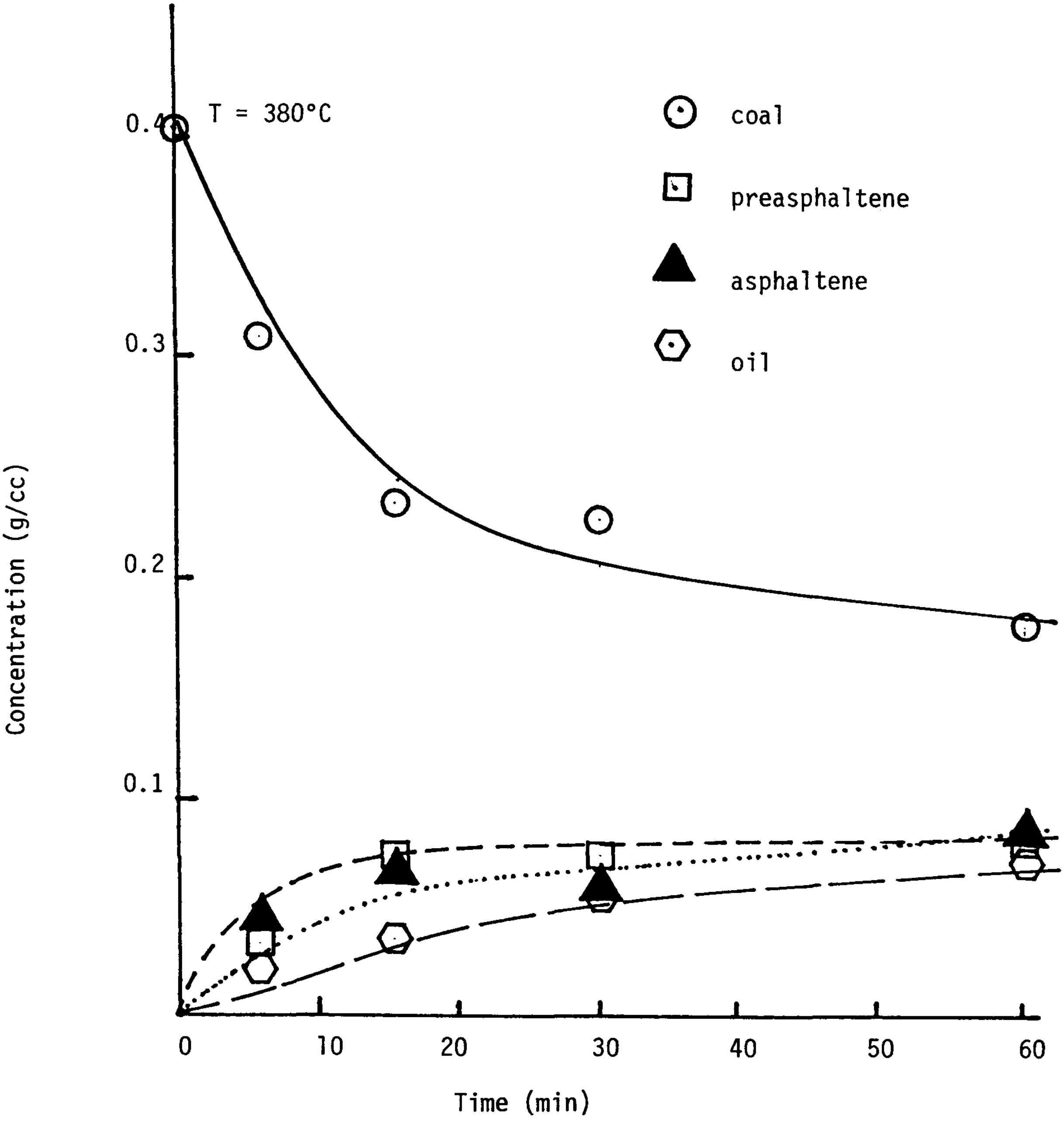


Figure 2.B.3. Product Distribution at 380°C

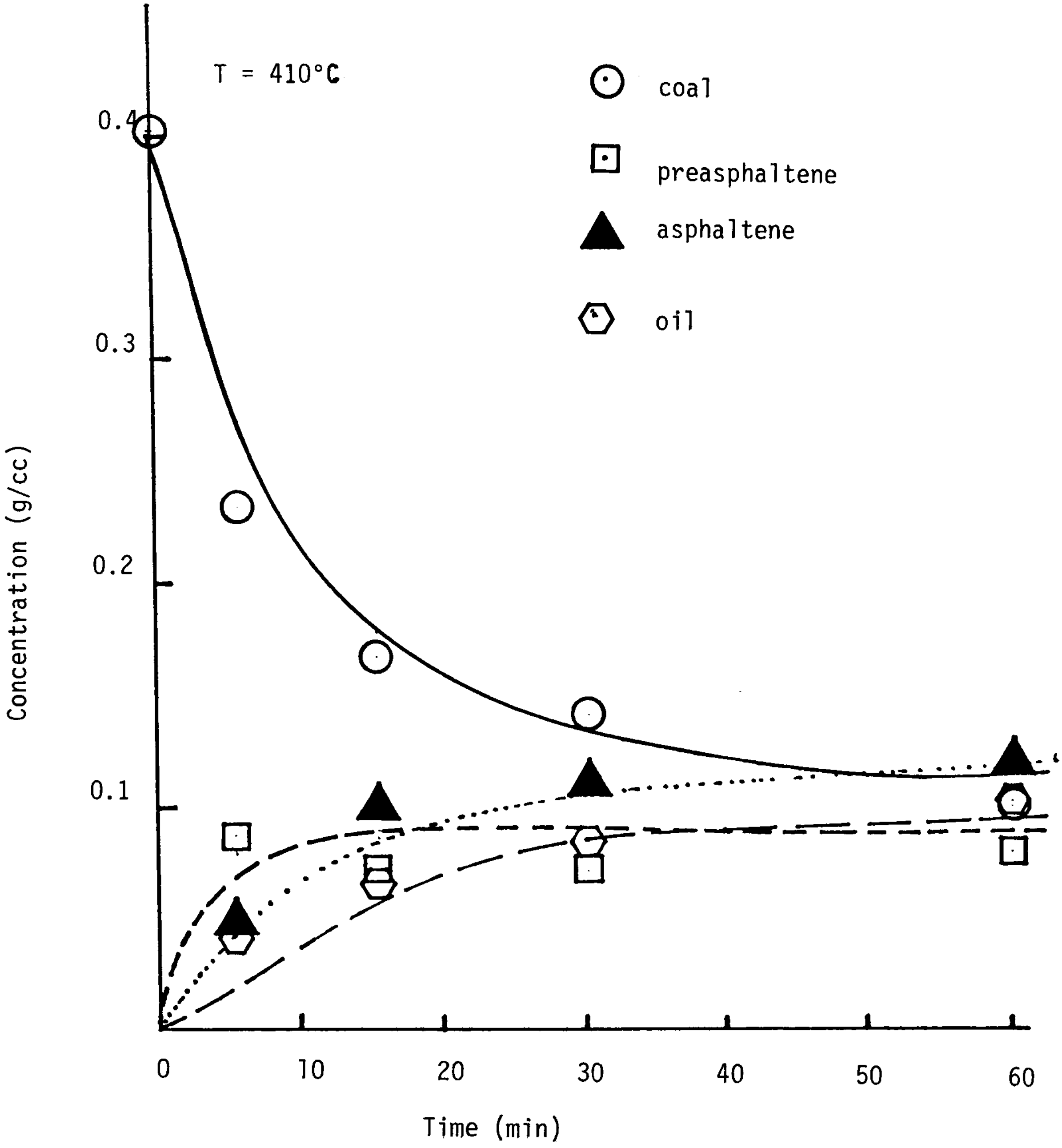


Figure 2.B.4. Product Distribution at 410°C

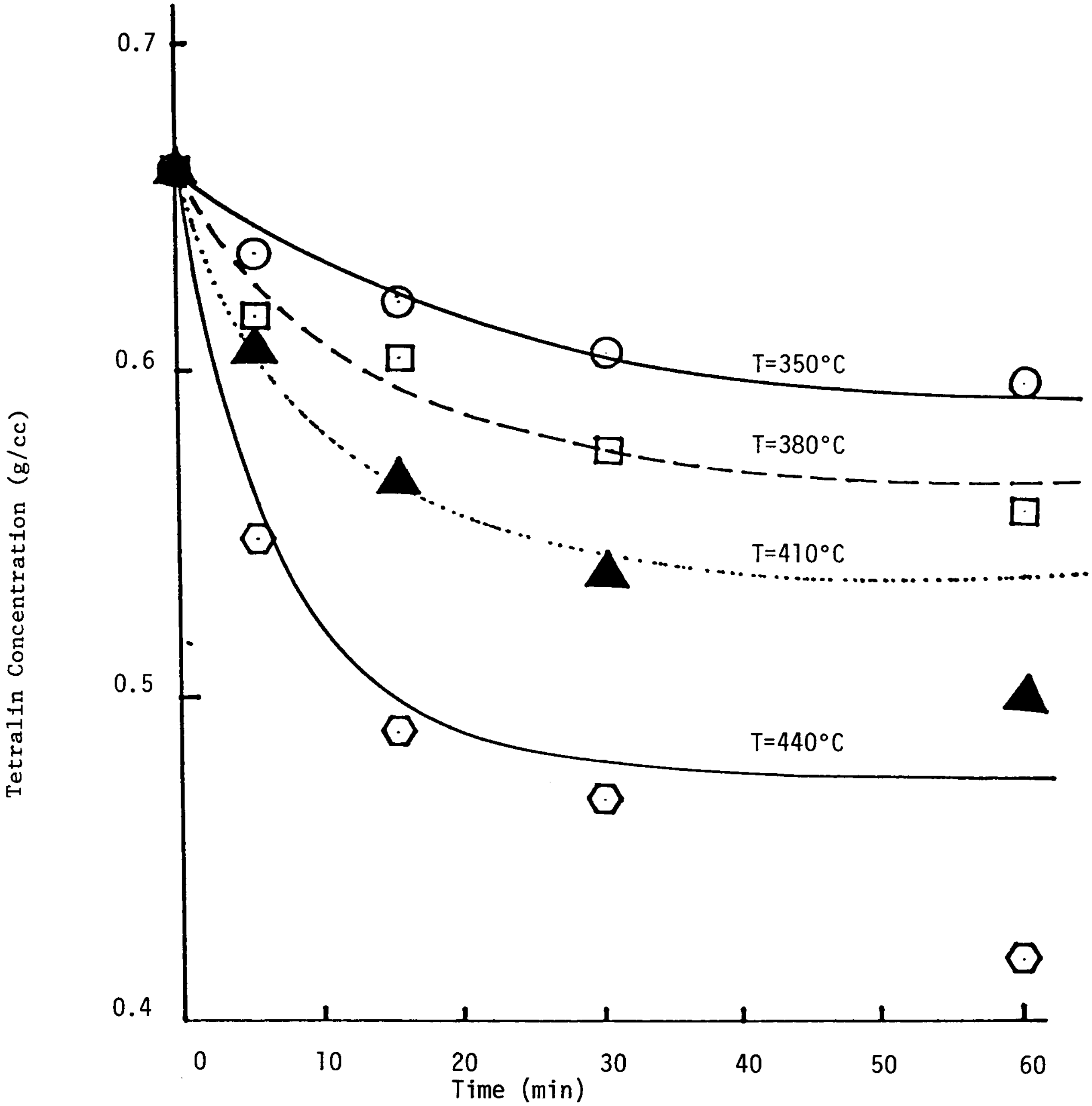


Figure 2.B.5. Tetralin Conversion vs Reaction Time

As shown in Figure 2.B.5, there appears to be a considerable amount of tetralin converted to naphthalene in coal liquefaction reactions. This hydrogen transfer reaction from tetralin to coal-derived free radicals provides stabilization of coal-derived products such as gases, oil, asphaltene and preasphaltene. Tetralin conversion to naphthalene seems directly related to the coal liquefaction yield, furthermore to the product distributions. Hence, we have considered the tetralin concentration term in our new kinetics model of coal liquefaction, which makes the overall process, second, rather than first order. Since each reaction product seemed to reach an equilibrium state, reversible reactions were also included in the kinetics model.

The proposed kinetics scheme is as follows:

$$\text{coal} + \text{tetralin} \underset{k_4}{\overset{k_1}{\rightleftharpoons}} \text{preasphaltene} + \text{Naphthalene}$$

$$\text{preasphaltene} \underset{k_5}{\overset{k_2}{\rightleftharpoons}} \text{asphaltene}$$

$$\text{asphaltene} \underset{k_6}{\overset{k_3}{\rightleftharpoons}} \text{oil} + \text{gases}$$

In deriving the kinetic expression, several assumptions have been made:

1. Active coal is based on daf coal
2. Unreacted coal is defined as pyridine insoluble.
3. For each component, i.e., for coal, preasphaltene, asphaltene, oil, and tetralin, first order kinetic expressions are assumed.
4. Concentration for each component is expressed in $\left[g/cc\right]$. Also, the volume of this heterogeneous mixture is assumed to be constant during the reaction.
5. A stoichiometric coefficient α was used, meaning that α parts (based on weight) of tetralin are needed for the stabilization of 1 part of coal.

6. The effect of naphthalene in the reverse reaction is assumed to be negligible (based on the results in Task 1.C.).

Based on the above proposed kinetics scheme and assumptions, the following kinetics equations have been obtained:

$$\frac{dC_c}{dt} = -k_1C_cC_T + k_4C_p$$

$$\frac{dC_r}{dt} = k_1C_cC_T - k_4C_p - k_2C_p + k_5C_A$$

$$\frac{dC_A}{dt} = k_2C_p - k_5C_A - k_3C_A + k_6C_o$$

$$\frac{dC_o}{dt} = k_3C_A - k_6C_o$$

$$\frac{dC_T}{dt} = \alpha(-k_1C_cC_T + k_4C_p)$$

where

C_c	= Conc. of coal	$[g/cc]$
C_p	= Conc. of preasphaltene	$[g/cc]$
C_A	= Conc. of asphaltene	$[g/cc]$
C_o	= Conc. of oil and gases	$[g/cc]$
C_T	= Conc. of tetralin	$[g/cc]$
k_i's	= rate of constants	$k_1\left[\frac{cc}{g.min.}\right]$ k_2 to $k_6\left[\frac{1}{min.}\right]$

$C_c = C_{c0}$ at $t = 0$

$C_p = C_A = C_0 = 0$ at $t = 0$

$C_T = C_{T0}$ at $t = 0$

These nonlinear differential equations were solved simultaneously using the computer, and the results are presented in Fig. 2.B.2, 3, 4, and 5. The values of ki's and α at each temperature were shown in Table 2.B.2. Even though the reaction temperature is different, the average value of α is almost the same. The value, α, at 410°C appears less accurate, compared to those at 350 and 380°C. this means that α grams of tetralin is needed to stabilize the free radicals, which are produced by the thermal rupture of coal, to pyridine soluble.

The computer simulation using the Parameter Estimation method gave a close fit to the experimental values, except for the tetralin conversion data for 60 minute reaction at 410°C. Under our coal liquefaction reaction conditions the proposed kinetics scheme can be observed to represent fairly well the mechanism of coal dissolution and hydrogen transfer reaction in coal liquefaction processes.

Table 2.B.2. α and Rate Constants at Each Reaction Temperature

Temp. Rate Const.	k_1	k_2	k_3	k_4	k_5	k_6	α
350°C	0.0380	0.1784	0.1759	0.0836	0.1917	0.1935	0.43957 ±0.0369
380°C	0.0843	0.2089	0.1811	0.1066	0.1961	0.2422	0.42988 ±0.0610
410°C	0.1551	0.2539	0.2104	0.1129	0.1971	0.2659	0.43211 ±0.0894

Task 3. Development and Utilization of New Analytical Techniques

Objective

The objective of this task is to develop analytical methodology for direct application and utilization in the characterization of coal-derived liquids, coal minerals, and solvent refined coals.

3.A. Development of High Pressure Liquid Chromatography Methodology for Coal Derived Liquids

Objective

The purpose of this work is to develop procedures using High Pressure Liquid Chromatography (HPLC) and Gel Permeation Chromatography (GPC) to separate, identify, and quantitate the organic constituents and heteroatom species present in coal liquids and solvent refined coals.

Progress

The objective of this work is to characterize the Solvent Refined Coal (SRC) solid product in terms of chemical species present in the complex matrix. To this end, we have employed high pressure liquid chromatography (HPLC) in a two stage analytical scheme. The basis of this procedure is a preliminary molecular-size separation (via GPC) of the THF soluble portion of SRC into six arbitrary fractions, which serve to group the species into principally "oils" and "asphaltenes/preaphaltenes"; followed by further separation into individual components by means of affinity mode (reverse and normal phase) HPLC. The highly complex chemical nature of SRC, both in terms of the range of molecular weight and chemical functionality of the species present, dictates that some sort of multi-stage scheme of analysis be followed. Farcasiu (1977) has employed a fractionation scheme based on sequential elution of the components in SRC by means of various solvents. Her first three fractions comprise components usually designated as "oils", i.e. primarily low molecular weight condensed ring aromatic systems. While later steps in the process comprise primarily asphaltenes and preashpaltenes. We propose that the oil and asphaltene, preasphaltene groups can be separated from one another by judicious collection of fractions obtained from a gel permeation chromatographic separation of SRC. Indeed, we have shown that those compounds designated as "oils" elute within a rather narrow range of elution volumes, whereas asphaltenes, preasphaltenes are not resolved and encompass a much broader region. Fractions collected from the "oil" region of the GPC curve have been shown by affinity mode (reverse phase) HPLC to be similar to coal derived "recycle oil" and to contain in four instances the same component.

Materials

The solvents used in this study were as follows:

(1) Tetrahydrofuran (Glass distilled, UV grade), Burdick and Jackson laboratories

(2) Acetonitrile (nanograde), Mallinckrodt laboratories

(3) Isopropanol (ACS grade) J. T. Baker

(4) Hexane (Spectrometric grade)

(5) Glass distilled water

All solventswere filtered through a 0.2 micron pressure filter (Millipore Corporation) prior to use to remove particulate matter, but otherwise were used as received without purification. The chromatograph used for all separations was a Waters Associates ALC/GPC-201 equipped with an M 6000A pump, UGK Universal injector, and differential refractometer. Additionally, an auxiliary UV detector Schoffel Spectroflow model 70 was employed. Chromatograms were recorded on a Texas Instrument Model PS02W6A Servowriter II dual pen recorder. The columns used were μ-Bondapak C_{18} (2), μ-Parasil, and μ-Styragel (500 Å (1); 100 Å (2)).

Experimental Procedures

A. Gel Permeation Chromatography

Samples were prepared for gel permeation chromatography by dissolving SRC in THF or the basis of 100 mgms of SRC per milliliter of THF. To aid in dissolution samples were agitated in an ultrasonic bath for 20 minutes. Following sonication samples were removed, allowed to cool to room temperature, and centrifuged for 30 minutes to settle out solids or THF insoluble materials, which amounted to approximately 15% of the weight of the original starting material. Following centrifugation the supernatant liquid solution of SRC was decanted and filtered through a syringe filter kit (containing a 0.2 micron filter) prior to injection into the gel permeation chromatograph. Injection volume was normally 100 ml. The gel permeation chromatography system consisted of three μ-Styragel columns (500 Å (1); 100 Å (2)) in series with a mobile phase of THF at a flow rate of 1 ml/min. Molecular sized fractions were obtained from the THF soluble SRC by collecting fraction from the GPC effluent stream at three minute interval beginning at the point detector response departed baseline and continuing over the duration of the run (run complete in 36 minutes). The detector for GPC analysis was the differential refractometer at 32X attenuation. In order to obtain on the order of milligram quantities of material in each collected fraction, multiple injection and collections were necessary. Collected fractions were concentrated for subsequent analysis by air evaporation of the THF solvent from the samples under a fume bond. Accurate determinations of mass balance relations proved exceedingly difficult due to the fact that under the experimental conditions employed it was found that the samples retained on the order of 10-15 weight percent of absorbed THF.

B. Affinity Mode HPLC

(1) Reverse Phase

Reverse phase HPLC analysis was chosen as the mode of separation for fractions 5 and 6 for three reasons:

a. Other works done in this laboratory with autoclave and tubing bomb reaction mixtures showed that 5 and 6 elute at volumes comprarable to those obtained for components designated as "oils".

b. Relative solubility determinations in common organic solvents normally employed for reverse phase analysis indicated a fair degree of solubility of both fractions in an equal volume mix of acetonitrile and o-propanol.

c. Reverse phase analysis has been successfully employed in this laboratory and elsewhere - for the analysis of coal derived "oils".

Samples were prepared for reverse phase analysis on the basis of a concentration rate of 10 mgm of material to 1 milliliter of solvent ($CH_3CN(50)$/o-PrOH). Samples were sonicated, centrifugal, and filtered prior to injections. 25 ml of sample solution was normally injected into the reverse phase system which was composed of two, μ-Bondapak C_{18} columns in series with a mobile phase ternary mixture consisting of equal volumn ratios of H_2O:CH_3CN: i-Propanol at a flow rate of 0.6 ml/min. Detection was accomplished by monitoring the LC effluent stream UV absorbance at 254 nanometers.

(2) Normal Phase

The normal phase mode of analysis was chosen for the study of Fractions 1 through 4. Relative solubility studies of these materials showed them not to be appreciably soluble in any of the common chromatographic as solutions of 10 milligrams per milliliter in THF. Normal injection volume was 5 ml. The normal phase system used was a μ-porasil column with hexane (95)/o-PrOH and hexane (75)/i-PrOH molbile phases at a flow rate of 1 ml/min. Detection was by UV absorbance of the LC effluent stream at 254 and 313 nanometers.

Results and Discussion

Reverse phase analytical separations of Fractions 5 and 6 are shown in Figures 3.A.1 and 3.A.2. Tentative identification of the species present in Fraction 6 has begun. Spiking experiments have indicated the presence of fluoranthene, phenanthrene, dibenzothiophene, and pyrene. Independant examination of Fraction 6 by gas chromatography also indicates the presence of these components. These species are also present in recycle oil used in the solvent refining process, which causes a question as to the origin of these species in the solid product fraction. Two distinct possibilities exist:

a. These species could represent the remnants of non-removed recycle oil from the product, or

b. They could be components which comprise the actual organic matrix of the SRC.

Work is currently underway to further identify and quantitate the components present. A complete identification will hopefully lead to a further understanding of the SRC product.

Normal phase analysis of Fractions 1 through 4 has been much less successful than the analysis of Fractions 5 and 6. Analytical separations are extremely poor. Table 3.A.1 summarizes work to date. Based on work with smaller condensed ring standards (phenanthrene, anthracene, dibenzothiophene, and Rubrene), which elute at V_0 under our experimental conditions, it appears that the components in fractions 1-4 comprise either higher condensed ring systems, polar compounds, or both. The principal obstacles to the application of HPLC to Fractions 1-4 appears to be:

a. In reverse phase mode, the very poor solubility of the samples in most common solvents employed: CH_3CN, CH_3OH, H_2O, etc.

b. In normal phase, the inability of the solvents commonly employed (Hexane, $CHCl_3$, CCl_4, THF, etc.) to force elution of the components from the column within

Figure 3.A.1

Reverse Phase Chromatogram of Amax GPC Fraction 5

*Column(s): μ-Bondapak C_{18} (2)

Mobile Phase: H_2O (1): CH_3CN(1): $\mathrm{CH_3\underset{\underset{CH_3}{|}}{C}H_2OH}$(1)

Detector: UV at 254 nm; 0.1 AUFS

Sample: 10 μl; 10 mgm/mℓ

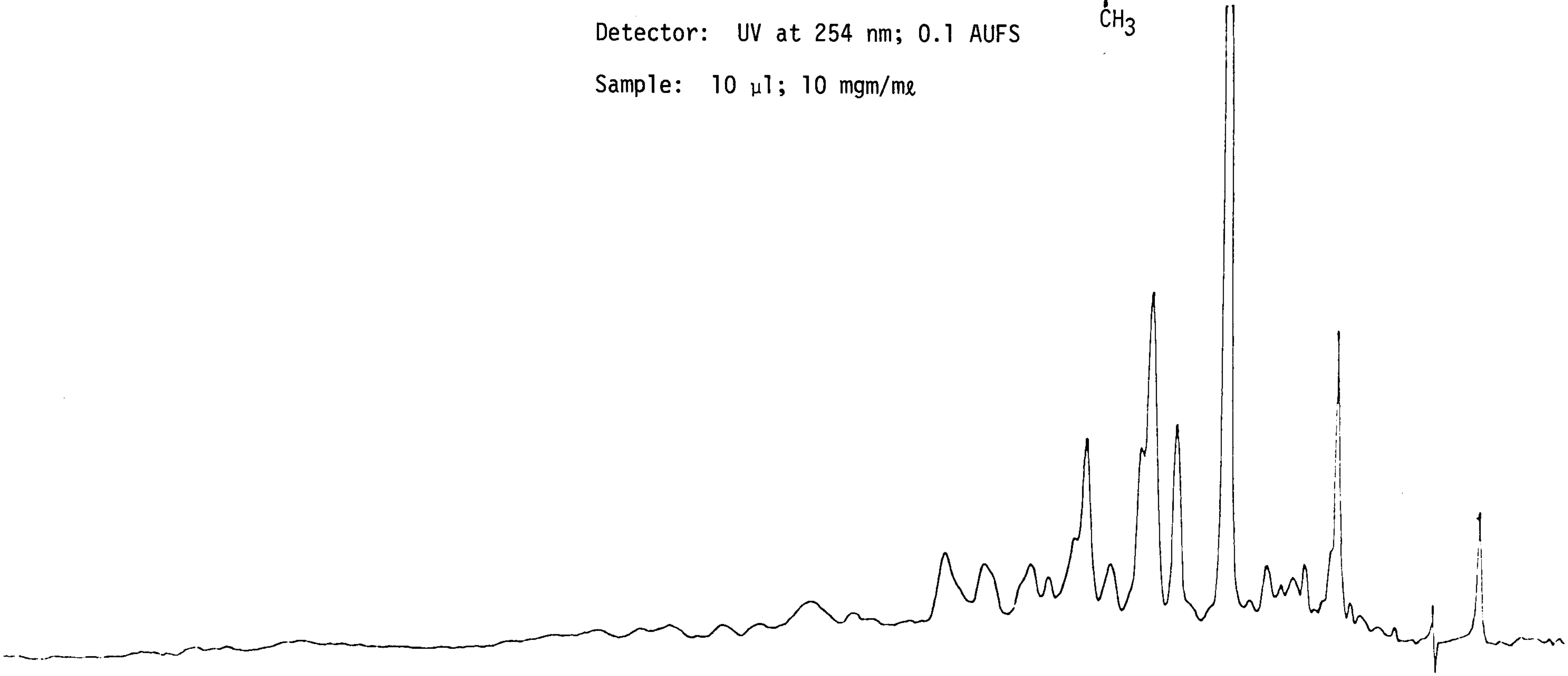


Figure 3.A.2

Reverse Phase Chromatogram of Amax SRC GPC Fraction 6

*Exp Cond. same as in Fig. 3.A.1

Peak Labels: 1-Phenanthrene
2-Dibenzothiophene
3-Fluoranthene
4-Pyrene

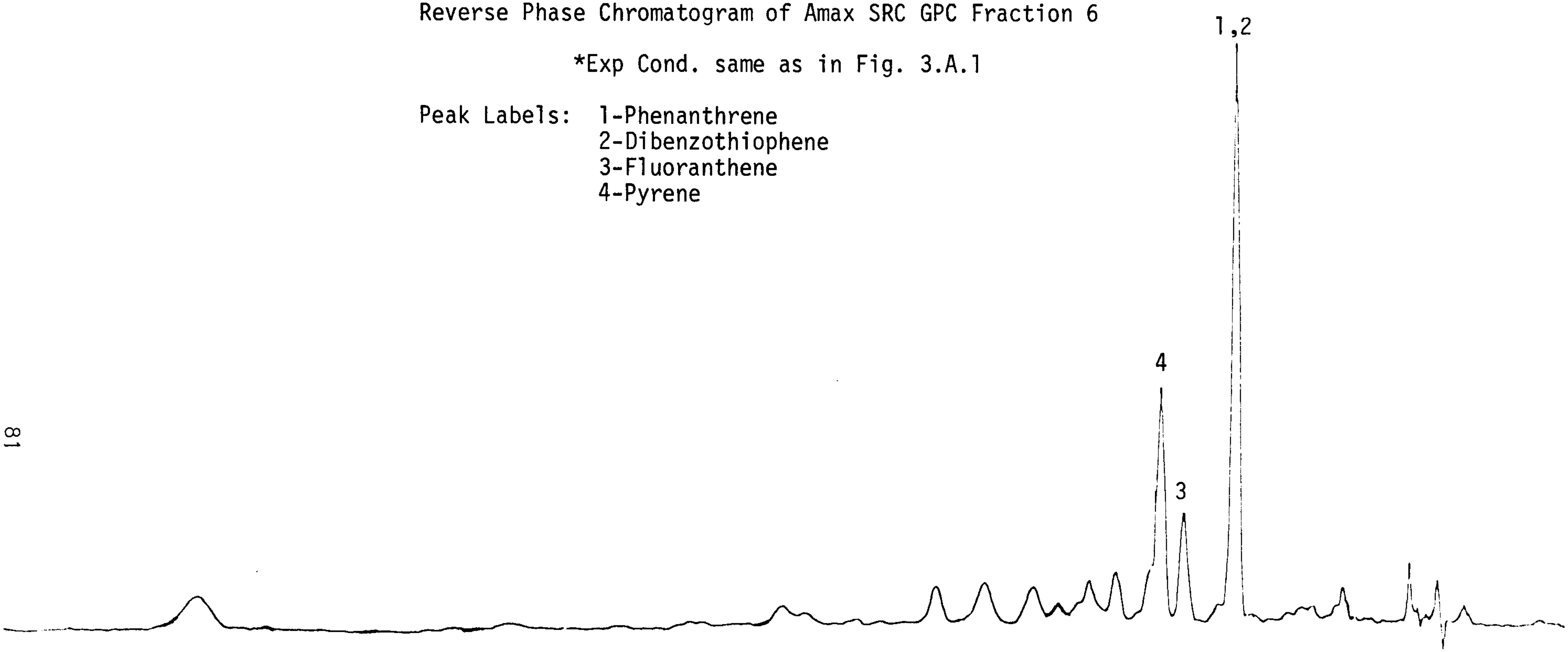


Table 3.A.1. Comparison in Normal Phase Analysis of Fractions 1 through 4

Fraction Number	Mobile Phase	
	Hexane (95%)/2-Propanol (5%)	Hexane (75%)/2-Propanol (25%)
I	No bands to $k' = 20$	Two broad bands, $1 < k' < 4$
II	No bands to $k' = 20$	Two broad bands, $0 \cong k' < 1.8$
III	13 peaks as poorly resolved bands, $k' < 20$	Single broad band, $k' = 0$
IV	3 bands, $0 < k' < 1$	Single band, $k' = 0$

reasonable length of time. Obviously, much developmental work remains to be done. For example, investigation into gradient modes of analysis has hardly begun.

Molecular Weight Distributions of Coal, SRC and Coal-Derived Products by Gel Permeation Chromatography

During this quarter, the molecular weight distributions of feed coal, SRC and coal liquefaction reaction products were determined by gel permeation chromatography (GPC). The GPC of oils, asphaltenes and preasphaltenes were studied to give a deeper understanding of their roles in the coal liquefaction. The molecular weight distribution (MWD) as determined by GPC can be used as a measure of rate of degradation and product quality. The effects of reaction time and temperature on the degradation of coal were also studied by GPC.

Experimental

The equipment used was a model ALC-GPC-201 system (Waters Associates, Milford, Mass.) mounted with a refractive under detector. Accessory equipment included a model 6000 solvent delivery system and a model U6K injector. A model SF 770 spectroflow monitor UV/VIS detector (Schoeffel Instrument Corp., Westwood, N.J.) was used for ultra-violet detection.

The columns used were μ-styragel (Waters Associates), two feet with 100 Å and one feet with 500 Å exclusion limits. The eluting solvent was tetrahydrofuran (THF) (UV grade, distilled in glass, Burdick and Jackson Lab., Inc.). The solvent was filtered through a 0.2 micron filter (Millipore Intertech, Inc., Bradford, Ma.) prior to use. A solvent flow rate of 1 ml/min which is the optimum flow rate for the μ-styragel columns was used for all the separations. The system was maintained at ambient temperature. When refractive index detector was used, a sample amount of 1 ~ 5 mg was injected. When the UV detector was used, the wavelength was set either at 313, 300 or 254 nm and a sample amount of 0.1 ~ 5 mg was used for injection.

The SRC samples were obtained from Catalytic Inc., SRC pilot plant (Wilsonville, Alabama). The tubing bomb reactor and autoclave reaction products were obtained from the studies in Tasks 1 and 2.

Oils, asphaltenes and preasphaltenes were obtained by following conventional solvent extraction scheme with the autoclave or tubing bomb reactor reaction products (refer to Progress Report, FE-2454-2). Here we define oils as pentane soluble compounds, asphaltenes as benzene (or toluene) soluble and pentane insoluble compounds and preasphaltenes as pyridine soluble and benzene insoluble compounds.

The solid or liquid samples were dissolved in pure THF to yield the bulk concentration (which is the weight of soluble and insoluble divided by the solvent volume) and filtered through a 0.2 micron filter prior to injection. However, due to the solubility limitation of the samples in THF, the actual concentration is lower than the bulk concentration.

A complete gel permeation chromatographic run takes about 40 minutes. Before each injection, the system must be allowed to reach an equilibrium state which is indicated by a stable baseline of the detector output.

Results and Discussion

The gel permeation chromatographic separation is recorded in the form of a chromatogram which is a plot of the RI or UV detector output as a function of retention time. If the recorder response is taken as being proportional to the mass of the eluting sample and a calibration curve of elution volume versus molecular weight is available, we can plot weight percent versus molecular weight from which the number molecular weight and molecular weight distribution can be determined.

When we apply GPC to determine the MW distribution of coal type materials, we must face the following problems:

1. The solubility of the sample in the solvent. The actual MW distribution is distorted by the solvent effect. If a sample is not very soluble in the eluting solvent, we might get a wrong MW distribution which is lower than it actually is. Thus, experiments with other solvents are needed.

2. The aggregation of sample in the solvent. Because of this phenomenon, the

method used, the sample concentration and size, the temperature and the type of solvent are all dominant in the determining of MW distribution and MW. Aggregation phenomenon would cause the MW to be higher and result in earlier elution.

3. Adsorption of solute to column packing. This phenomenon would cause chromatogram tailing, incomplete recovery and delayed elution which would distort the MW distribution toward the low MW end. The column and solvent used must be selected carefully in order to avoid this adsorption phenomenon.

4. The dependence of TI or UV on MW or molecular structure.

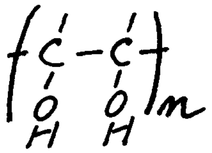
The solution to this problem is the use of a detector which responds directly to mass, rather than a physical property. We can collect fractions of the eluting sample and solvent on a constant interval basis, then evaporate the solvent and obtain the weight of each fraction and construct a weight versus retention volume chromatogram.

5. The lack of suitable MW distribution standards. Coal type materials are complex organic compound mixtures. Various hydrocarbons have their own size-molecular weight relationship. Separate calibration is needed for every type of homologous series.

If coal type fractions with narrow MW distributions are available, we can determine their number MW by vapor phase osmometry or MS techniques and use them as GPC calibration standards.

A standard calibration curve for the purpose of MW calculation of coal type material was not attempted here. However, one calibration curve of aliphatic homologous series (straight chain saturated hydrocarbons) was completed with polyethylene glycols in high MW range, and one of aromatic homologous series (alkyl benzenes) was calculated to give a scale for the comparison of molecular weight distribution. The standards used are listed in Table 3.A.2. The retention time for each standard was obtained individually on the THF μ-styragel system with a 1 ml/min flow rate. The calibration curves are plotted in Fig. 3.A.3.

Table 3.A.2. GPC Calibration Standards

Compound	Structure	M.W.	Retention Time
Straight Chain Saturated Hydrocarbons			
n-hexane	$CH_3(CH_2)_4CH_3$	86.2	27.5
n-undecane	$CH_3(CH_2)_9CH_3$	156.3	24.6
tetradecane	$CH_3(CH_2)_{12}CH_3$	198	23.3
Nanadecane	$CH_3(CH_2)_{17}CH_3$	268.5	21.6
Polyethylenglycol			
1		285-315	21.2
2		570-630	19.1
3		950-1050	17.6
4		1300-1600	16.8
Alkyl Benzene			
Toulene	Bz CH_3	92.13	30
n-propyl benzene	Bz $(CH_2)_2CH_3$	120.1	27.9
n-hexyl benzene	Bz $(CH_2)_5CH_3$	162.1	26.0
n-decyl benzene	Bz $(CH_2)_9CH_5$	218.1	24.0

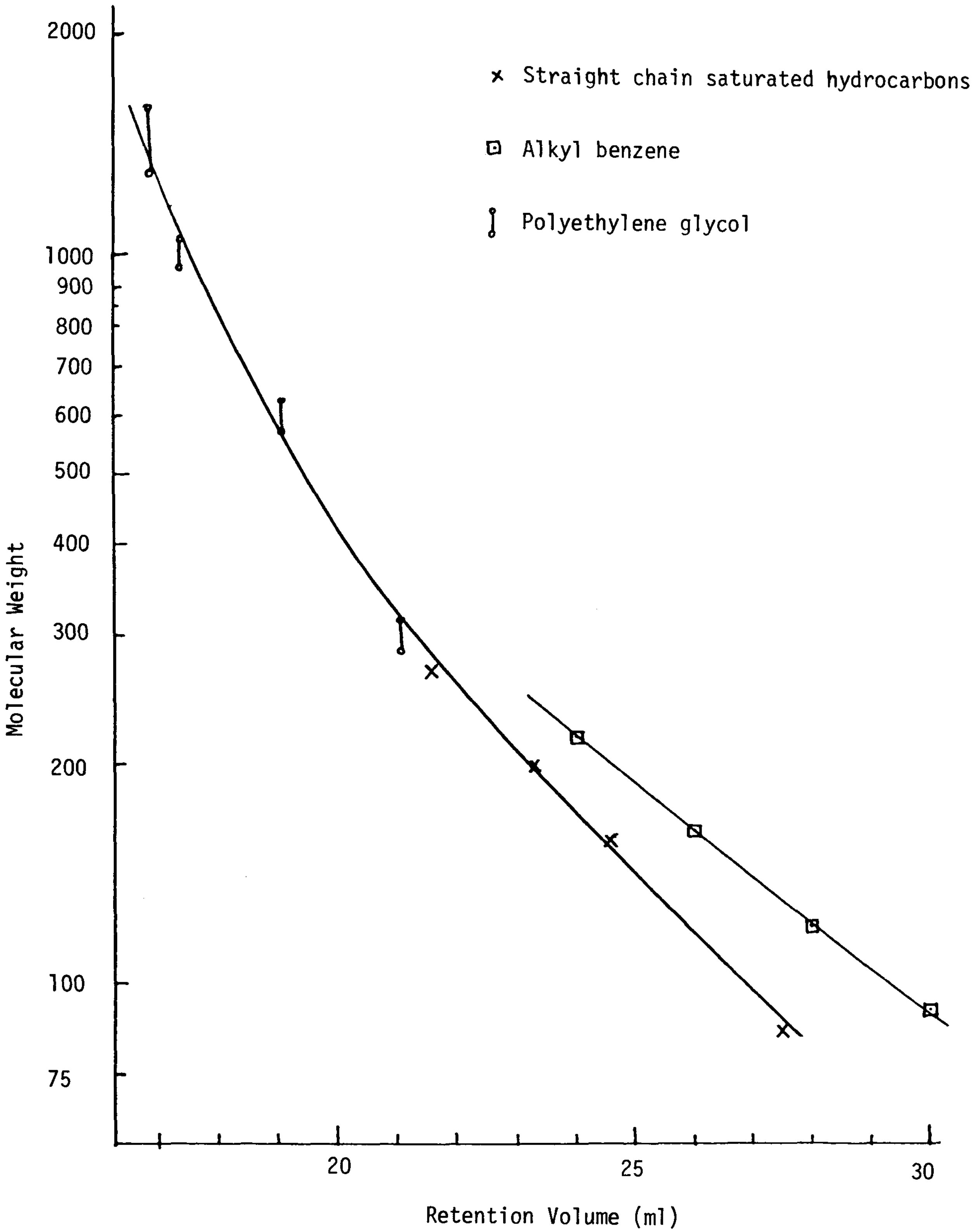


Figure 3.A.3. GPC Calibration Curve

The GPC of different types of unreacted feed coal were compared in Fig. 3.A.4. All samples were prepared to have the same bulk concentration and filtered prior to injection. We can see the THF solubles of different coals are quite different in MW distribution. Monterey feed coal has the highest solubility in THF and its THF soluble portion has the heaviest MWD (molecular weight distribution). Amax feed coal has the lowest solubility in THF and its THF soluble portion has the lightest MWD.

SRC from different kinds of coal are more soluble in THF than feed coal and are similar in MWD as shown in Fig. 3.A.5. This indicates that after the solvent refining process, different types of coal have been transformed into very similar SRC products, in the view of molecular weight distribution. Fig. 3.A.6 compares the MWD of Monterey feed coal and Monterey SRC, and the THF soluble portion of Monterey SRC has a lighter MWD or smaller molecules which maybe due to the breakage of larger molecules during the SRC process. This may not be true because the THF soluble portion of feed coal is very small in the amount and does not represent well the feed coal.

As shown in Figure 3.A.7, the GPC of oil, asphaltene and preasphaltene obtained from the autoclave reaction products were compared to the total reaction product mixture which is a combination of these fractions. The autoclave reaction products were obtained by reaction of W. Kentucky coal with recycle oil (weight ratio 1:2) at 410^{o}C. The reaction time was 120 minutes.

The oil and asphaltene portions are quite soluble in THF. The GPC of oil portion is very similiar to that of recycle oil and has a light molecular weight distribution. The asphaltene portion has a higher molecular weight distribution, and the GPC of its THF soluble portion is very similar to that of SRC. Preasphaltene portion which has the heaviest molecular weight distribution is only partially soluble in THF. The RI detector can hardly detect this amount of THF soluble preasphaltene portion. The high peak in the GPC of the total reaction product corresponds to

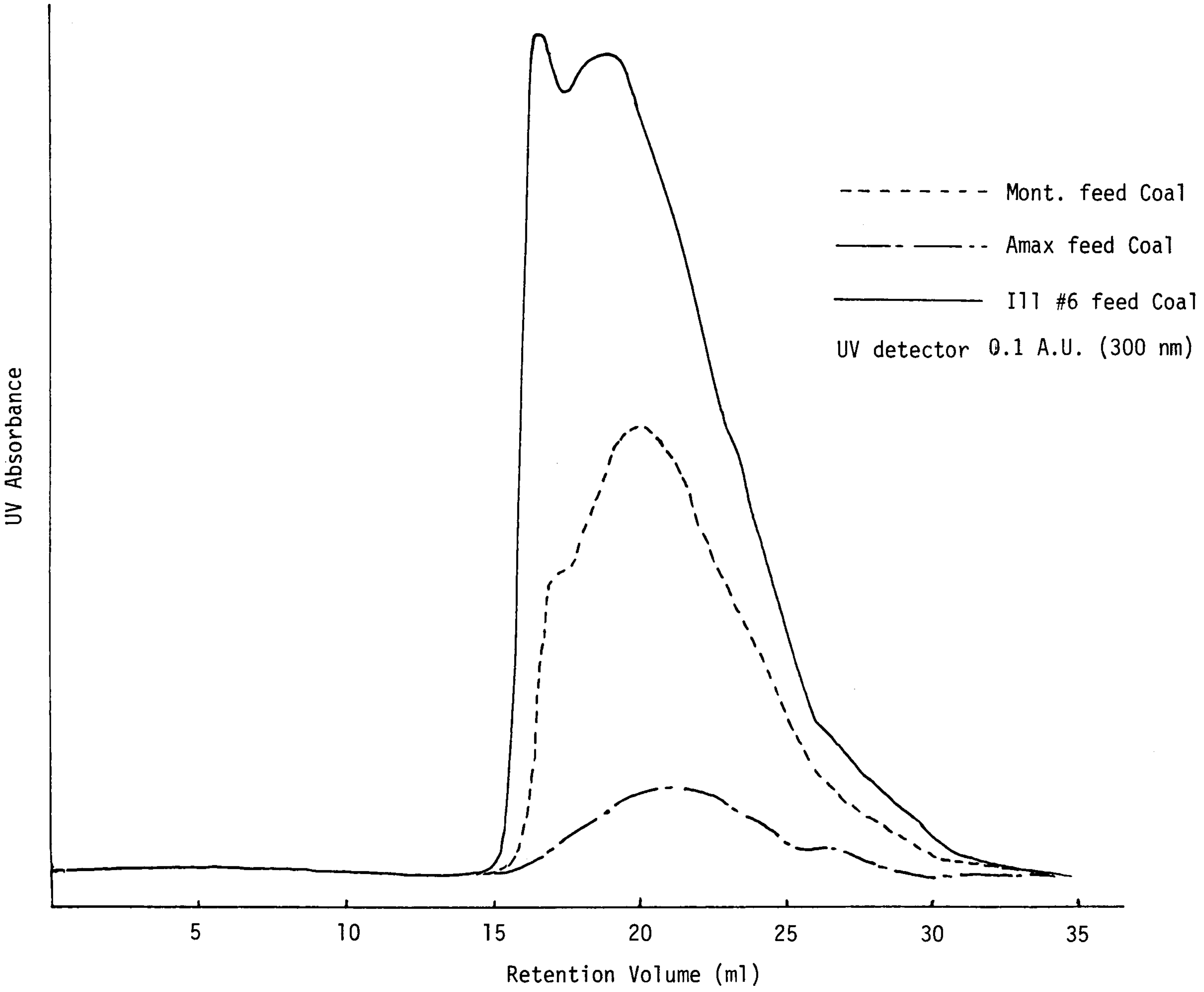


Figure 3.A.4. Comparison of THF Soluble Portion of Different Feed Coal

Figure 3.A.5. Comparison of THF Soluble Portion of Different SRC

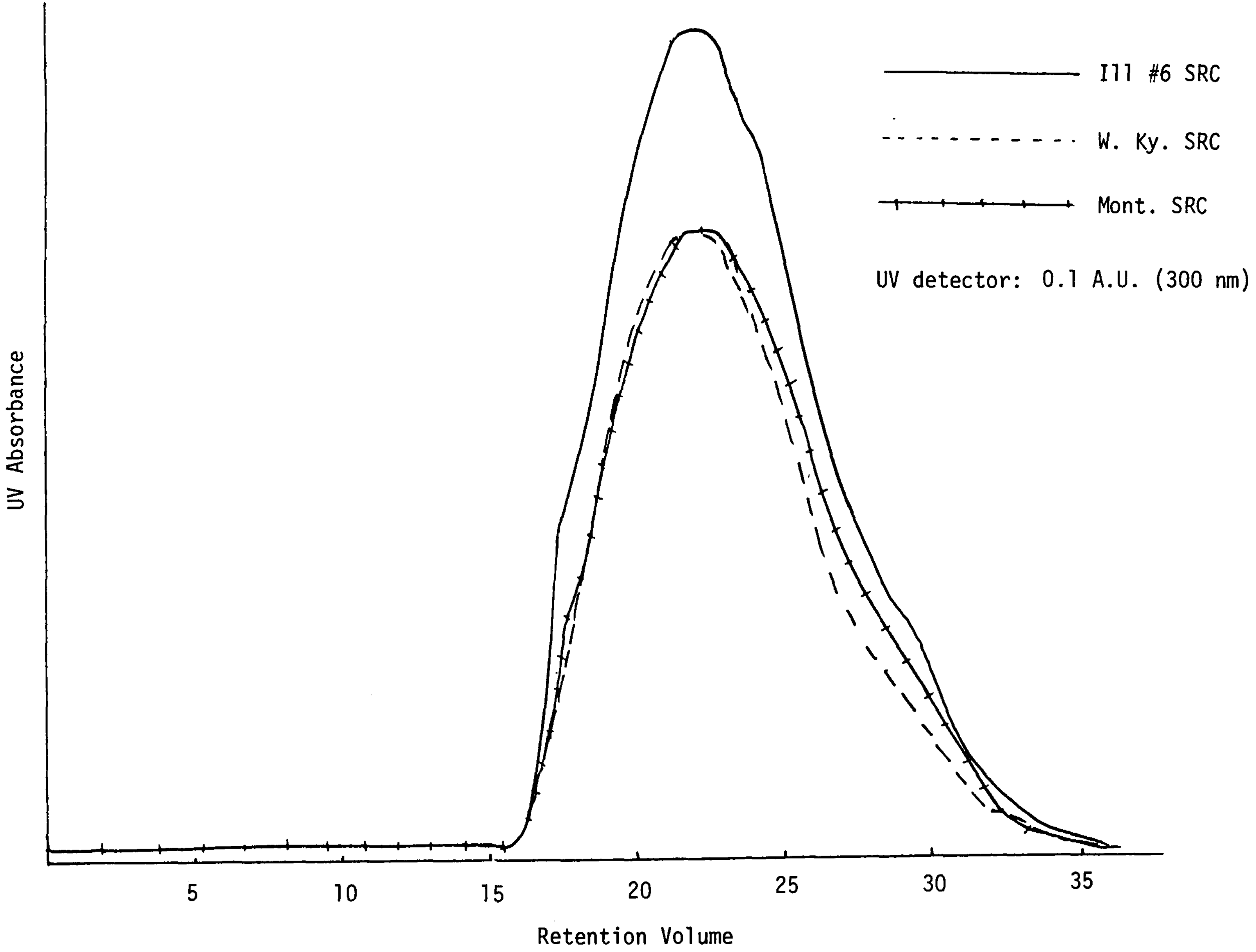


Figure 3.A.6. Comparison of Mont. Feed Coal and Mont. SRC

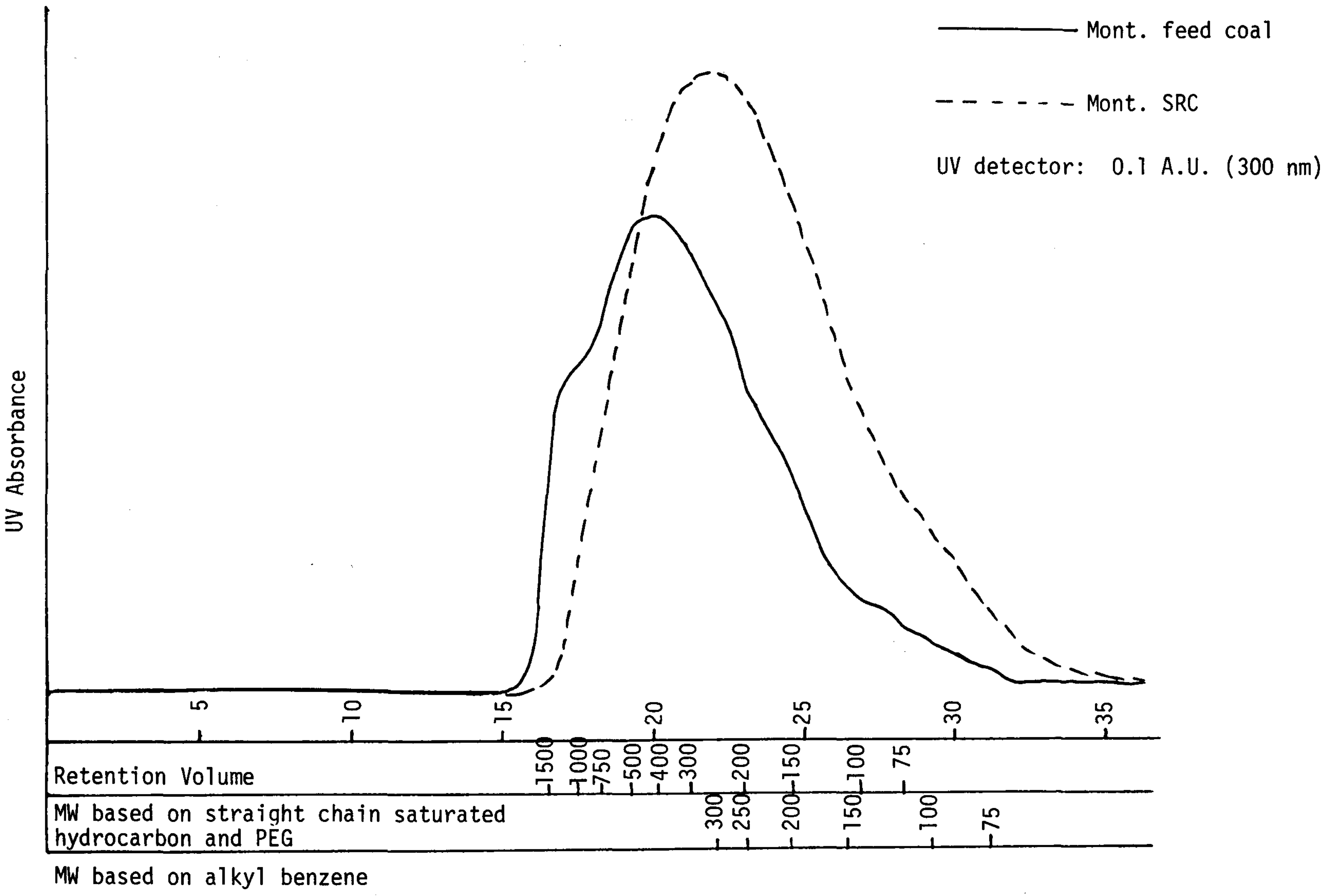
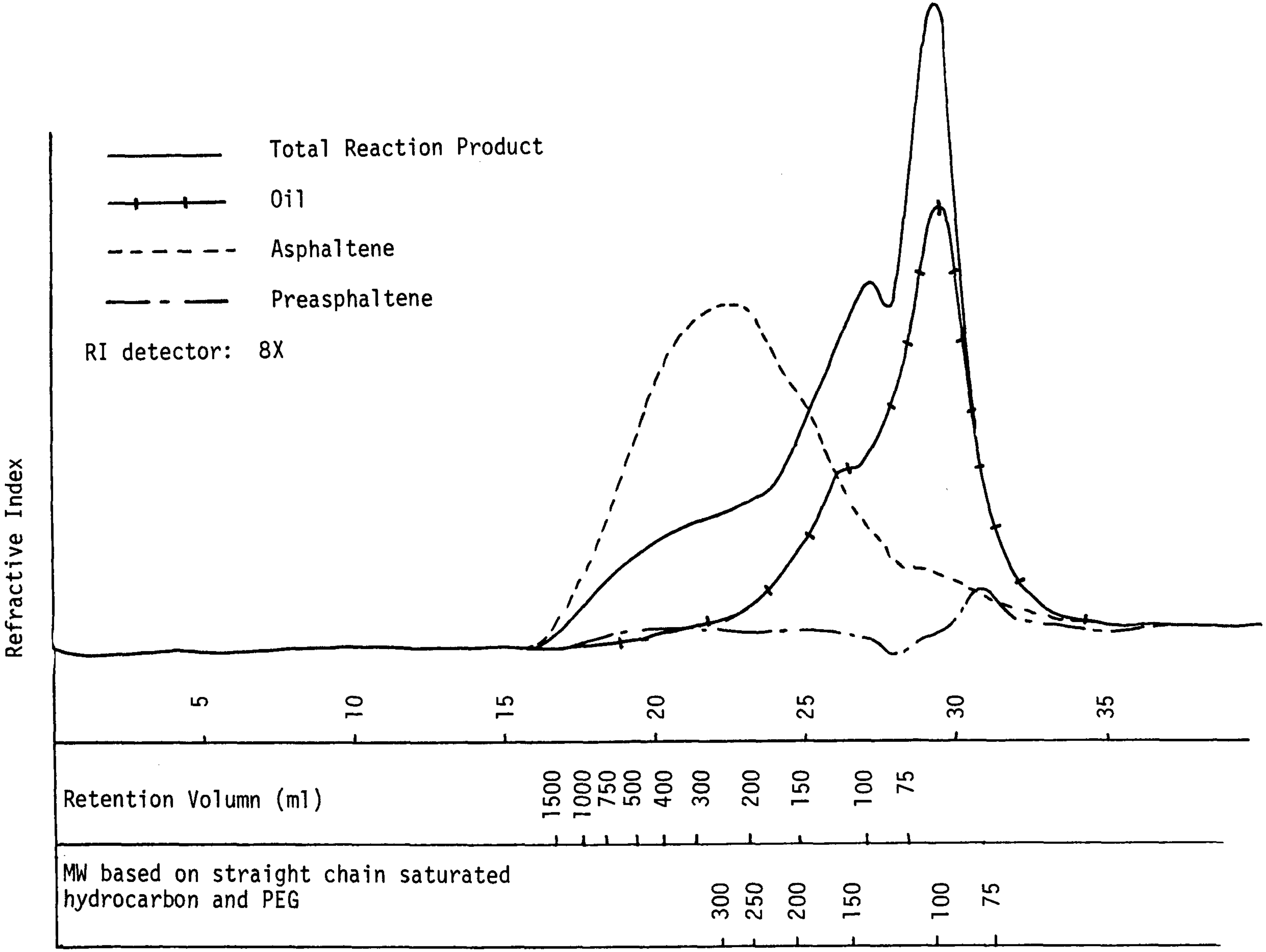
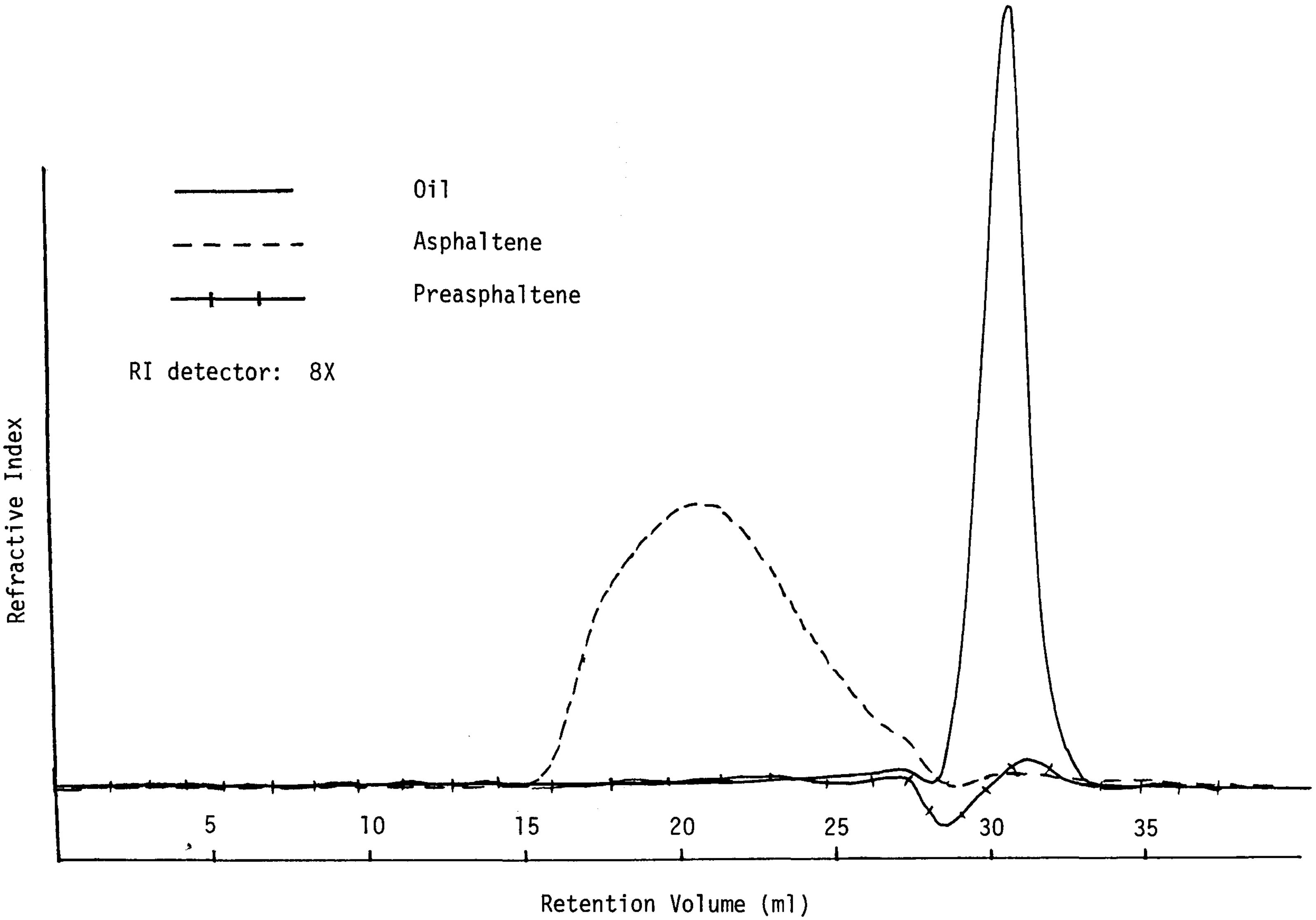


Figure 3.A.7. GPC of Autoclave Reaction Product and Its Oil, Asphaltene, and Preasphaltene Fractions



·MW based on alkyl benzene

Figure 3.A.8. GPC of Oil, Asphaltene and Preasphaltene from Tubing Bomb Reactor Product



oil portion and the plateau corresponds to asphaltene portion. Preasphaltene, due to its low solubility in THF, has very little contribution to the total reaction product RI chromatogram. The GPC of oil, asphaltene and preasphaltene portions from the tubing bomb reactor products were also obtained (Figure 3.A.8.). The reactants used for the tubing bomb reactor run were W. Kentucky coal and tetralin, thus the oil portion obtained contains mainly tetralin and shows a much narrower molecular weight distribution than that from the autoclave reaction products which used recycle oil and W. Kentucky coal as reactant.

Time and Temperature Effects on Coal Breakage

The GPC of THF soluble asphaltene from the tubing bomb reactor reaction products for different reaction time and reaction temperature reveals the change in the molecular weight distribution, from which the rate of disappearance of high molecular weight materials as a function of time can be determined.

Fig. 3.A.9 depicts the effects of reaction time on molecular distribution for different reaction temperature. The RI of large molecules (corresponding to short retention volume) is decreasing with reaction time and the RI of small molecules (corresponding to long retention volume) is increasing with reaction time. Since the RI is assumed to be proportional to mass concentration, the arbitrary ratio of RI at some high retention volume (here we take 22 ml) to the RI at some low retention volume (here we take 17 ml) represents the ratio of the mass concentration of small molecules to that of large molecules, and is a good indication of the molecular weight distribution. Higher RI ratio means that more small molecules are present in the sample.

The 22 and 17 ml were arbitrarily chosen such that they would be in the most representative position of the chromatogram. Retention volumes 22 and 17 ml correspond to a molecular weight of 250 and 1,200, respectively, based on the polyethylene glycol and straight chain saturated hydrocarbon calibration curve. Fig. 3.A.10 correlates the RI ratio for asphaltene portions obtained from various conditions to reaction

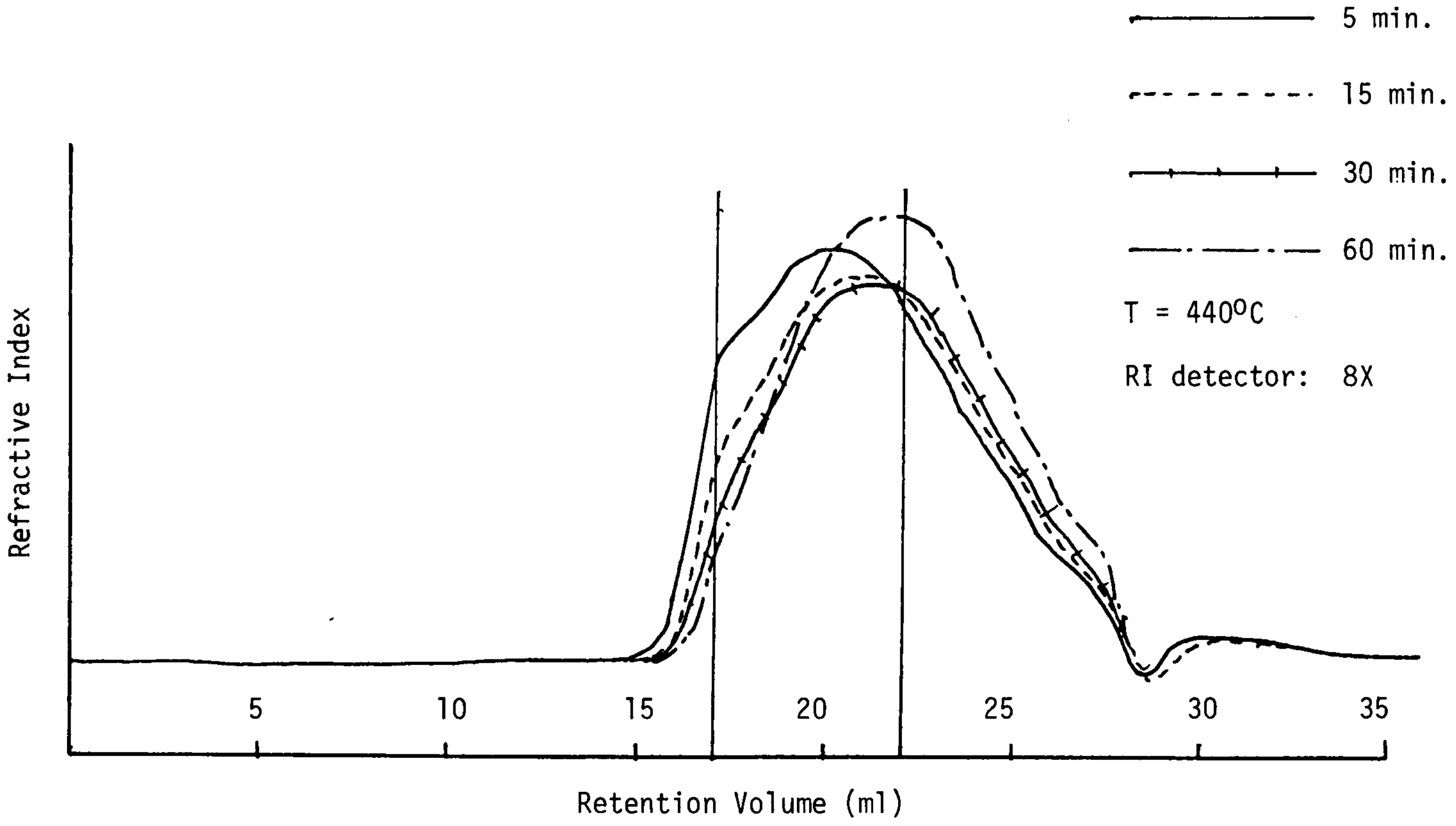


Figure 3.A.9. Effects of Reaction Time on M.W. Distribution Asphaltenes from Tubing Bomb Reactor Products

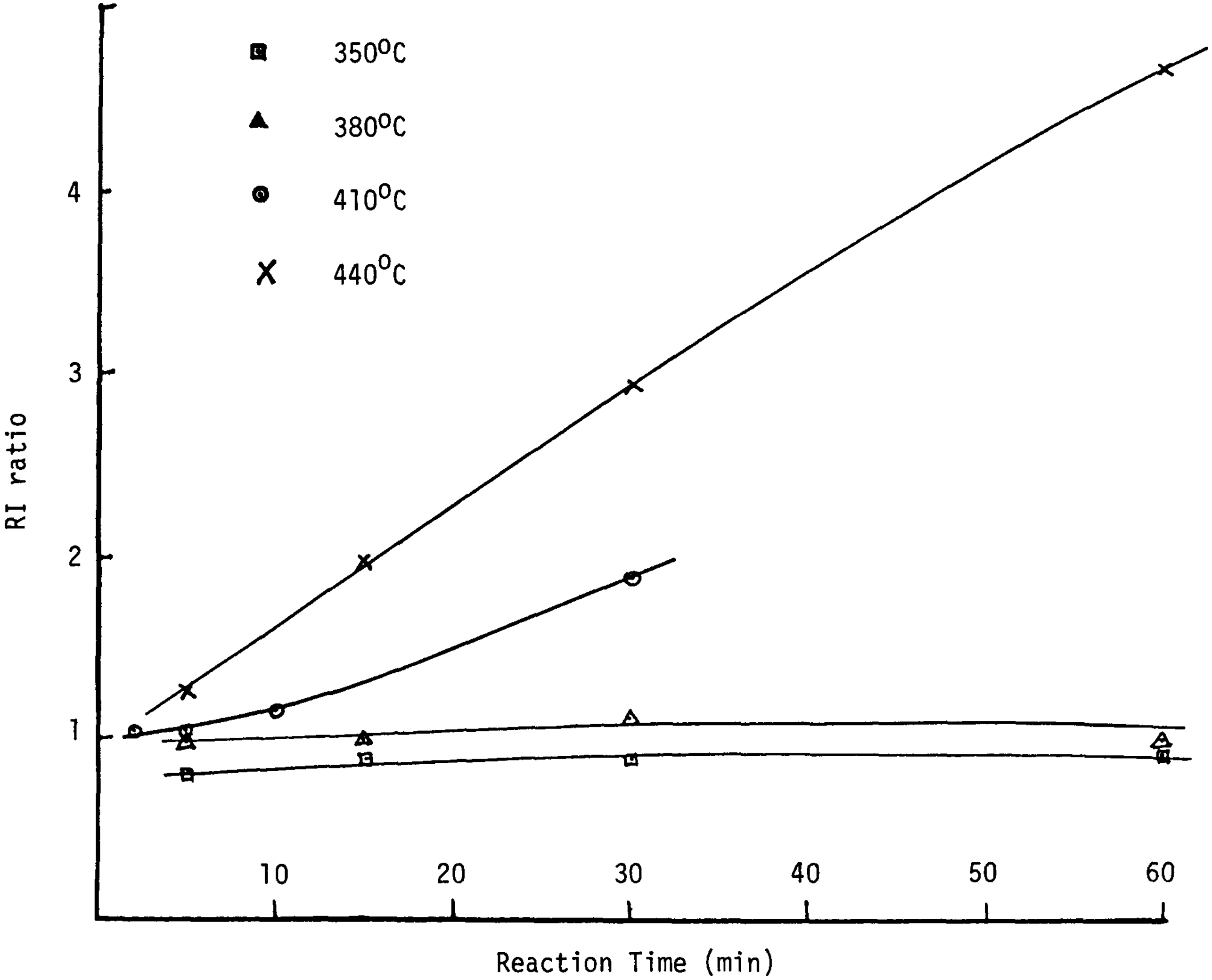


Figure 3.A.10. Correlation of the RI Ratio to Reaction Time for Different Temperature

time. At 410°C or 440°C the RI ratio is increasing quickly with reaction time which indicates that the MWD is shifting toward the low MW end. At 350°C or 380°C, the MWD appears to change little with variation in the reaction time, because the RI ratio was observed to be constant over the different reaction time (0 to 60 minutes). However, according to the results of Task 2.B., the asphaltene yield increased as the reaction time increased. These RI ratio results indicate that at the high reaction temperature, 410°C or 440°C, the degradation of coal substances or coal derived asphaltene was significantly occurred, while not apparent at the low reaction temperature, 350°C or 380°C.

In Fig. 3.A.11 the temperature effects are shown by plotting the RI ratio versus reaction temperature with variation in the reaction time. The higher the reaction temperature was the higher the RI ratio was observed, which means that more small molecules were formed at higher temperature.

Planned Work

In order to eliminate the solubility and reverse elution effect, experiments with other solvents such as pyridine will be performed. GPC calibration standards which have coal-like structure and composition will be obtained. A calibration curve for coal-type material will be constructed and used for the calculation of molecular weight of coal-derived products. The possibility of using GPC as a quick method to determine the product distribution will also be studied.

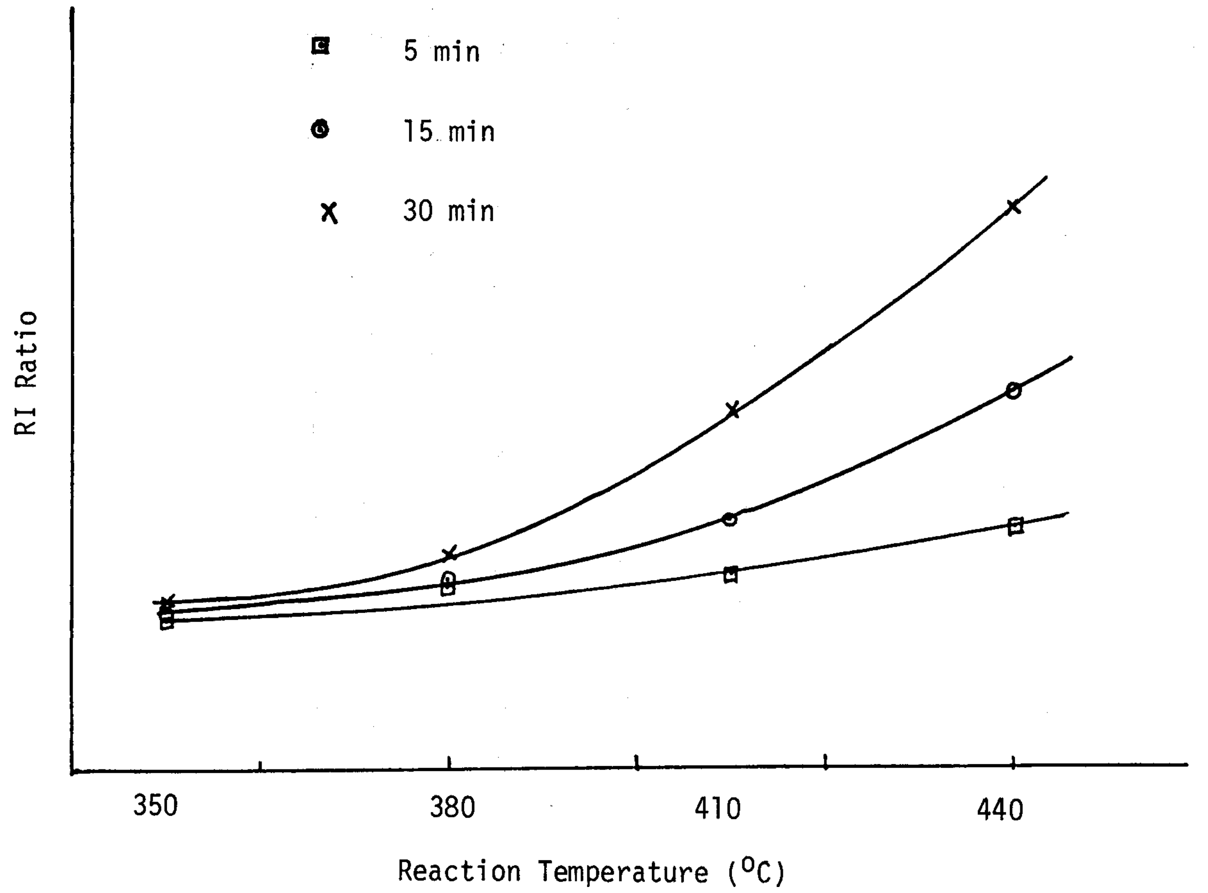


Figure 3.A.11. Correlation of the RI Ratio to Reaction Temperature for Different Reaction Time

3.B. Gas Chromatography of Coal Liquids and Coal-Derived Products

Objective

The objective of this subtask is to develop gas chromatographic techniques for the separation, identification, and characterization of coal liquids and sulfur containing coal species by using, 1) capillary columns and a flame photometric GC detector, 2) on-the-fly infrared spectroscopy of GC coal liquids effluent, and 3) usual GC detectors, FID and TC. Through the development of these gas chromatographic techniques, the determination of a solvent quality index and the characterization of coal and SRC by their GC chromatogram pattern will be achieved.

Progress

During this quarter, several representative liquid samples obtained from the studies of catalytic hydrodesulfurization of model sulfur containing compounds (benzothiophene, thiophene, phenyl sulfide and dibenzothiophene) have been extensively analyzed by using a gas chromatograph equipped with a flame photometric detector (sulfur sensitive detector) and quantified each reaction product by integration of each GC peak area. These samples were obtained mostly by reaction with hydrogen in the presence of iron or pyrite, which showed different reaction behavior in the hydrodesulfurization reaction presumably becuase of the presence of H_2S produced from pyrite (refer to the previous progress report). Some reaction products or intermediates, containing sulfur in their molecular structures, have been identified in order to verify reaction courses and to provide a basis for kinetic studies. Further identification of unknown peaks are in progress.

Experimental conditions of GC analysis have been summarized in Table 3.B.1. Typical GC chromatograms are shown in Figures 3.B.1., 3.B.2., 3.B.3., and 3.B.4. Current progress in identification of each reaction product or intermediate has been tabulated in Tables 3.B.2., 3.B.3., and 3.B.4. Preliminary quantitative analysis of each product in the benzothiophene runs has been done based on the GC peak area of dodecane solvent (Table 3.B.5). The possibility of finding a better internal standard for quantitative analysis is also in progress because we use a sulfur sensitive, flame-photometric detector.

Discussion

Essentially, the same compounds were identified in the Benzothiophene model series. Three apparent differences occurred between those samples containing pyrite and ironcatalyst. They are an unknown compound and more ethyl phenyl sulfide were present in the pyrite sample and more ethyl benzene was present in the iron-sample(Figures 3.B.1., and 3.B.2). An unknown sulfur compound was present only in the phenyl sulfide sample catalyzed by pyrite (Figures 3.B.3., and 3.B.4); whereas the compound was absent in the sample with iron.

Planned Work

Future work is to include identification of the compound present in the phenylsulfide model sample catalyzed by pyrite and identification as well as quantitation of thiophene and benzothiophene model samples.

Table 3.B.1. Experimental Conditions of GC Analysis

GC: Varian Model 3700

Detector: Flame-Photometric Detector

Column: SP 2250, 10 ft, 1/8 inch diameter

Gases:		
	Helium (carrier)	30 ml/min
	Air #1	80 ml/min
	Air #2	170 ml/min
	Hydrogen	140 ml/min

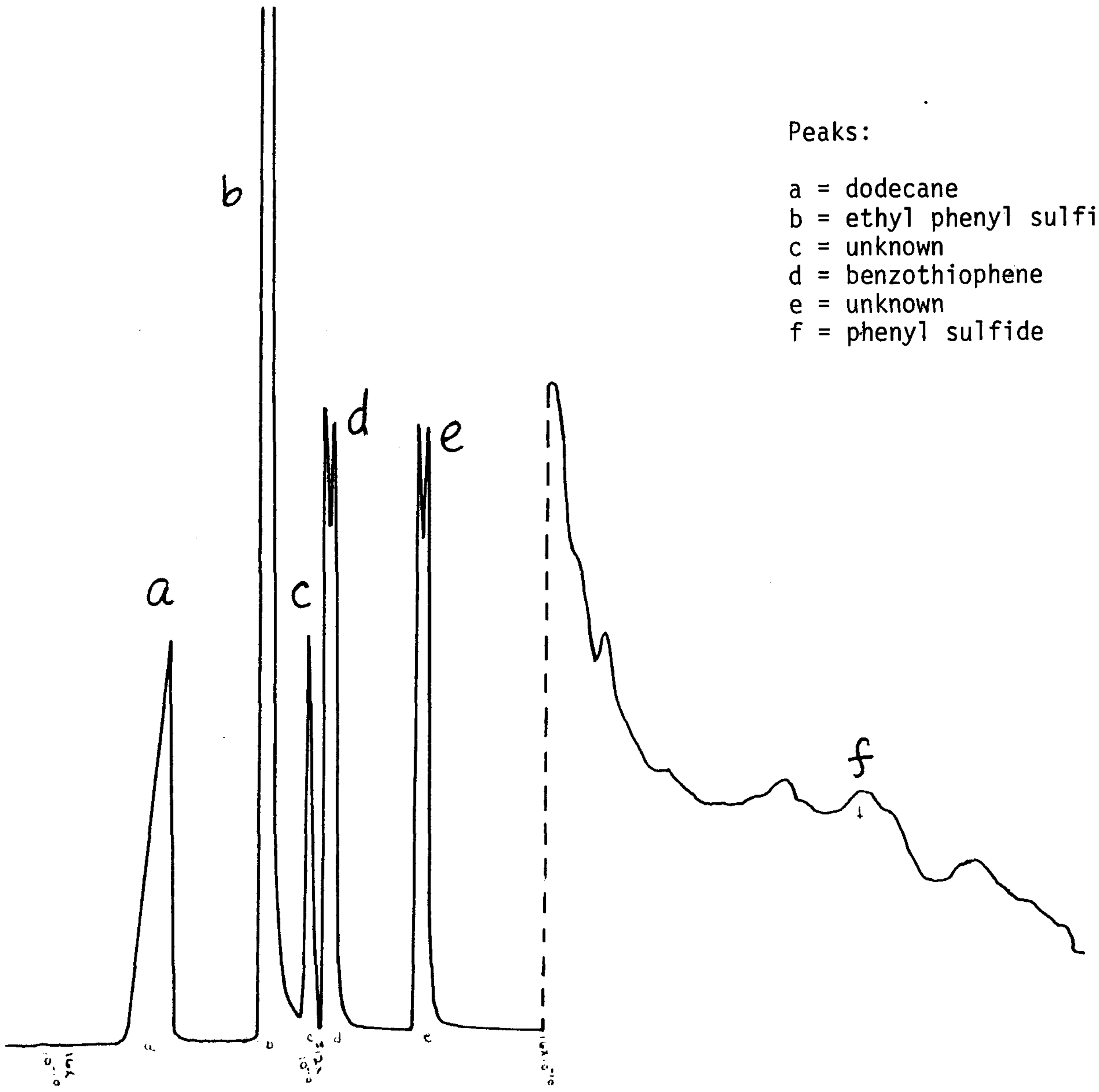
Samples:
8.8 wt% Benzothiophene in Dodecane
10 wt% Thiophene in Dodecane
10 wt% Phenyl Sulfide in Dodecane
3 wt% Dibenzothiophene in Dodecane

Hydrodesulfurization Conditions

$T = 410^{o}C$
$Pi = 1200$ psig H_2
30 min, 1000 pm
10 wt.% catalyst (Iron or Pyrite)

GC Operation:		
	Injection Amount	0.5 μl
	Temperature Program	100 to 200°C at 5°/min hold at 200°C 5 min
	Attenuations	varied according to sample
	Chart Speed	1 cm/min

Retention Times (cm):		
Benzothiophene		
	Ethyl Benzene	2.6
	Dodecane	6.6
	Ethyl Phenyl Sulfide	8.6
	Benzothiophene	9.8
	Phenyl Sulfide	20.0
Thiophene		
	2-methyl thiophene	3.0
	Thiophene	3.6
	n-butyl sulfide	6.1 or 7.3
	Dodecane	9.1
Dibenzothiophene		
	Dodecane	3.0
	Dibenzothiophene	16.5



Peaks:

a = dodecane
b = ethyl phenyl sulfide
c = unknown
d = benzothiophene
e = unknown
f = phenyl sulfide

Figure 3.B.1. GC Chromatogram-Benzothiophene Run with Pyrite as Catalyst

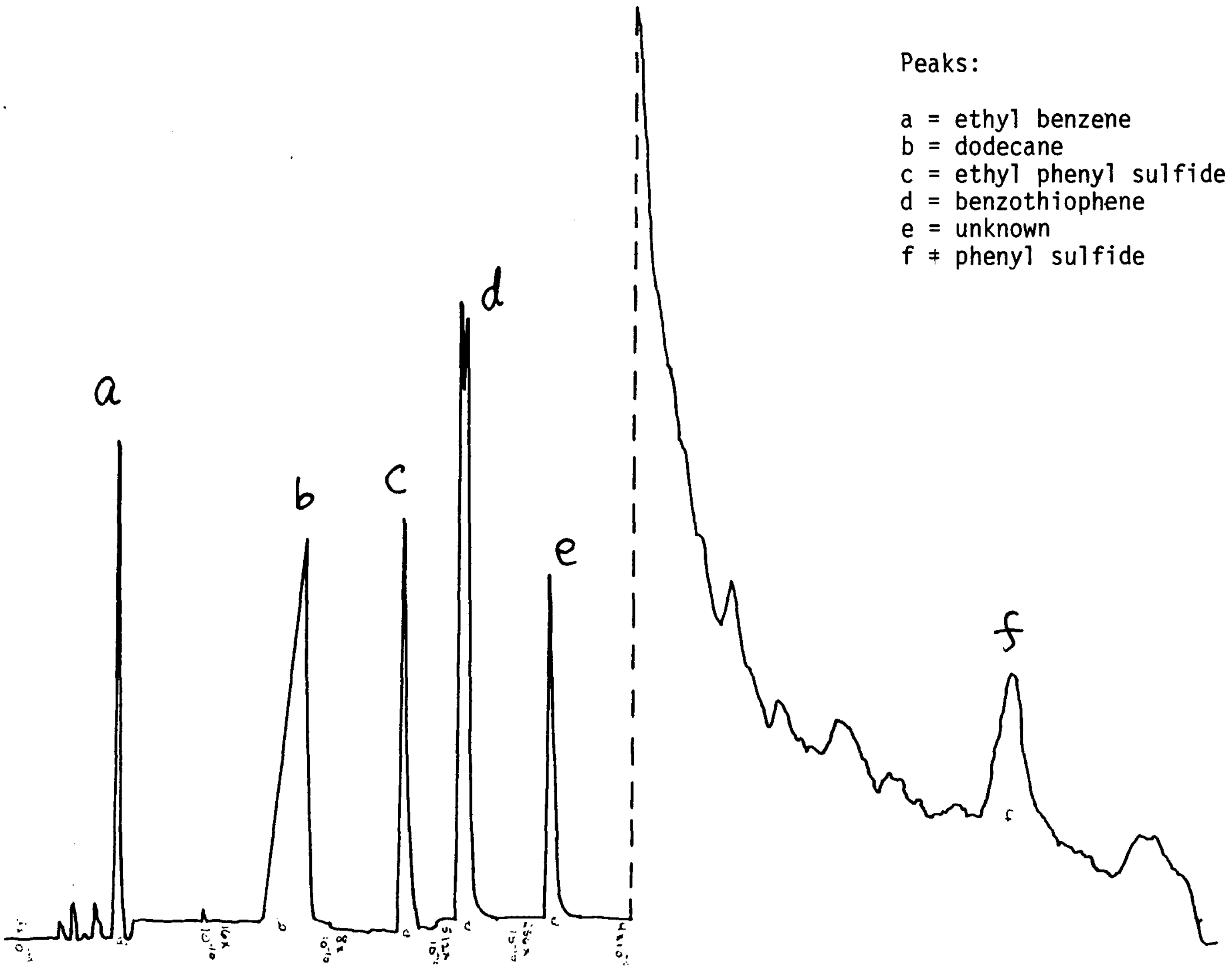
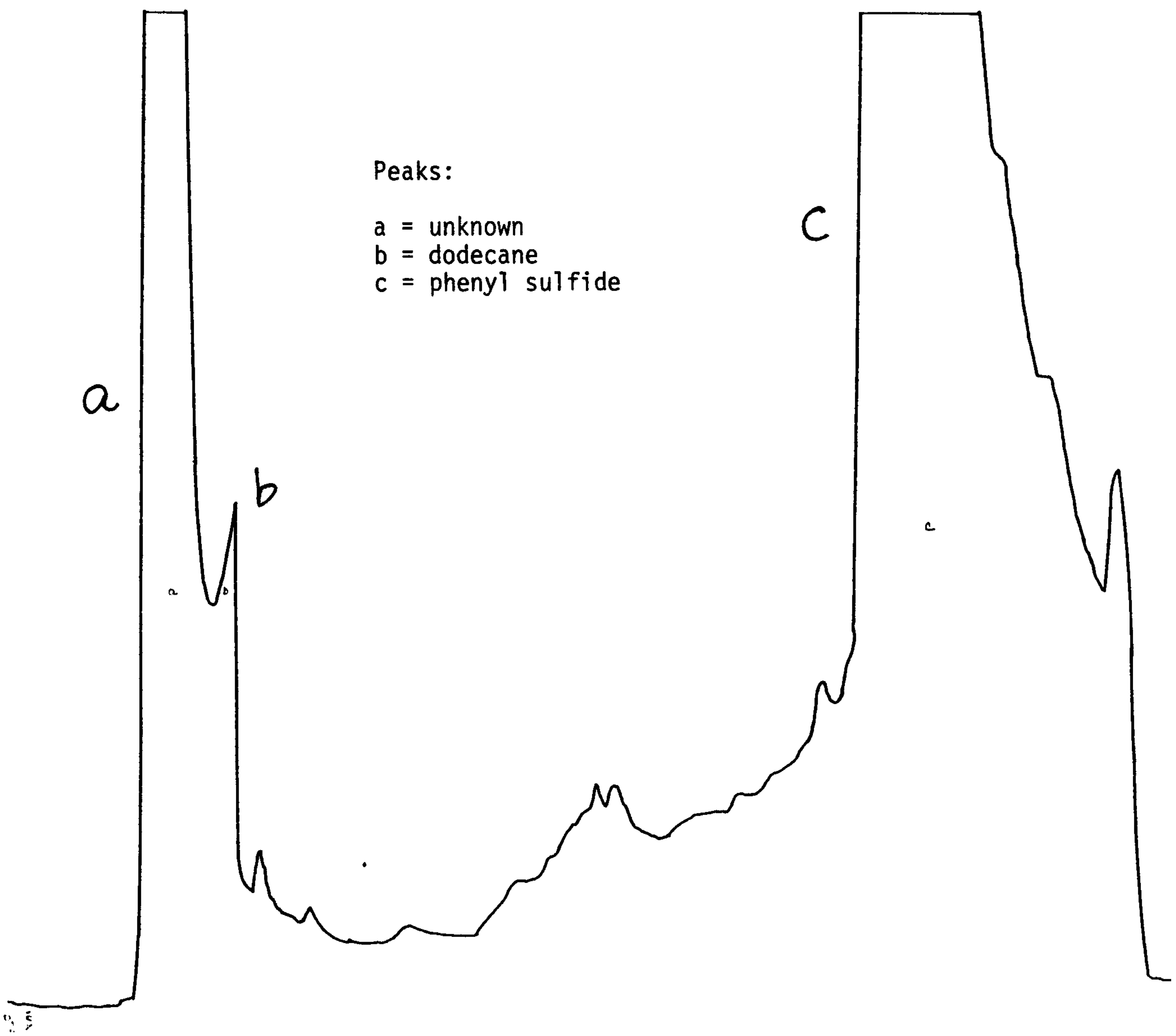


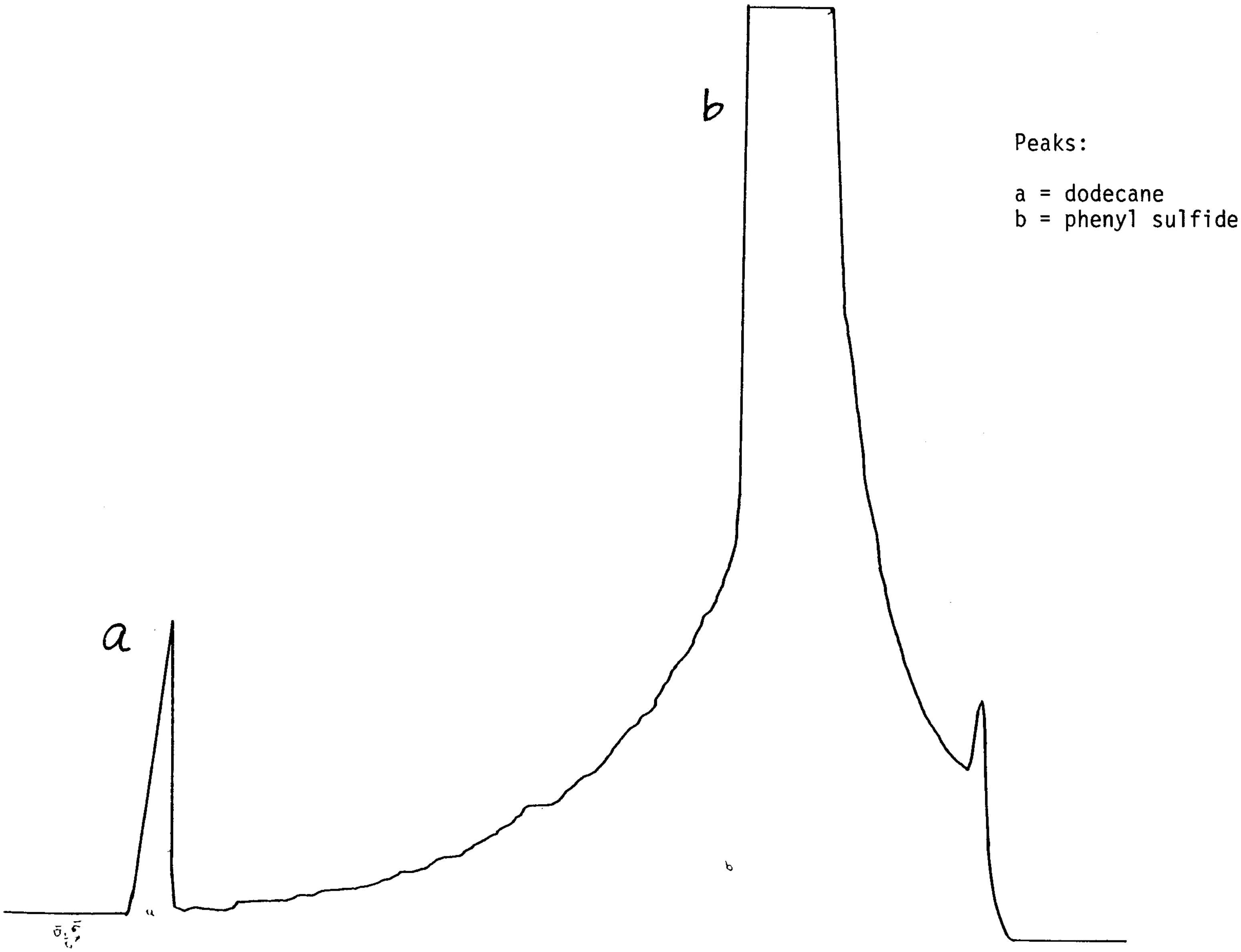
Figure 3.B.2. GC Chromatogram-Benzothiophene Run with Iron as Catalyst



Peaks:

a = unknown
b = dodecane
c = phenyl sulfide

Figure 3.B.3. GC Chromatogram-Phenyl Sulfide Run with Pyrite as Catalyst



Peaks:

a = dodecane
b = phenyl sulfide

Figure 3.B.4. GC Chromatogram-Phenyl Sulfide Run with Iron as Catalyst

Table 3.B.2. Benzothiophene Runs Identification

Sample	TD 9B	TD 5C	TD 2
Solvent	Dodecane	Dodecane	Dodecane
Catalyst	Pyrite	Iron	Blank
Peaks Identified	Dodecane Benzothiophene Phenyl Sulfide Ethyl Benzene Ethyl phenyl sulfide	Dodecane Benzothiophene Phenyl Sulfide Ethyl Phenyl Sulfide Ethyl Benzene	Dodecane Benzothiophene
Major Peaks	5	4	
Sulfur peaks	3	3	
Hydrocarbon	1	?	
Not identified	2	1	

Table 3.B.3. Thiophene Runs Identification

Sample	PD 10	PD 8	PD 2
Solvent	Dodecane	Dodecane	Dodecane
Catalyst	Pyrite	Iron	Blank
Peaks Identified	Thiophene Dodecane	Thiophene Dodecane n-butyl sulfide 2-methyl thiophene	Thiophene Dodecane
Questionable Peaks		Dodecane thiol	
Major peaks (not solvent)		5	
Sulfur Peaks		4	
Hydrocarbon (not solvent)		?	
Not identified		1	

Table 3.B.4. Dibenzothiophene Runs Identification

Sample	DD1-A	DD-2	DD-5
Solvent	Dodecane	Dodecane	Dodecane
Catalyst	Original	Blank	Iron
Peaks Identified	Dodecane Dibenzothiophene	Dodecane Dibenzothiophene	Dodecane Dibenzothiophene
Major Peaks (not solvent)	1	2	2
Sulfur Peaks	1	2	2
Not Identified		1	1

Table 3.B.5. Quantitative Analysis of Benzothiophene Runs Based on Dodecane Peak Area

Sample	GC Peak Area Ratio to Dodecane				
	Ethyl Benzene	Ethyl Phenyl Sulfide	Benzothiophene	Unknown	Phenyl Sulfide
Blank	-	0.003	$8.3\text{x}10^2$	$9.9\text{x}10^1$	-
	-	0.003	$8.4\text{x}10^2$	$9.51\text{x}10^1$	-
Iron	0.029	0.148	$3.56\text{x}10^3$	$4.4\text{x}10^2$	0.185
	0.027	0.157	$3.5\text{x}10^3$	$4.2\text{x}10^2$	-
Pyrite		7.3	$2.9\text{x}10^3$	$4.5\text{x}10^3$	0.33
Original	-	-	$8.36\text{x}10^2$	-	-
	-	-	$8.13\text{x}10^2$	-	-

3.C. Energy Dispersive X-Ray Fluorescence Analysis of Coal, SRC, and Coal Minerals

Objective

The objective in this subtask is to examine the trace elements present in coal and SRC by developing a reliable coal standard and a subsequent catalogue of trace minerals in various coals and SRC's, by studying the effect of mineral catalysts on the trace metals present in SRC and by performing mineral balances on sulfur and iron in the SRC process stream.

Progress

With the Kevex^R Energy Dispersive X-Ray Unit we have, it is possible to analyze both solid and liquid samples. Several secondary targets are provided with this instrument, allowing a rather wide range of elements to be analyzed with a high degree of efficiency.

Solid samples are normally prepared by the procedure of Kuhn (Illinois Geological Survey, circular #499, 1977). This procedure consists of first grinding the sample to a fine (-325) powder. A rough pellet of the ground sample is then made, and a boric acid backing is added. The combination of pre-formed pellet and backing is then converted into a finished pellet by pressing in a hydraulic press for approximately thirty minutes at a pressure of twenty tons. This gives a suitable surface for X-Ray analysis. The pellets are then placed in the X-Ray chamber, which is then evacuated to a residual air pressure of around 100 μm of Hg. The analysis is then carried out, using the procedure indicated below.

Liquid samples are treated differently, as befits their nature. The samples are placed in "Somar^R" cups, with the end of the cups sealed with polypropylene filler. There are no problems with the surface of the sample, as a liquid always presents a suitable surface. The samples are then placed in the X-Ray chamber, and the chamber is flushed with Helium gas, at ambient pressure, with a slight positive pressure maintained to prevent back filling with air. This is done to minimize X-Ray absorption between the sample and the detector. This avoids the possible problems caused by the relatively high vapor pressures of the liquids under analysis. Occasionally, solid samples are treated by the same method, with the powdered smaple being placed in the analysis cup. This is done whenever the sample is needed for later tests, so that the presence of the backing material is unsuitable, or when insufficient quantity of sample exists to pelletize.

The X-Ray analysis is normally carried out using Ti, Ge, and Mo targets. This allows for the analysis of all elements from Al to Zr by their K transitions (these are the most intense X-Ray emission lines, and allows the greatest accuracy of analysis). Elements of higher atomic weights are also analyzable using their L transitions, which are the second most intense transitions. This covers all of those metallic elements normally present in coal which are suitable for X-ray analysis. This allows the simultaneous analysis for typically fifteen or more elements.

X-Ray exposure (counting) times normally used are 200 and 500 seconds per target with Ti normally used at the lower time. This represents a good compromise between speed of analysis and good line shapes and signal-to-noise ratio. The higher times are usually necessary for the other targets, due to the (typically) much lower concentration of elements analyzed using these targets. This allows the simple and rapid determination of elements present in concentrations of less than 10 ppm.

Application of X-Ray Analysis in Elements Determination of SRC-and Coal-Related Samples

Several areas connected with the X-ray fluorescence analysis facility have shown considerable progress over the preceeding quarter. These include: 1) improvement in accuracy in analysis; 2) alternative analysis schemes; 3) alterations made to improve overall systems reliability.

The improvement in accuracy of the unit has resulted from the acquisition of coal standard samples from the Illinois Geological Survey. These standard samples have undergone extensive analysis (using the relevant ASTM determination for elemental concentrations), and are virtually the only standards for elemental concentrations in coal which are available. The use of these standards for the purpose of calibaration of the calculations using the XRF analyzer has allowed the accuracy determination of important trace and minor elements to be greatly improved. Further improvements in the accuracy through use of other standards is anticipated although the values obtainable currently exhibit an accuracy that lies with sampling errors of the specimen under investigation.

The use of these standards will also lead to an improvement through their incorporation (as standards) in the NRLXRF program for the reduction of X-Ray fluorescence data. This program is being used in an IBM 370/158 for determining the elemental concentration in a given sample from the X-Ray emission spectrum. This program will significantly upgrade the ability to make accurate concentration determinations both through the greater versatility of the calculational algorithm and through the greater variety of line types which can be analyzed. Previously, only $K\alpha$, $L\alpha$, and $M\alpha$ lines have been usable for analysis. This program will also allow the use of $K\beta$, $L\beta_1$, and $L\beta_2$ lines for concentration determination. This is a major advance, as overlaps can make data reduction more difficult when only a single line in a double is used for the analysis. When both lines are used, the probability of overlaps occurring in both lines is greatly reduced. This program uses a fundamental parameters method for the calculation of elemental concentrations combined with an empirical approach. Thus the incorporation of additional standard spectra with this program should lead to significant improvements in available accuracy.

The combination of both these features should enhance the accuracy and versatility of XRF analysis of coals and coal-related products (such as SRC).

Also, some alterations, additions, and changes to the XRF system have been made to improve system accuracy. These include replacement of defective power supplies in the system, addition of a helium-flow system to permit the high-accuracy analysis of liquid samples, and overall system maintenance. In the near future, improvements are anticipated in sample preparation facilities.

Currently, work is in progress on materials balances in the SRC process using XRF analysis. It is anticipated that the information derived from this study will allow improvement in the SRC process through an understanding of the source of abrasive materials noted at the Wilsonville SRC pilot plant. It is hoped that the information may also lead to an improvement in understanding the effects of process parameters on trace elements distribution among the reaction products, and their effect on the overall process.

It has been noted that in the course of this study that a significant amount of material is leached from the reactor walls. Details of this factor will be studied also.

CONCLUSIONS

1. The effect of the initial particle size of a coal on the final particle size of the product was observed by Coulter Counter analysis to be significantly dependent on the types of coals; Amax coal, a slow dissolving subbituminous coal, showed radical changes in mean particle size of the reacted coal when the initial particle size was varied, while Kentucky 9/14 coal, a fast dissolving bituminous coal, showed very little effect.
2. In the presence of tetralin as solvent, the solvent/coal ratio (1 to 4) had little effect on the coal dissolution yield with different reaction times (0 to 60 minutes). LRO and creosote oil as solvents behaved differently from tetralin in the coal dissolution, which could be due to a combination of two governing factors, hydrogen transfer reactions and physical solvation of coal-derived species to prevent char formation.
3. Pretreatment of coal with $Fe_2(SO_4)_3$ solution resulted in a sulfur removal of about 20%; when followed by tetralin-liquefaction an additional 30% of the sulfur was removed. An addition of pyrite (25% of the coal) in liquefaction decreased significantly the hydrodesulfurization rate, that is, % liquid sulfur increased from 0.21 to 0.38. $Fe_2(SO_4)_3$ pretreatment of Kentucky 9/14 coal had little effect in the sulfur content of the liquid product upon liquefaction possibly due to the low content of pyrite in the coal. Liquefaction yield was not affected by $Fe_2(SO_4)_3$ pretreatment.
4. In coal liquefaction with LRO as solvent, Kentucky coal ash and SRC residue ash, representative coal minerals, significantly enhanced the rate of sulfur removal, that is, the percent liquid sulfur decreased from 0.4% without catalyst to 0.3% in the presence of these mineral catalysts. Both coal ash and SRC residue ash enhanced solvent quality based on tetralin/naphthalene ratio, possibly due to the catalytic hydrogenation activity of these mineral catalysts.

5. The pretreatment of coals by acid extraction or magnetic separation methods for demineralization appeared not to alter significantly the reactivity of organic material in the coal when reacted in the tetralin solvent in the presence of Co-Mo-Al catalyst.
6. The interaction between coal mineral matter and solvent LRO significantly altered the coal liquefaction behavior. Coal mineral matter enhanced the dissolution yield about 15 to 24% and the hydrogenation reaction, based on benzene solubles, about 11 to 15%. In contrast with LRO as solvents, the interaction in the presence of tetralin as solvent had little effect in the coal dissolution and hydrogenation reactions. These could be due to different characteristics of each solvent, that is, the hydrogen transfer reaction is the major governing reaction step in the presence of tetralin, while the combination of two factors, the hydrogen transfer reaction and the solvation of coal-derived species, are important in the presence of LRO.
7. Coal minerals, such as Fe, SRC residue ash and pyrite had moderate hydrodesulfurization activity with phenyl sulfide, but not with dibenzothiophene, which is the most difficult sulfur-containing compound observed in hydrodesulfurization.
8. Mathematical modeling of reaction kinetics in coal liquefaction with tetralin as solvent was achieved by using the Parameter Estimation method. Coal dissolution and hydrogen transfer kinetics expressions were obtained based on the second order assumption in the following reaction scheme:

$$\text{Coal} + \text{Tetralin} \rightleftharpoons \text{Preasphaltene} + \text{Naphthalene}$$

$$\text{Preasphaltene} \rightleftharpoons \text{Asphaltene}$$

$$\text{Asphaltene} \rightleftharpoons \text{Oil} + \text{Gases}$$

9. By GPC analysis of coal, SRC and coal-derived products (oil, asphaltene and preasphaltene), the pattern of GPC molecular weight distribution of THF soluble portion of coal and SRC was found to be generally broad and very similar regardless of the rank of coal (Monterey, Amax and Illinois #6). The Monterey

feed coal showed a heavier distribution than its SRC. GPC chromatograms of asphaltene and oil fractions were clearly discernable, but that of pre-asphaltene was not observed, probably due to its solubility in THF. The arbitrarily defined RI ratio of each GPC chromatogram of asphaltene at different reaction time showed that at the high reaction temperature, 410°C 440°C, the degradation of coal substances or coal-derived asphaltene occurred significantly, while it was not apparent at the low reaction temperature, 350°C or 380°C.

10. The flame photometric detector (sulfur sensitive) was helpful in identifying each unknown sulfur-containing compounds such as phenyl sulfide, ethyl phenyl sulfide, n-butyl sulfide and 2-methyl thiophene as trace side products in hydrodesulfurization of benzothiophene, thiophene, phenyl sulfide and dibenzothiophene.

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*U.S. GOVERNMENT PRINTING OFFICE : 1979 0-620-097/2231