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

Quarterly Report for the
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ABSTRACT

This report summarizes work done in the first year as well as in the fifth quarter of a program designed to better understand and improve the Solvent Refined Coal and related liquefaction processes. The research is concerned primarily with the chemical and physical principles of coal liquefaction, hydrogenation, and desulfurization. A major focus is on the variables and conditions affecting the reaction kinetics, yields and product distribution of the Solvent Refined Coal (SRC) process. These studies are closely related to the operation of the SRC pilot plant at Wilsonville, Alabama, and are carried out in cooperation with Southern Company Services and Catalytic, Inc., who operate the pilot plant. This close cooperation with a large scale (6 tons/day) coal conversion plant promotes urgency in the research program as well as indicating important areas of practical concern for increased research emphasis.

The ongoing program under the current contract can be subdivided into four broad areas; namely: (1) mechanistic studies of coal particle dissolution, (2) macroscopic reaction kinetics of coal liquefaction, and heteroatom removal, (3) detailed high pressure liquid chromatographic and analytical studies of coal liquefaction kinetics, (4) development and application of improved analytical techniques for coal liquids and coal conversion products.

Considerable progress has been made in several specific areas during the five quarters. Some of the most important accomplishments are:

(1) development of a Coulter Counter particle size method for measuring particle size in SRC process streams as an indication of filterability,
(2) determination of the selectivity of certain coal minerals for catalyzing hydrogenation/desulfurization reactions,
(3) development of a comprehensive multi-phase axial dispersion model for the continuous SRC reactor for predicting coal converison, desulfurization, and hydrogenation consumption in the SRC preheater/dissolver system,

(4) development of an X-ray fluorescence technique for the determination of metals, sulfur, and ash in SRC and feed coals,

(5) a detailed study of the effect of initial coal particle size on coal conversion in the SRC process,

(6) solubility data for hydrogen, methane, and carbon dioxide in SRC recycle solvent at process temperatures and pressures,

(7) experimental data elucidating the viscosity peaks occurring during the early coal depolymerization period in the SRC preheater,

(8) development of an in-situ sulfur scrubbing process for the SRC dissolver,

(9) confirmation of the dependence of coal dissolution rate upon hydrogen donor content of the solvent,

(10) correlation of qualitative dissolution behavior observed in a transparent wall microreactor with actual operating results from the Wilsonville SRC pilot plant,

(11) data showing that agitation rate is a significant rate limiting step in the presence of an active hydrogenation catalyst,

(12) data showing that iron containing compounds represent the most active coal mineral catalysts.

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 results 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

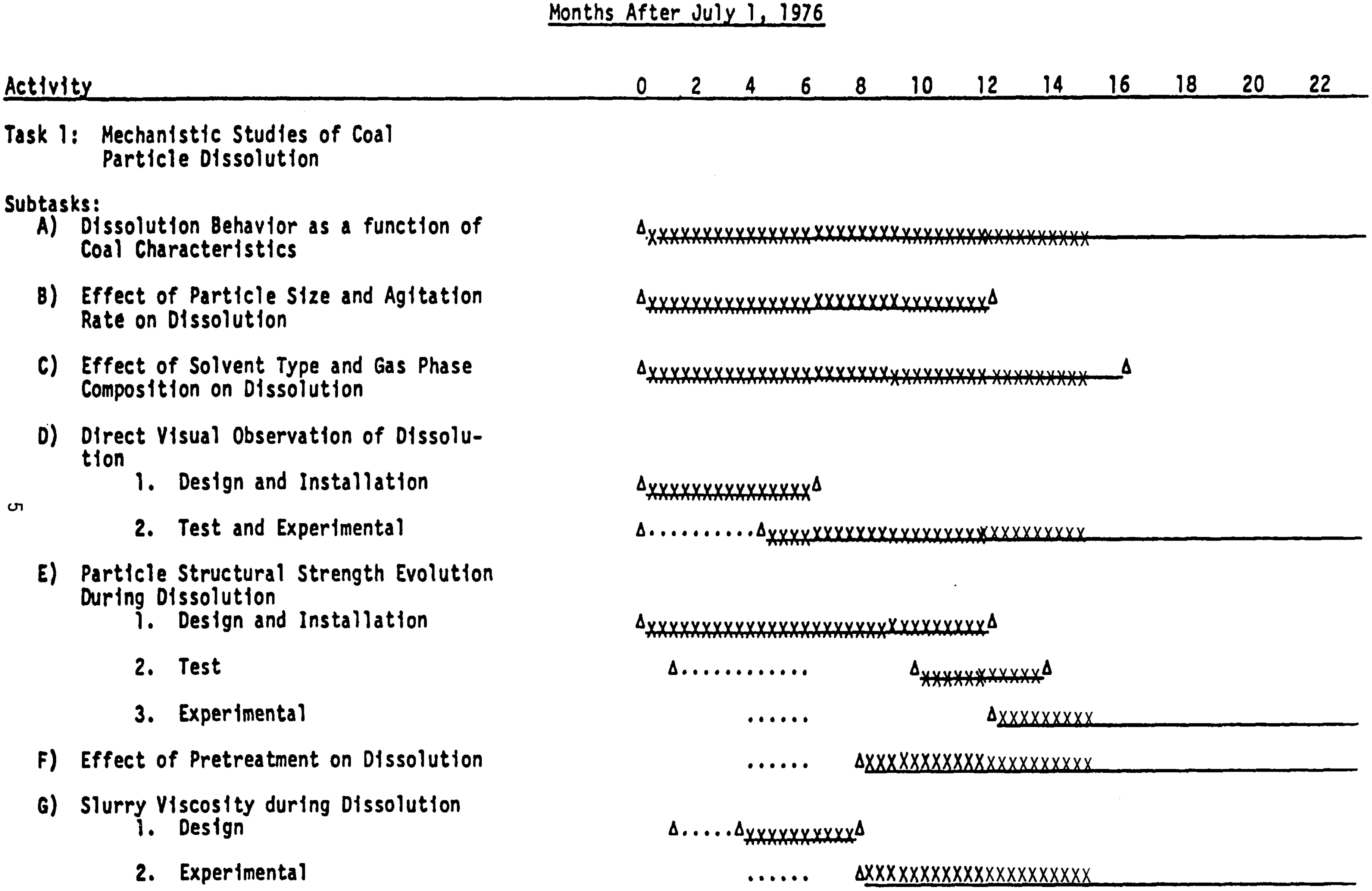


Figure 1. Work Schedule

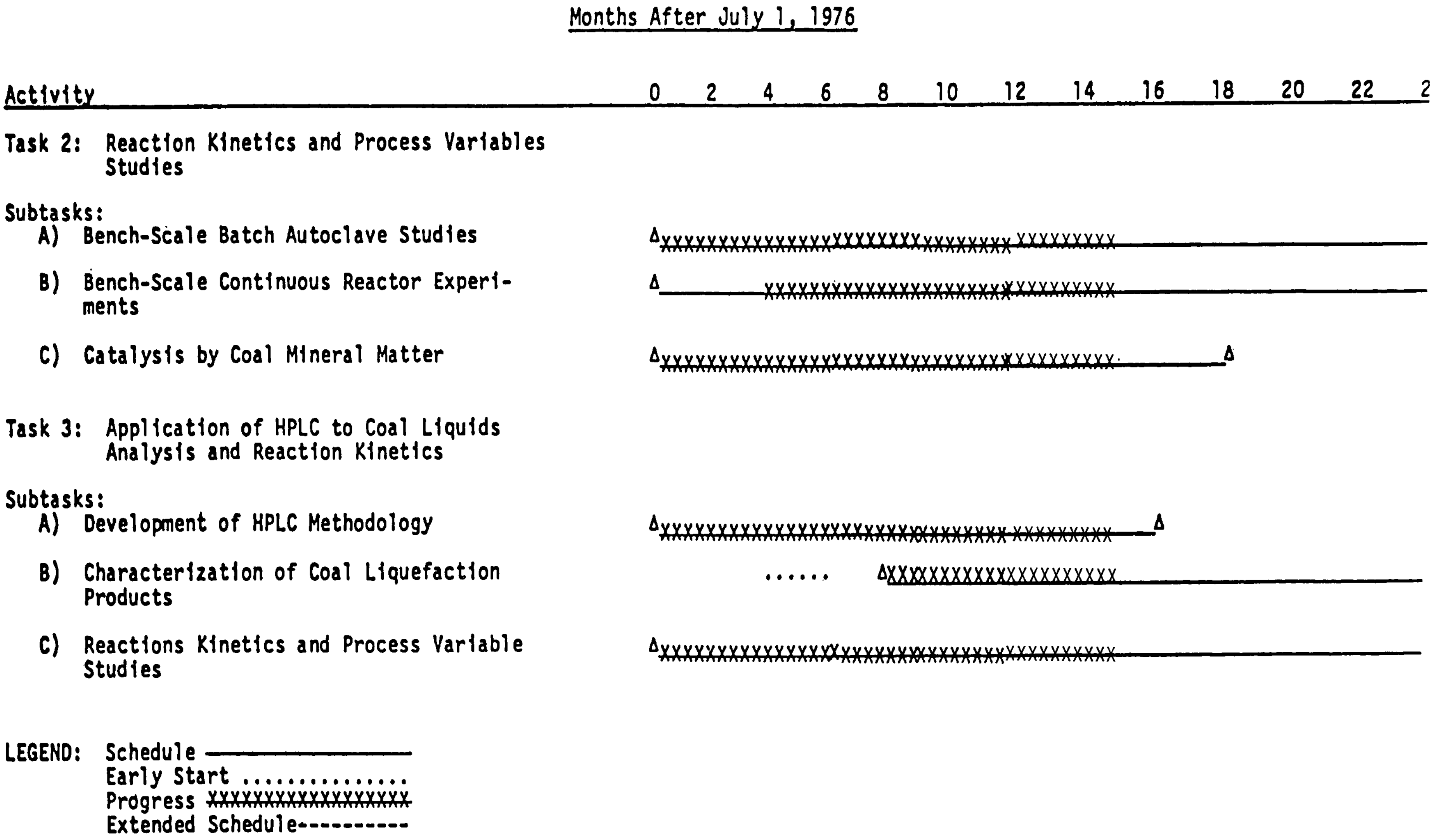


Figure 1 (continued)

TECHNICAL PROGRESS BY TASKS

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.

Summary of Progress

Thus far, several coals have been investigated for their overall dissolution behavior. These include Kentucky 9/14 coal mixture, Pittsburgh No. 8, Illinois No. 6, and an Amax subbituminous coal from Wyoming. Analyses of these coals are given in Table 1.A.1. All of these coals have been processed by the Wilsonville SRC pilot plant and our dissolution results have generally agreed with their observations. As an example, typical results of a batch dissolution experiment are pictured in Figure 1.A.1, comparing the dissolution kinetics of bituminous Kentucky 9/14 coal mixture with that of subbituminous Amax coal.

From Figure 1.A.1, it is obvious that the Amax coal performs much more poorly under SRC liquefaction conditions than does the Kentucky coal. Similar

TABLE 1.A.1.

CHEMICAL ANALYSIS OF PITTSBURGH NO. 8 COAL

Ultimate Analysis

Carbon	76.09%
Hydrogen	5.14%
Nitrogen	1.22%
Chlorine	0.11%
Sulfur	2.57%
Ash	8.11%
Oxygen (by diff.)	6.76%

Proximate Analysis

Moisture	0.32%
Ash	8.09%
Volatile Matter	39.63%
Fixed Carbon	51.96%

CHEMICAL ANALYSIS OF OF AMAX COAL

Ultimate Analysis

Carbon	67.97%
Hydrogen	4.87%
Nitrogen	1.04%
Chlorine	0.01%
Sulfur	0.64%
Ash	6.65%
Oxygen (by diff.)	18.83%

Proximate Analysis

Moisture	6.61%
Ash	6.21%
Volatile Matter	41.90%
Fixed Carbon	45.28%

CHEMICAL ANALYSIS OF ILLINOIS NO. 6 COAL

Ultimate Analysis

Carbon	70.57%
Hydrogen	4.93%
Nitrogen	1.10%
Chlorine	0.04%
Sulfur	3.58%
Ash	10.57%
Oxygen (by diff.)	9.21%

Proximate Analysis

Moisture	5.76%
Ash	9.96%
Volatile Matter	45.75%
Fixed Carbon	38.53%

CHEMICAL ANALYSIS OF KENTUCKY NO. 9/14 MIXTURE

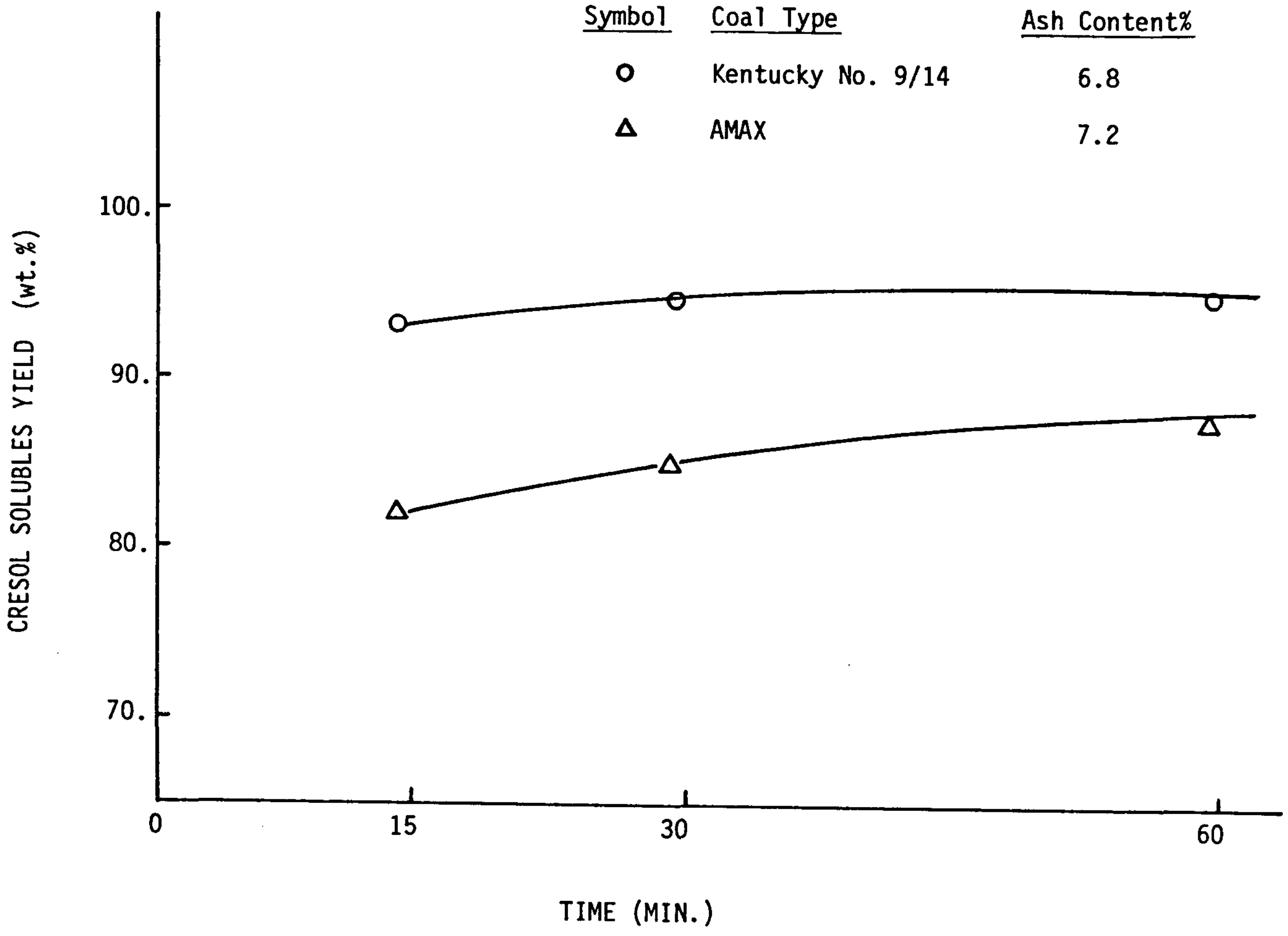
Ultimate Analysis

Carbon	70.70%
Hydrogen	5.02%
Nitrogen	1.43%
Chlorine	0.06%
Sulfur	3.75%
Ash	10.43%
Oxygen (by diff.)	8.61%

Proximate Analysis

Moisture	2.22%
Ash	10.20%
Volatile Matter	38.01%
Fixed Carbon	49.57%

Figure 1.A.1. Effect of Coal Type on Rate of Cresol Solubles Generation



Reaction Conditions

T= 410°C
P_i= 2000 psi H_2
2:1 recycle solvent-to-coal ratio

processing behavior was also observed at the Wilsonville pilot plant. The same relative trend between the two coals was observed in other solvents such as creosote oil (hydrogenated and unhydrogenated) and tetralin, although the absolute value of the yield was altered slightly by the different solvents.
The dissolution behavior of these coals has also been examined further under the remaining subdivisions of this task and will be further discussed herein. Although the results shown for the Kentucky (bituminous) and Amax (subbituminous) coals might be expected on the basis of rank, additional experiments have shown that rank alone is not a valid criterion by which to predict liquefaction behavior. For example: Bighorn coal -- a western, subbituminous coal -- was observed to dissolve at a rate that, although it was not as high as that of Kentucky No. 9/14, it was significantly higher than that of Amax coal, which is also a western subbituminous coal. As of yet, we have been unable to establish a comprehensive set of criteria so as to predict a-priori the liquefaction behavior of various coals; however, it is clear that factors such as rank, chemical, petrographic, and mineral matter composition, and even the physical treatment of the coal prior to liquefaction will affect its behavior. These facts are evidenced by the work performed in the other parts of this contract, as they are all related to various aspects of coal liquefaction. All the ramifications of each result toward coal dissolution behavior will not be brought out at this point, but will be discussed as appropriate under each task as they occur. Needless to say, since one does not know the exact chemical (molecular) structure of any particular coal, (and even if one did, the liquefaction behavior would still not be immediately forthcoming), one must of necessity rely on macroscopic properties such as rank, elemental analysis, petrography, etc., for some idea as to liquefaction behavior. Of course, even then, the behavior of any single coal will vary widely with

particular liquefaction conditions such as solvent type, and process variables. The effects of these latter factors upon coal liquefaction behavior are also considered in subsequent parts of this task.

A major effort in the particle dissolution work has been concentrated on developing a technique for the observation of discrete and/or populations of coal particles during the early dissolution/liquefaction period. At this point, the research has culminated in the development of a technique, based upon Coulter Counter analysis, which is able to provide the detailed observation method which is required to discern among the dissolution behavior of various coals.

The Coulter principle was originally applied to blood cell counting (1) and is now widely used in the biomedical area for cell counting and size distribution (2). Industrial use of the Coulter technique is now widespread (3). The Coulter technique has been applied in coal research in the size analysis of pulverized coal, coal dust, and fly-ash (4). Our interest in the Coulter technique stems from our study of particle size distributions in the SRC process. Interest in the effect of the mean particle size in the effluent from the SRC dissolver on filtration along with the problem of dissolver solids accumulation has shown the need for a reproducible method of determining particle size in SRC process streams. In addition, the observation of a known particle size distribution of coal particles during dissolution would provide much more detailed information on liquefaction mechanisms than would, say, the observation of only a macroscopic property such as conversion or yield.

The Coulter technique measures the particle volume size distribution. The optimum volume measurement range is 2 to 40% of the aperture size used with lower measurements possible when a low noise background is maintained.

The particle diameter range effectively measured using SRC process samples is 1.0 to 92.0 μm. So far particle size distributions have been obtained for the Wilsonville SRC Pilot Plant filter feed and for certain Auburn University autoclave reaction mixtures. Development of a reproducible and reliable sizing technique using Coulter analysis has required close examination of three procedural variables: 1) the solvating ability of the electrolyte, 2) the length of sonication time and 3) the effect of solvent residence time on the particles. In each of the size distributions obtained, size distribution measurements were repeatedly reproduced within ±10% error. The mean particle size has been 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.

The effect of two dramatically different solvent systems on particle size distribution in SRC process samples is shown in Figure 1.A.2. The mean particle size for Emery coal filter feed is 7.5 μm in 2-propanol/LiCl and 3.5 μm in DMF/NH_4SCN. This difference can be attributed directly to the solubility of SRC in these two electrolytes. Solubility studies using Western Kentucky 9/14 SRC show that this SRC is 80% soluble at the 20 mg/ml level in DMF; whereas, in 2-propanol the solubility of SRC at that concentration level is 20%. Therefore, SRC particles which have settled out of the oil slurry after sampling account for the substantial difference in the SRC mean particle size in the two electrolytes. Another factor responsible for this difference in mean particle size is that DMF is a good solvating agent for the oil coating the SRC particles, while 2-propanol acts more as an anti-solvent causing the oil to cling to the SRC particles or possibly even to precipitate. The solvent of choice, therefore, in our further studies will be DMF since it is a good solvent for SRC and for the oil slurry. In solvating these two interfering substances, DMF

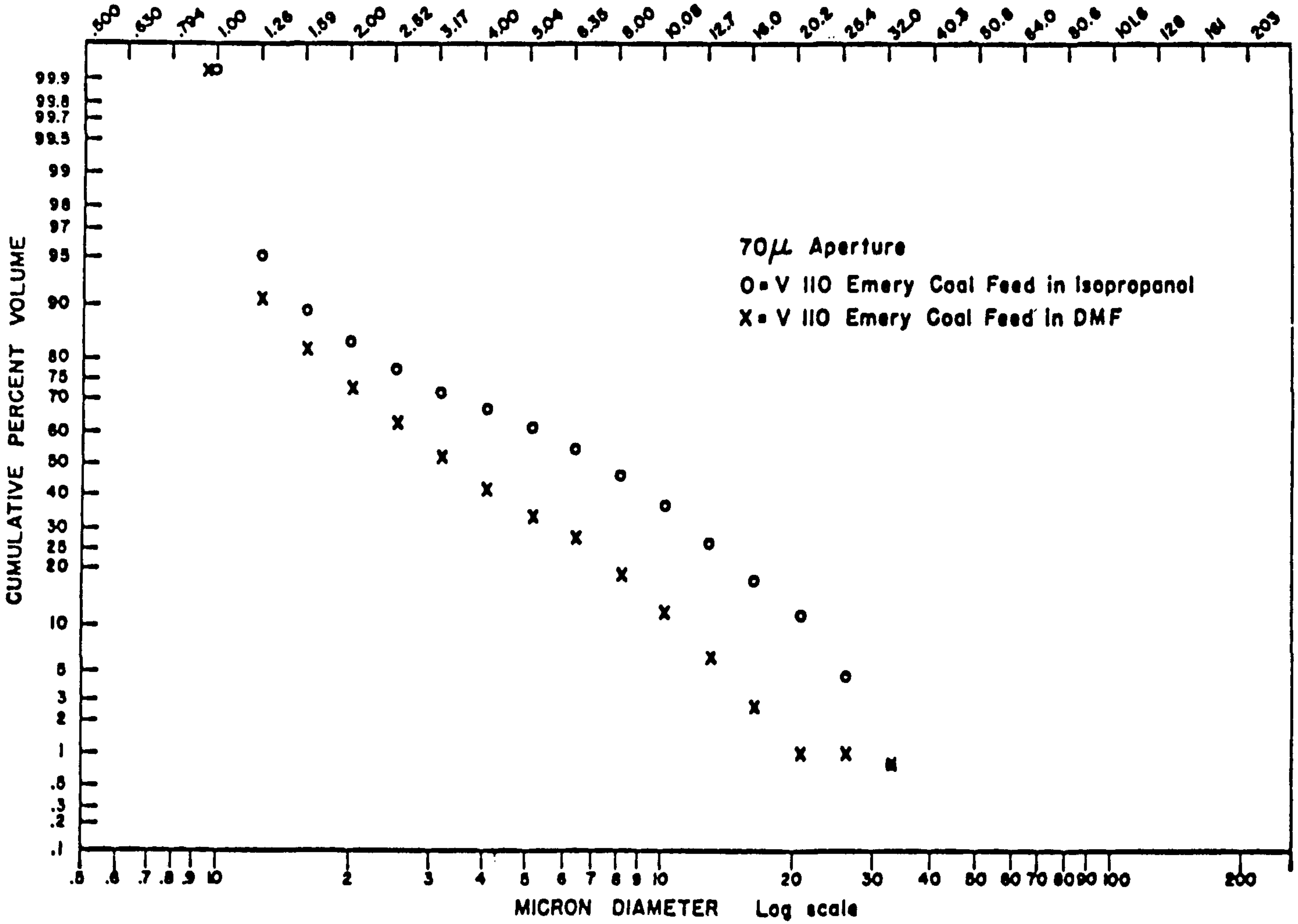


Figure 1.A.2. COMPARISON OF DMF AND ISOPROPANOL IN COULTER ANALYSIS OF SRC FILTER FEED USING 70μm APERTURE

provides a method of determining the true particle size of the mineral matter or "dirt" on the process stream.

To determine the effect of dissolution in DMF/NH_4SCN, a coal/oil slurry which had been sonicated 15 minutes was dispersed in electrolyte, stirred for one minute and then immediately analyzed. The particles from the SRC process are not affected by dissolution in the DMF electrolyte. Further studies (see Figure 1.A.3) demonstrated that the particle size remained essentially constant after two months of dissolution in DMF/NH_4SCN.

The reproducibility obtained using the resulting technique is excellent. As was recommended by Coulter, Inc., Xerox toner was used here as a calibration standard. As shown in Figure 1.A.4, our analysis of the Xerox toner agrees very well with that by Coulter, Inc.

Further verification of the Coulter technique by optical microscopy was also performed using the rigid polystyrene calibration spheres, 9.99 μm, shown in Figure 1.A.5 under 500 X magnification to have a diameter of 10.0 μm. Subsequent analysis of the polystyrene particle size by Coulter Counter agreed completely with the microscopy (Figure 1.A.6).

Thus far particle size distributions have been obtained for autoclave reaction mixtures produced at the Auburn University Coal Conversion Laboratory and for Wilsonville filter feed of Amax, Western Kentucky 9/14, Pittsburgh seam and Illinois Monterey coals. The particle size distributions for the Wilsonville filter feed closely resembled the distributions for the autoclave reaction mixtures for all the coals studied except Western Kentucky 9/14. The Wilsonville Kentucky 9/14 particle size distributions showed a significant shift to smaller particles when compared to the autoclave produced samples. Complete results of these experiments are presented at the Chicago ACS meeting in August, 1977.

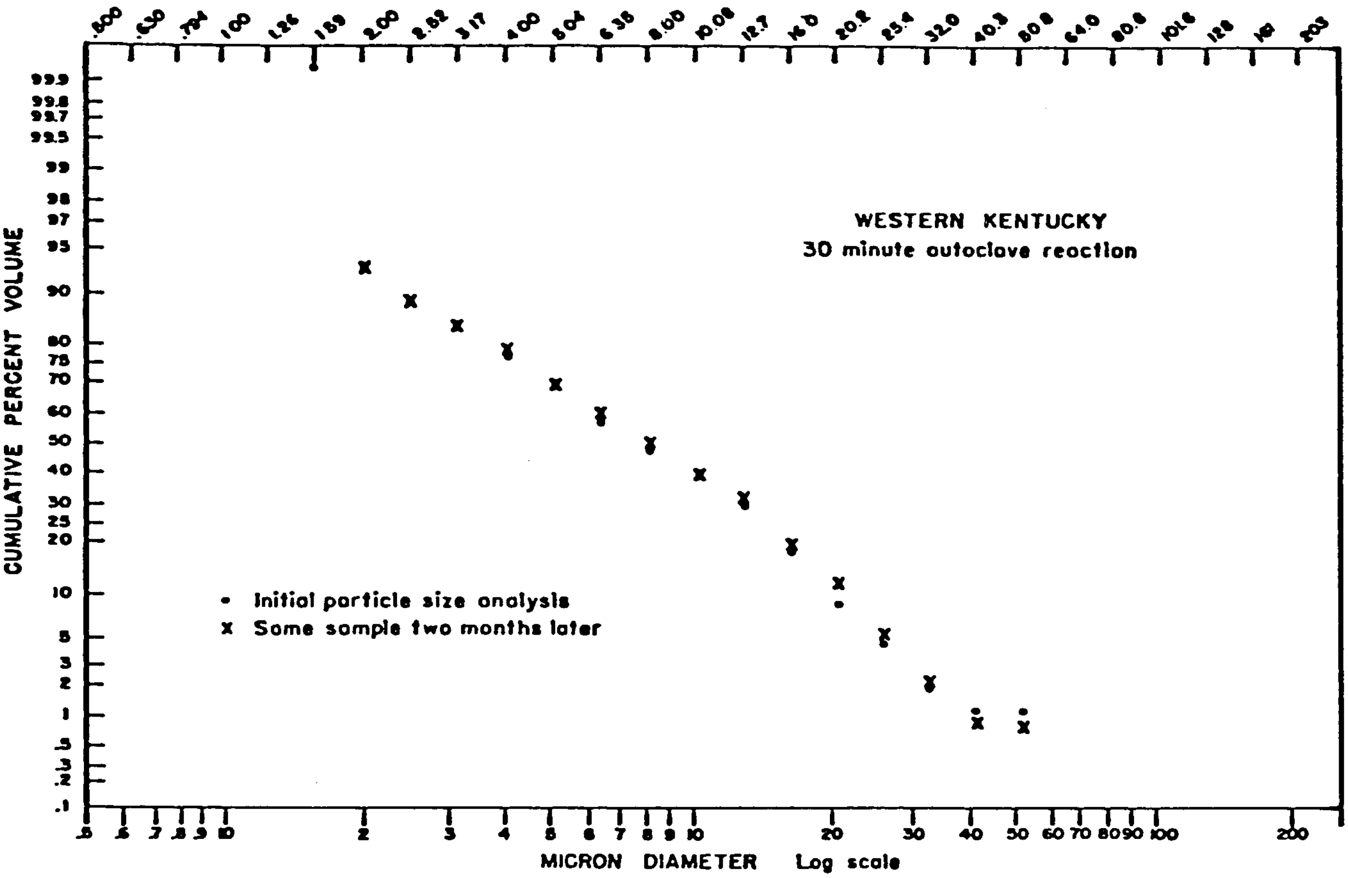


Figure 1.A.3. EFFECT OF TIME AND SOLVENT ON PARTICLE SIZE ANALYSIS

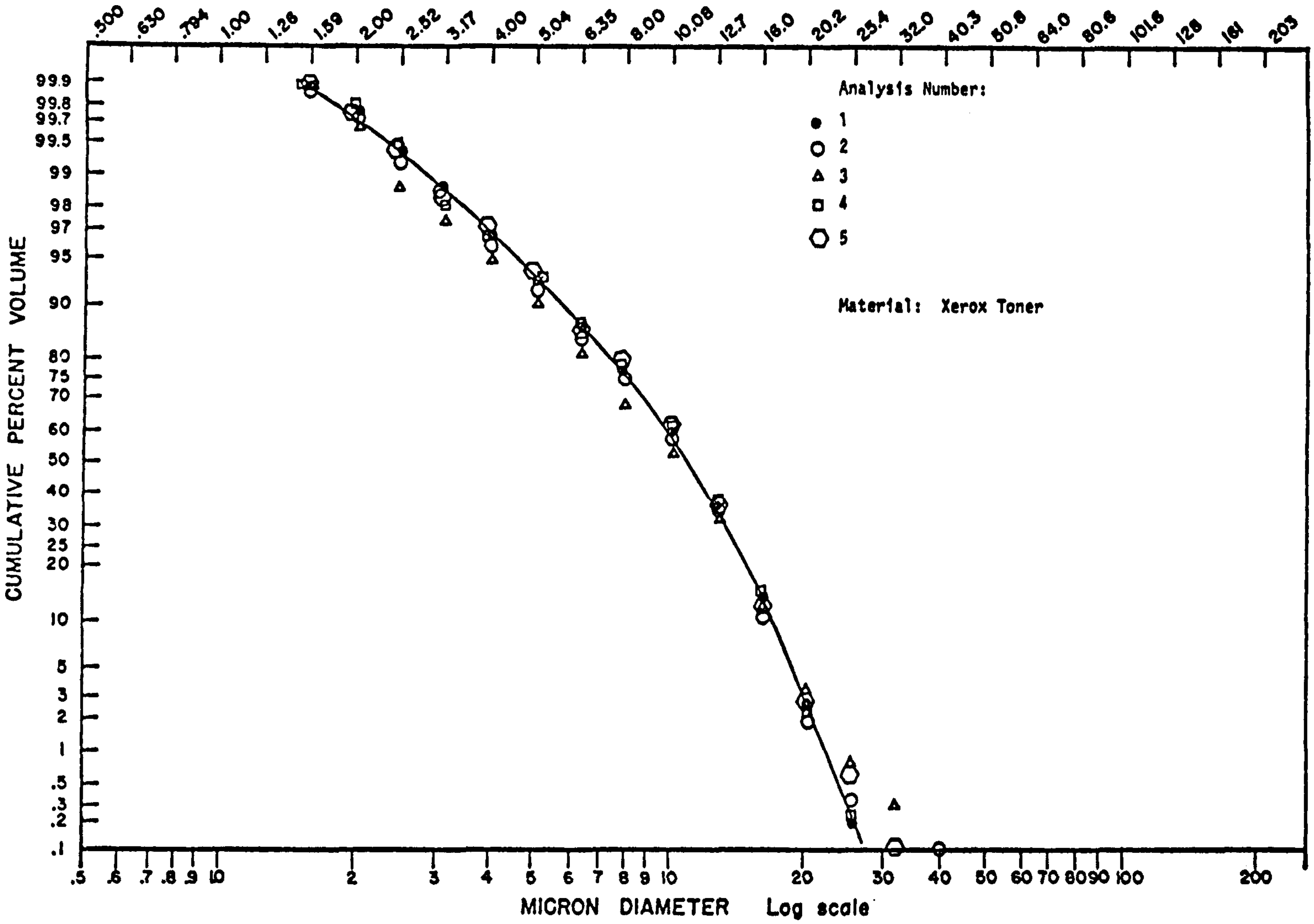


Figure 1.A.4. **An Evaluation of Degree of Internal Duplication Obtained for Size Analysis of Calibration Standard.**

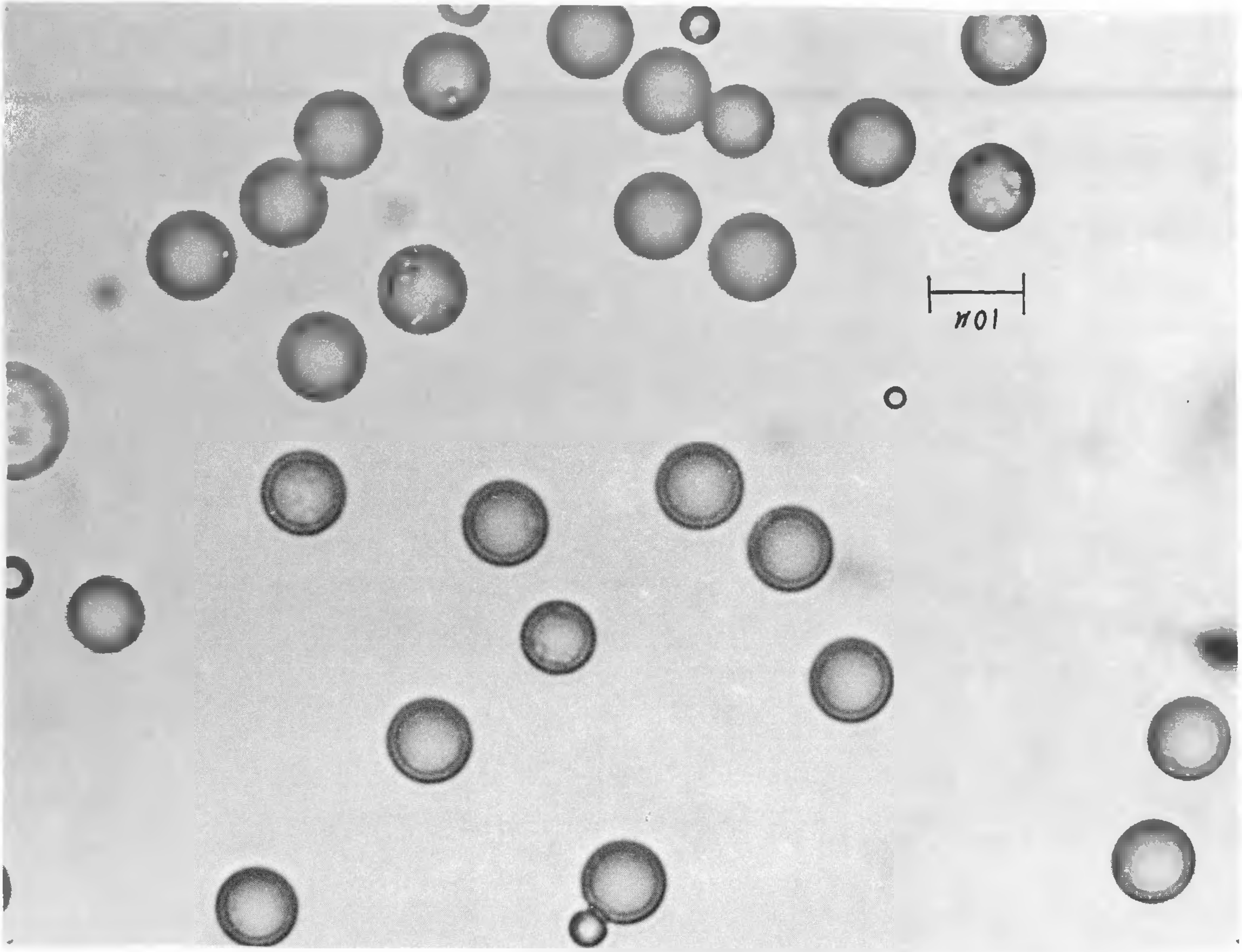


Figure 1.A.5. Photomicrograph of Polystyrene Spheres Used to Calibrate Coulter Counter

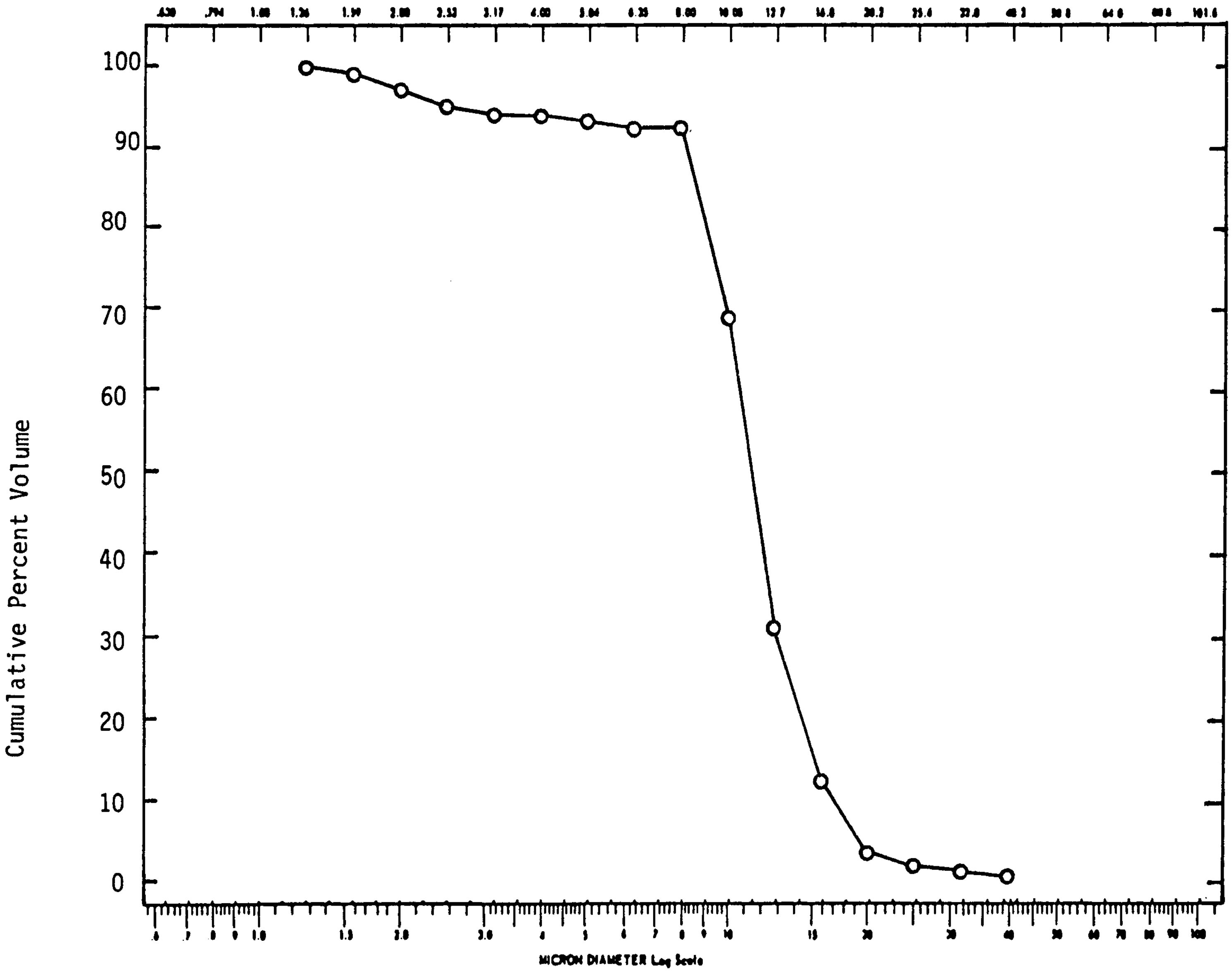


Figure 1.A.6. Particle Size Distribution of Polystyrene by Coulter Counter

Since the batch autoclave reaction particle size distributions correspond to those under actual process conditions, the effect of reaction time on particle size distributions of the four previously mentioned coals was studied through batch autoclave reactions. Although some of the coals showed significant changes in particle size distribution during reaction time, within the limited time range studied, the mean particle size of two bituminous coals, Monterey and Pittsburgh Seam, remained essentially constant. In addition, the mean particle size of Western Kentucky 9/14, another bituminous coal, increased with time - 7.0 μm at 15 minutes, 10 μm at 60 minutes. After 4 hours the mean particle size dropped to 6.3 μm. These rather interesting, though somewhat perplexing results indicate the need for additional research to determine the exact mode of dissolution and liquefaction of coal particles with time and other reaction conditions. The reason for the increase in mean particle size of the Kentucky coal is unknown. Obviously, these first studies have only scratched the surface in following the evolution of coal particle size distribution during liquefaction and much work remains to be done before a complete understanding of the phenomenon is obtained. A large amount of time so far has been spent developing the above procedure which is actually ready to apply for the first time now.

A practical application of the Coulter Counter work concerns prediction of the filterability of the SRC slurry after the dissolver reaction, a problem of major concern in the SRC and related coal liquefaction processes. The filterability of a solid/liquid slurry depends on the size distribution of the particulates entrained in the slurry, viscosity, adhesive forces among the particles (i.e. whether the particles are sticky or discrete and unattractive) as well as other factors. A major objective of this work is to determine whether mean particle size determined by Coulter Counter analysis can be correlated to filterability or, more specifically, cake resistivity. To this end: the mean particle size of particulates in the SRC dissolver effluent for the coals studied so far have been compared with their associated cake resistivities.

Filtration rates for Amax, Western Kentucky 9/14 and Monterey coal/oil slurries have been extensively studied under test conditions and without the incorporation of bodyfeed at the Wilsonville SRC Pilot Plant (5,6). Pittsburgh Seam coal/oil slurries have only been tested with bodyfeed. Table 1.A.2 shows the cake resistivities calculated for the slurries processed without bodyfeed. Indeed, correlations are evident between the ease of filtration (i.e. cake resistivity) and mean particle size. Amax coal/oil slurries which have the lowest cake resistivity and are, therefore, the most easily filtered of the three types of slurries considered have the largest mean particle size. Monterey coal/oil slurries have the highest cake resistivity, are the most difficult to filter, and have the smallest mean particle size. When screen blinding is accounted for, Western Kentucky 9/14 ranks second in filterability.

TABLE 1.A.2

Correlation between Cake Resistivity and Mean Particle Size of Wilsonville Filter Feed

Coal	Cake Resistivity ft/lbm	ΔP (psi)	Mean Particle Size (μm)	
Amax	0.8×10^{12}	45	7.0	(Ref 6)
Western Kentucky	1.13×10^{12}	60	5.7	(Ref 9)
Monterey	1.22×10^{12}	60	4.0	(Ref 9)

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

Objective

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

Summary of Progress

The effect of initial particle size on dissolution yield (conversion to cresol solubles) has been determined for the four coals listed in Table 1.A.1. In these experiments tetralin was used as a hydrogen donor solvent and nitrogen gas as the gaseous atmosphere. Complete details of these experiments are given by Stino (7). Some of the experimental results are presented in Tables 1.B.1. From these results, one can note that the overall coal conversion was not affected significantly by the change in initial particle size. In fact, the large mesh size particles gave almost the same yields as the small mesh size particles and sometimes even slightly better under the conditions used in these experiments. It should be noted that thus far only one reaction time (30 min) has been studied and only overall conversion (not particle size distribution) has been measured. It is likely that when less rigorous conditions are used and shorter times are examined that significant differences in dissolution behavior will result from the different initial particle sizes. The results so far however, indicate that under the usual SRC operating conditions as encountered in commercial operation, the initial particle size will not be a major factor affecting overall coal dissolution. For this reason, a substantial savings may be realized by grinding the coal only to a small enough size to be pumped as a slurry. Additional grinding would be wasteful and do little to promote SRC yield.

The following additional experiment was performed to determine if the existence of a hydrogen non-donor vehicle in coal pores prior to reaction with a hydrogen-donor vehicle would affect the yield. For this experiment, 30 grams of -7 +8 mesh Kentucky No. 9/14 coal particles were soaked in paraffin oil for about 15 hours. The coal particles were removed and weighed. Approximately

Table 1.B.1. Effect of Initial Particle Size on Coal Conversion

Coal Type	Initial Particle Size (Mesh)	maf Coal Conversion (percent)
AMAX	-3½ +4	65.7
	-150	64.2
Pittsburgh No. 8	-3½ +4	87.4
	-150	86.7
Illinois No. 6	-3½ +4	82.0
	-150	82.0
Kentucky 9/14	-7 +8	88.8
	-200	86.9

2 grams of paraffin were absorbed. The particles were then mixed with 90 grams of tetralin and the mixture was used to make a run. The resulting yield was found to be the same as that obtained when the coal particles were not soaked in paraffin oil. It is believed that during the heat-up period, while the tetralin-coal slurry was agitated, the paraffin oil and the tetralin were mixed by diffusion in the coal pores and thus the yield was not affected. The results of the above experiments provide evidence that intraparticle diffusion and absorption mechanisms are not significant variables in the SRC process, if the reaction times are long enough (i.e. greater than 30 minutes). On the other hand, if the residence time can be decreased and still maintain adequate desulfurization (as the results of Task 2 indicate may be possible) then under these shorter residence times particle size and diffusional effects may be significant. Note also that we have as yet examined only the influence of initial particle size on overall coal conversion, not the individual yields of the various chemical species produced as products. Although the conversion could be the same in each case, the chemical species product distribution could be highly different (eg. consider the similar situation occurring in pyrolysis).

The effect of agitation rate on coal conversion also has been studied as shown in Figures 1.B.1 and 1.B.2 using a tubing bomb microreactor in a fluidized sand bath. Kentucky 9/14 coal containing 8.2% ash was used in the experiments and dissolution yields were calculated based on an ash balance on the cresol insoluble filter cake. The experimental conditions are shown in Table 1.B.2.

Table 1.B.2 Experimental Conditions for Agitation Experiments

$T = 410^{o}C$
Atmospheric Pressure (No hydrogen used)
Solvent: SRC recycle solvent (LRO)
LRO + Coal = 7.5 g
LRO:Coal = 2:1 (weight ratio)
Reaction Time = 15 min.
Agitation Rate = 0 to 600 rpm

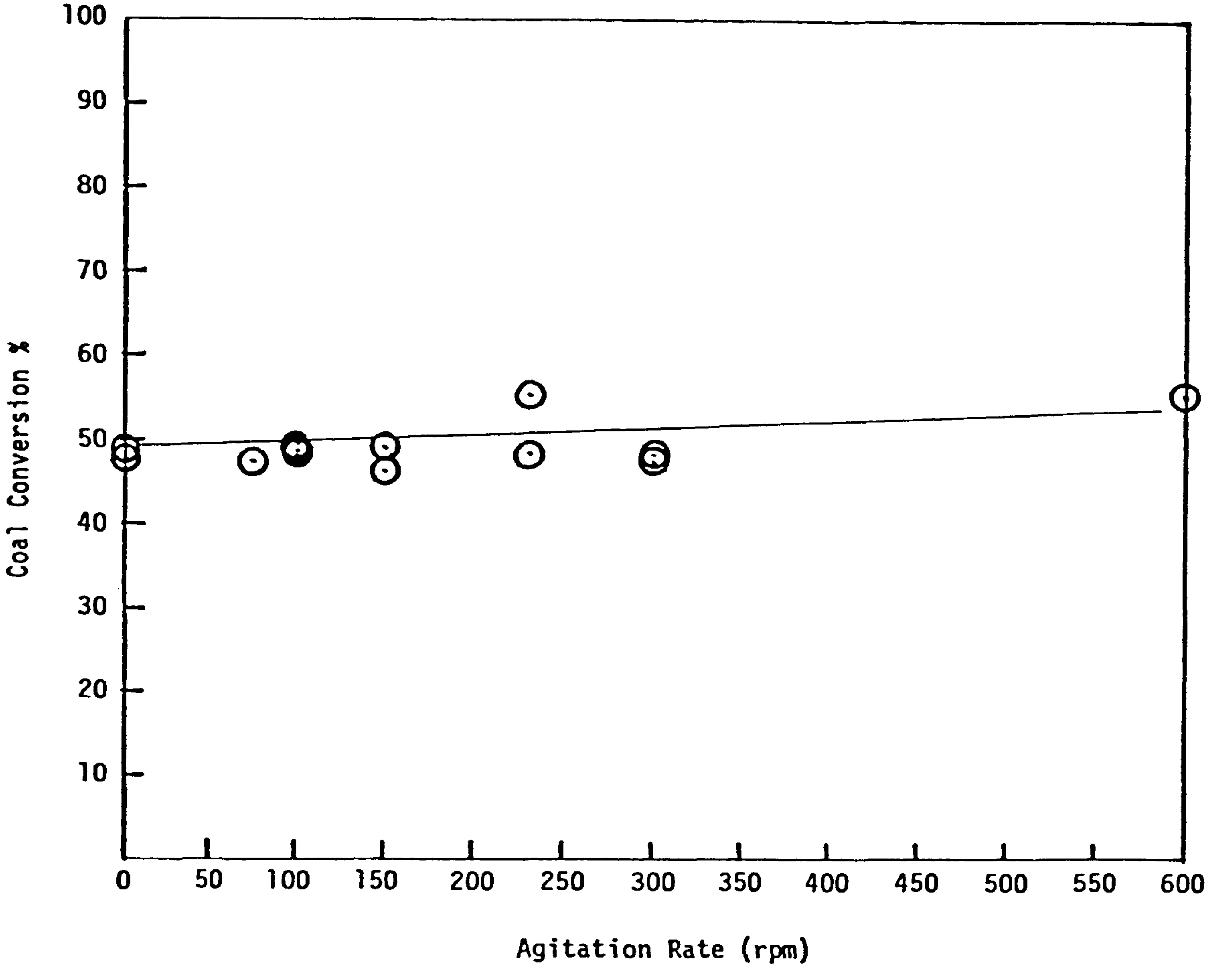


Figure 1.B.1. Effect of Agitation Rate on Coal Conversion

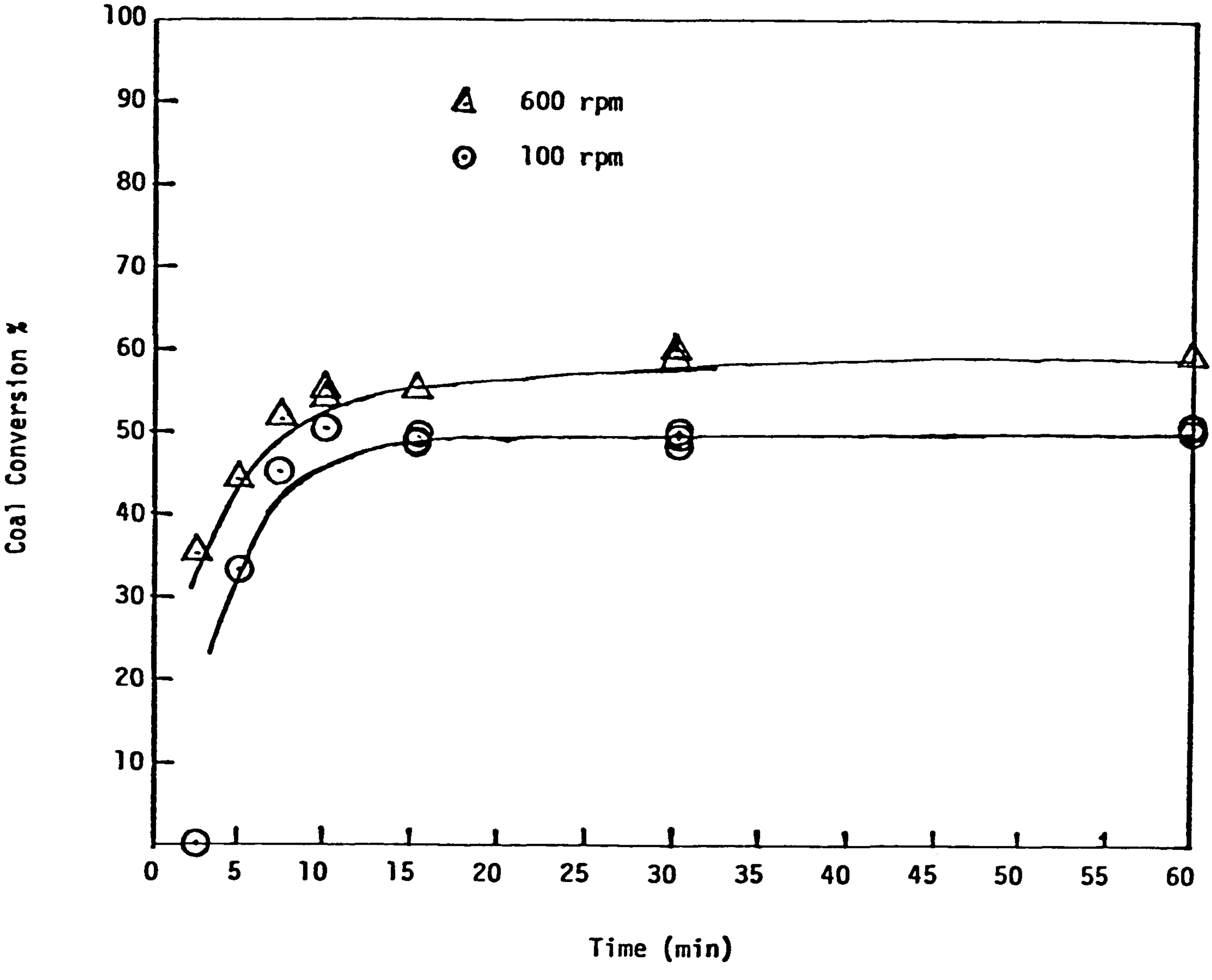


Figure 1.B.2. Coal Conversion Kinetics at Two Agitation Rates

The conversion of coal to liquids and gases was calculated according to the following

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

where M = percent ash in the cresol insoluble residue
F = percent ash in the original dry coal

The effect of agitation on the coal conversion rate is presented in Figure 1.B.1. These results indicate, for the coal and solvent used here (Kentucky 9/14 coal with SRC recycle solvent), that agitation is not a significant factor in determination of the coal conversion rate to gases and liquids. There is, perhaps, a five percent increase in the conversion when the agitation rate is increased from zero to 600 rpm, however, this probably is not significant in view of the experimental accuracy.

The results of the kinetics experiments at two different agitation rates (100 and 600 rpm) are shown in Figure 1.B.2. As shown in the Figure, there exists about a 10 percent greater conversion at the higher agitation rate of 600 rpm. At the present time, it is felt that this may be attributed primarily to a simple mixing phenomenon, rather than the result of solid-liquid mass transfer. Nevertheless, the 10 percent difference does seem to be a reproducible effect and further research is required to ascertain the exact reason for this behavior. Note that in these agitation rate experiments, no measureme~~nts other than overall~~ coal conversion have yet been made. The effect of agitation on other factors, (eg. hydrogen consumption, product distribution, SRC yield, etc.) has yet to be determined.

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 access the relative roles of dissolved hydrogen versus donor-hydrogen from solvent species in promoting particle dissolution.

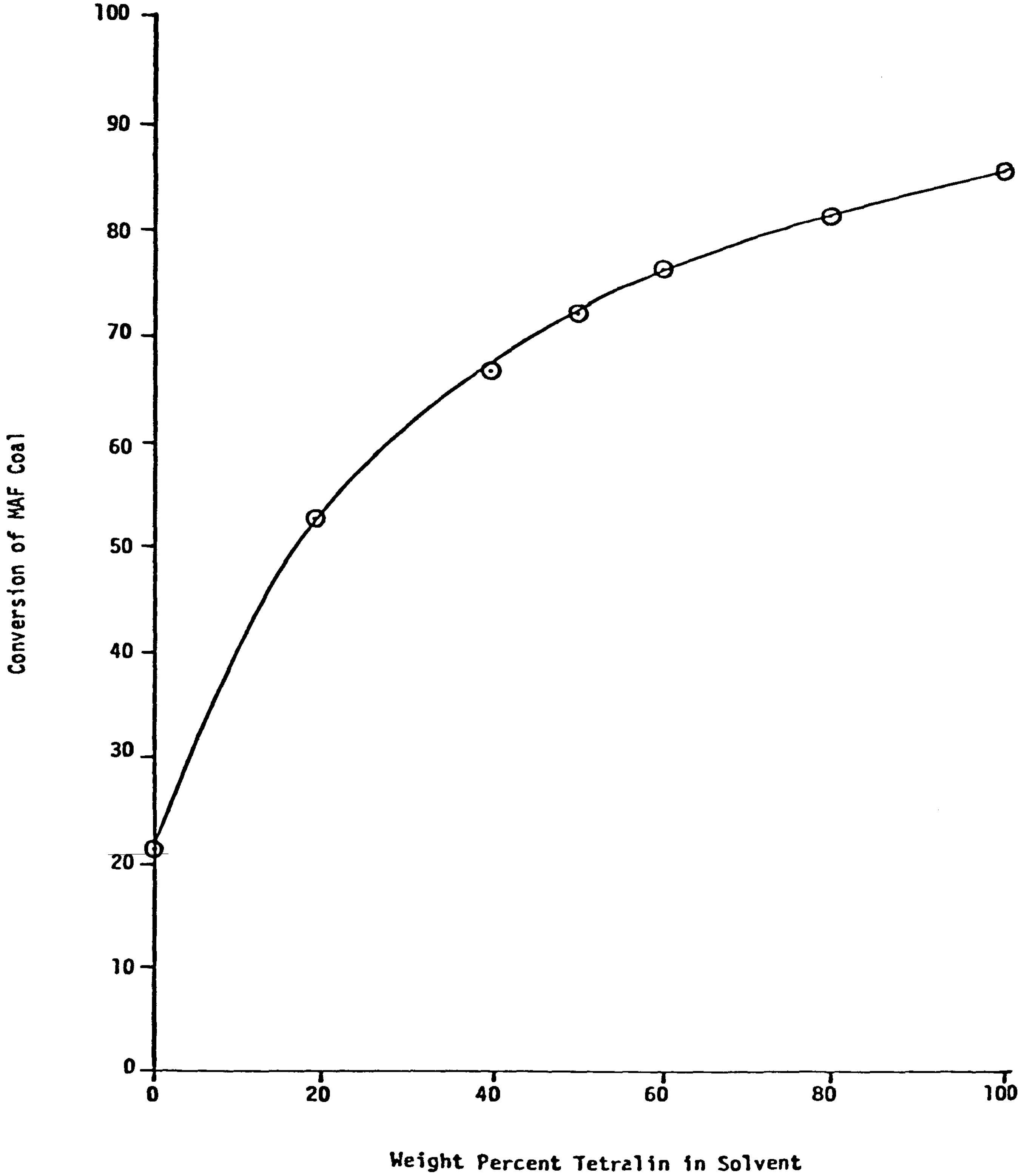
Summary of Progress

A series of experiments has been carried out to determine the effect of tetralin concentration, as a hydrogen donor vehicle, on the conversion of coal into liquids. These experiments were designed to test the hypothesis that the rate at which coal dissolves is a function of the hydrogen donor content of the solvent. Thus, they complement an associated hypothesis (Task 2) that a primary function of coal mineral matter is to produce hydrogen donor species within the solvent and to increase their concentration if they are already present. Materials and procedures for the experiments included:

Coal: Kentucky 9/14 mixture (80 percent, -325 mesh)
Solvent: Tetralin - Paraffin oil mixture
Gas phase: Nitrogen
S/C Ratio: 3 to 1
Total Weight of Charge: 120 g
Autoclave: 300 cc magnedrive
Agitation: 1000 rpm
Temperature: 410°C
Time of Reaction: 15 min.

The conversion of maf coal was calculated from an ash balance on the cresol insoluble filter cake. The experimental results are presented in Figure 1.C.1. From these results it is obvious that an increase in tetralin concentration gives rise to a corresponding increase in the coal conversion. This lends support to the hypothesis that the hydrogen donor content of the solvent is perhaps the single most important factor (although certainly there are others) in determining the extent of coal dissolution. Consequently, any solvent "quality" index, such

Figure 1.C.1. Effect of Tetralin Concentration on Coal Conversion



as for SRC recycle solvents, must take into account this factor. As shown later in the subsequent Task 3 analytical methods such as IR and NMR can provide a qualitative indication of hydrogen donor content, and hence solvent quality. Therefore, it appears that the effectiveness of a solvent for coal liquefaction depends, in large measure, upon its ability to donate hydrogen to coal radicals. To examine this aspect in more detail we have begun a series of experiments using an "artificial" solvent composed of tetralin and a number of related species. For example, a series of experiments was performed using an "artificial" solvent to check for the presence of synergistic effects on the rate and extent of a coal conversion. The first set of experiments was done using a mixture of cresol and tetralin as an artificial solvent. Kentucky 9/14 coal was used in all experiments. The purpose of these experiments was to see if the cresol, as a phenolic-type solvent species, would combine with the tetralin (hydrogen donor species) in a synergistic fashion so that the resulting mixed solvent would be more effective than either pure species alone. The results of these experiments are shown in Figure 1.C.2 where it may be seen that pure tetralin (0% cresol) gives the highest coal conversion, and that the conversion drops off smoothly as cresol is added to the tetralin. It is interesting that pure cresol itself gives around 52 percent coal conversion. There does not seem to be any synergistic solvent effect in the tetralin/cresol mixture as no maximum or minimum appears in the curve in Figure 1.C.2, but the conversion decreases in monotonic fashion as cresol is added to the tetralin.

A second series of experiments was performed using a ternary mixture of paraffin oil/cresol/tetralin. The percentage of tetralin in the solvent was held constant at 50 percent, while cresol was used to progressively replace the paraffin oil. As the results in Figure 1.C.3 show, the dissolution of coal improves as the paraffin oil is replaced by the cresol. Again, there does not appear to be any synergism present in the solvent mixture, as the curve increases in monotonic fashion with no maxima or minima. Both sets of experiments above

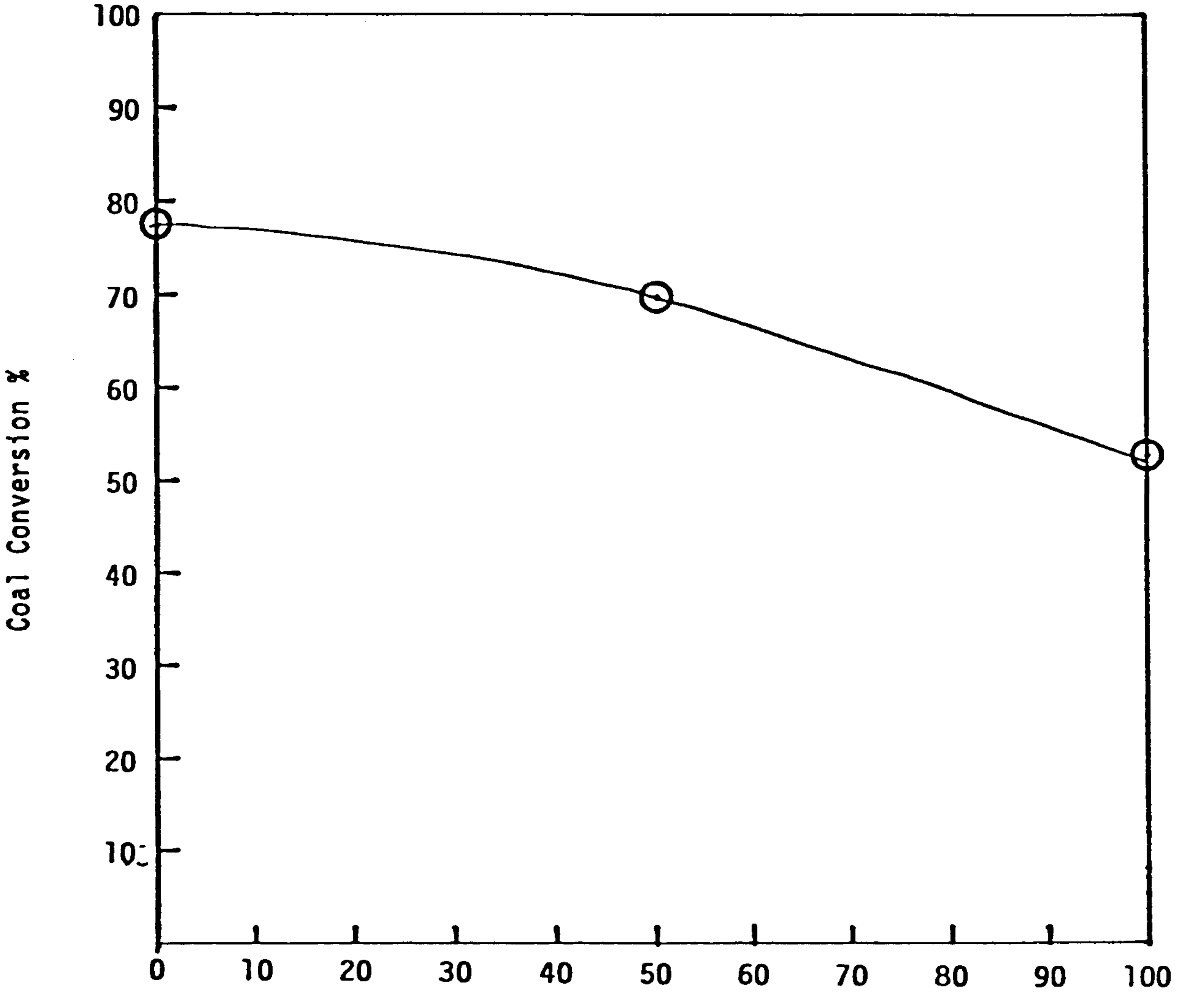


Figure 1.C.2. **Dissolution of Coal in Cresol-Tetralin Mixture**

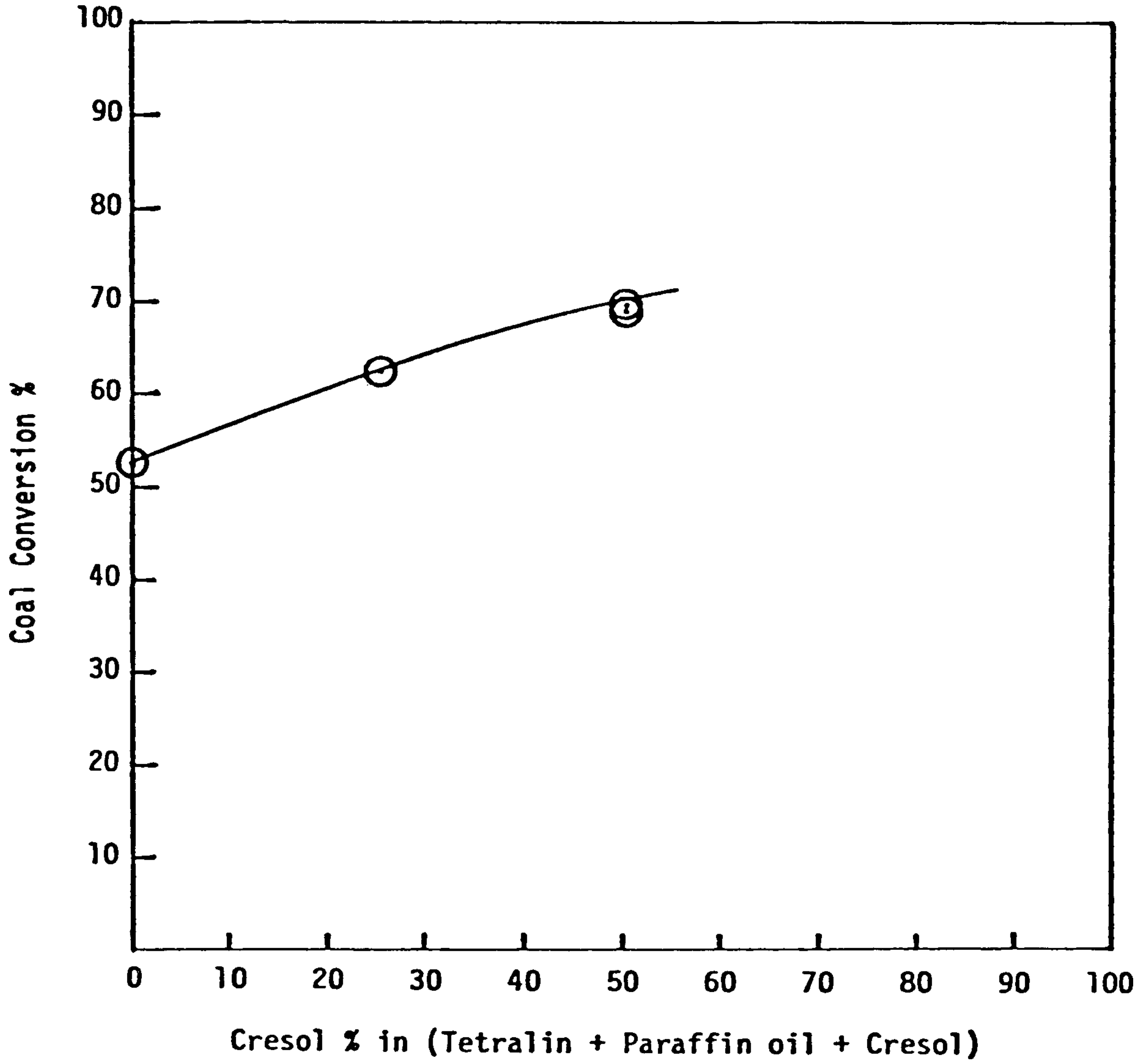


Figure 1.C.3. Coal Dissolution in Ternary Solvent Mixture

indicate the lack of a synergistic solvent action and indicate that the dominant effect in coal dissolution is the presence of the hydrogen donor species.

With respect to the effect of gas phase composition on particle dissolution, our research so far has shown that hydrogen gas acts primarily to rehydrogenate the donor species of the solvent, rather than directly interacting with the coal particles themselves, although the latter may occur to a minor extent. These results are presented and discussed in detail in the references 12 and 33. Therefore, since the gas phase effect on coal particle dissolution is predominately indirect (gas → solvent → coal) rather than direct (gas → coal), it is believed that the effort in this subtask should be more sharply focused on the solvent action in promoting coal dissolution and that the effect of the gas phase should be studied primarily as it relates to effecting changes in the solvent composition and hence, indirectly, the coal dissolution rate.

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

Objective

The objective of this task is to develop and employ a transparent, high pressure microreactor in which direct visual observation of dissolving coal particles may be accomplished at temperatures to 450°C and pressures to 1000 psig.

Summary of Progress

To date the research has resulted in the development of a unique and highly satisfactory visual microreactor which allows the direct observation of in-situ dissolution of coal particles at actual process reaction conditions. A schematic diagram of the microreactor system is shown in Figure 1.D.1 and of the microreactor itself in Figure 1.D.2. Basically, the apparatus consists of a vycor glass capillary tube, electrically heated, in which an appropriate solvent, gas, and coal particle may be pressurized and brought to reaction temperature. The coal particle is lighted from behind and may be observed through a small slot as the dissolution

Figure 1.D.1. VISUAL REACTOR SYSTEM

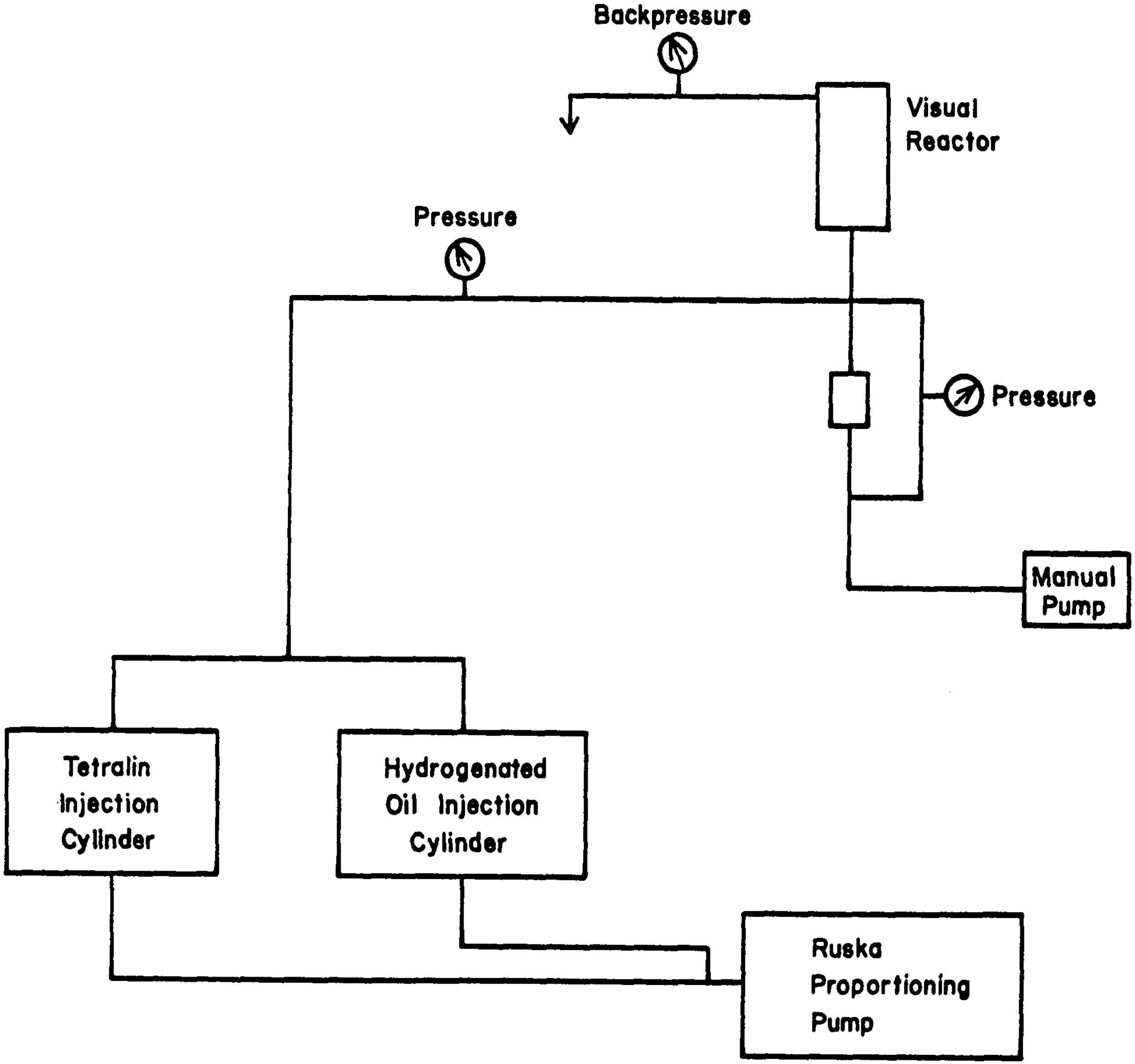
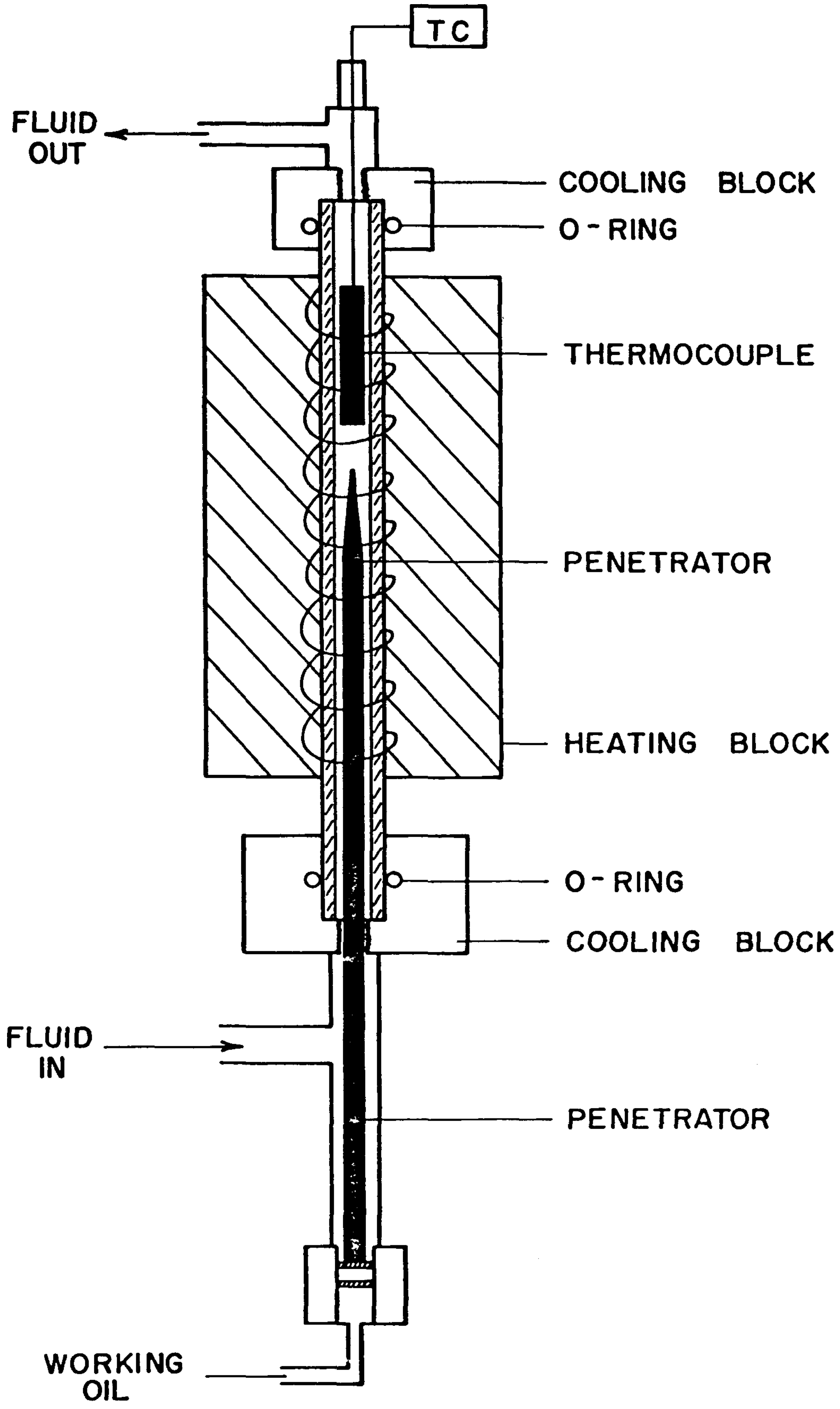


Figure 1.D.2. VISUAL REACTOR



proceeds. A metal rod, termed the penetrometer, is mounted in the top of the capillary tube and may be used to apply a known compressive stress to the coal particle during dissolution. Thus, the penetrometer may be used to test the consistency and the breakdown pressure for various coal particles in various solvents under a very wide variety of processing conditions.

To provide a permanent record for subsequent comparative study, etc., different types of cameras (e.g. time-lapse, pulse, rapid-sequence) and different lighting techniques (e.g. incandescent, infrared) have been evaluated for photographing the particle in the reactor. Because of the curved surface of the microreactor a wide depth of field is required; for correct lighting, on the other hand, a small F-stop (i.e., a wide camera aperture) has to be used. However, a satisfactory technique has now been developed for making micrographs, and our immediate attention is being focused on the photography of coal particles during their dissolution. A typical photomicrograph showing a coal particle in the reactor is pictured in Figure 1.D.3. A sequence of pictures such as 1.D.3 is made to record the dissolution process, eg. swelling, popping, disintegration, as it proceeds.

Perhaps the best method to illustrate the usefulness of the visual microreactor is by reference to an actual example, as shown in Figure 1.D.4. In Figure 1.D.4, a comparison is shown between the dissolution behavior of a bituminous (Kentucky) and a sub-bituminous (Amax) coal particle using the transparent-wall microreactor. A particle of Kentucky No. 9/14 coal submerged in creosote oil at 410°C and 1000 psig is shown in Figure 1A. In Figure 1B pressure is applied to the particle by pressing it between the penetrator rod (the pointed rod at the top of the picture) and the thermocouple rod (the flat-surfaced rod at the bottom). The particle of bituminous coal exhibited little structural resistance

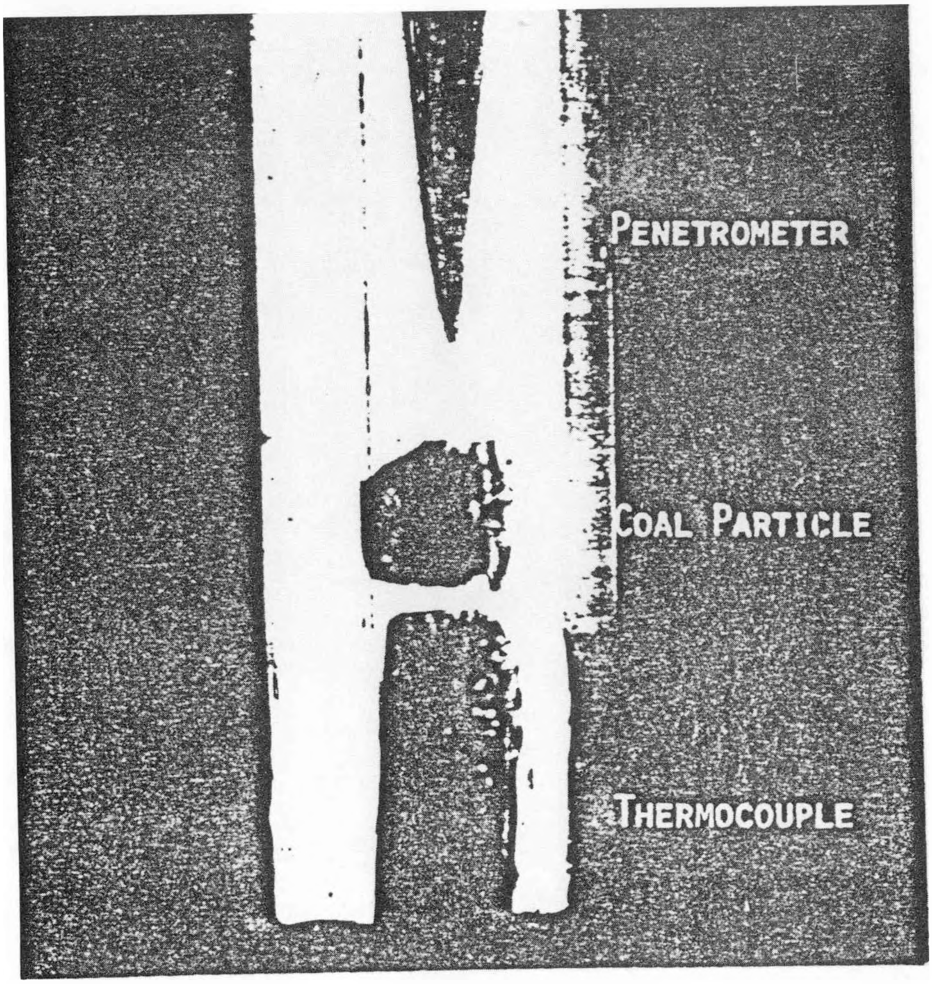


Figure 1.D.3. Original Particle of Coal in Solvent in Visual Reactor

NOTE: The pointed rod at the top is the penetrator; the flatedged rod at the bottom is the thermocouple well; and the particle is the object in the center.

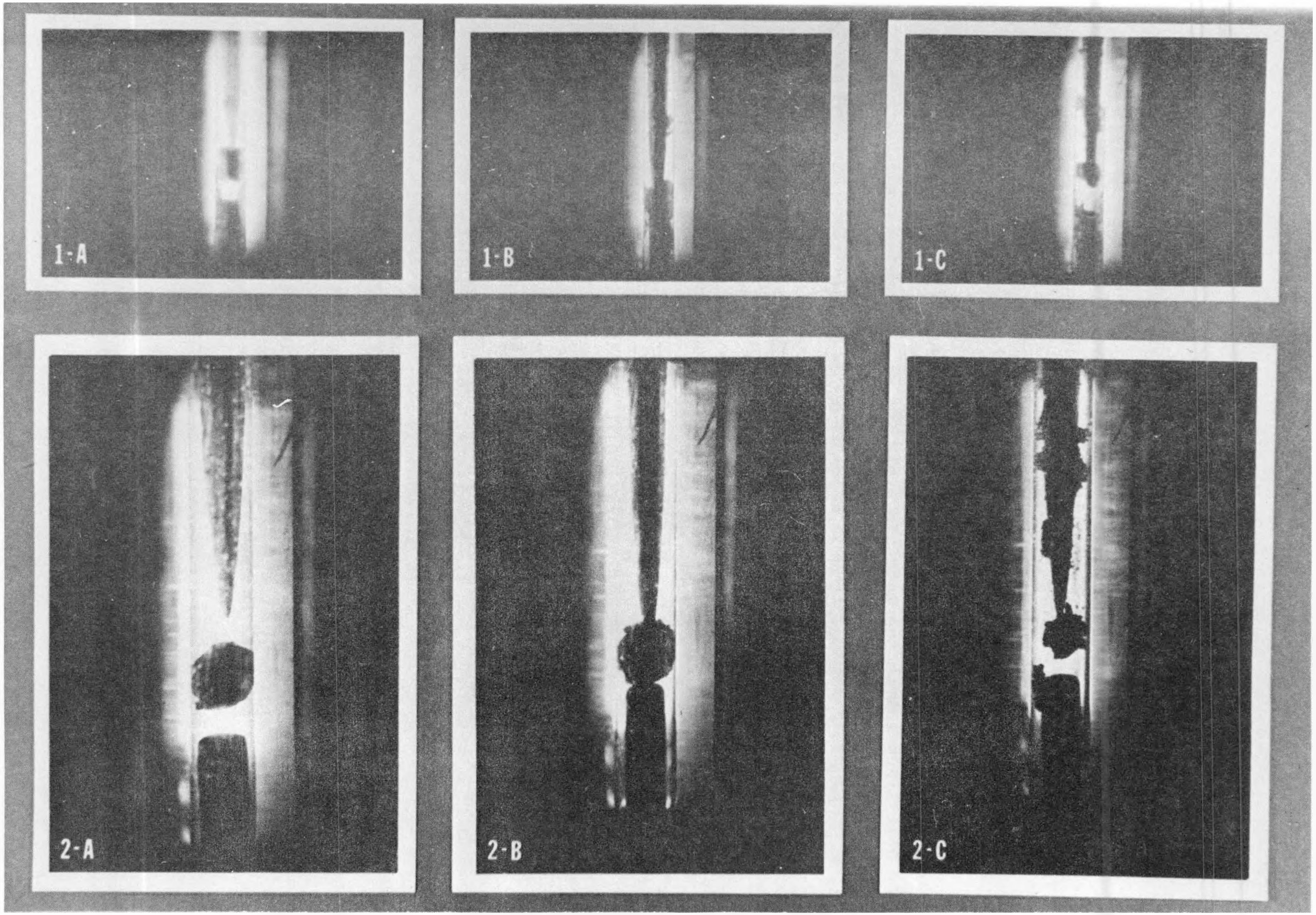


Figure 1.D.4.

to compression, and only a slight amount of pressure was required to penetrate the particle. During compression the particle of bituminous coal exhibited little structural resistance, and only a slight amount of pressure was required to penetrate the particle. During compression the particle easily flowed to fill the capillary reactor tube around the penetrator rod, exhibiting a gummy chewing-gum like consistency. The rheological properties of the particle are difficult to record photographically; however, in Figure 1C the particle is shown pulled into two pieces, half being stuck to the tip of the penetrator upon withdrawal and the remaining half stuck to the thermocouple. Had SRC recycle solvent been used in this experiment instead of the creosote oil, the particle of bituminous coal would have dissolved before reaching 410^{o}C, and with flushing of the reactor tube only slight amounts, if any, of the particle would have remained. In Figure 2A, a particle of Amax sub-bituminous coal is shown under the same conditions. In contrast to the bituminous coal, over 50 psi of penetrator pressure was required to penetrate the particle of sub-bituminous coal; for it remained very hard, showing little change (Figure 2B). Finally, upon a sudden crushing of the particle it fractured into hard, brittle, discrete particles (Figure 2C). In SRC process solvent the particle of sub-bituminous coal behaved very much the same. The contrast in behavior observed in the visual reactor between the dissolution behavior of the Amax and Kentucky coals was observed also in the Wilsonville pilot plant -- the Kentucky coal giving high yields (around 90 percent) while the Amax coal gave only around 50 percent conversion under the same processing conditions.

The observations made of the behavior of coal particles during dissolution also have implication as to the filterability of the product stream. For example, as observed above, Amax coal dissolved very slowly and maintained a very distinct particle integrity and a high structural strength -- like salt particles dissolving in water. Kentucky No. 9/14 and a Bighorn Western coal dissolved much faster than the Wyoming Amax coal; yet during dissolution the Bighorn coal particles broke down into smaller granular particles behaving similarly to Amax coal particles in that the particles, even the smaller ones formed, never became tarlike in consistency as did the Kentucky No. 9/14 coal particles. Based on these results then, Bighorn coal should be a relatively easy coal to process: dissolving readily, having high filtration rates, and presenting no significant plugging problems due to solids accumulation in the reactor/dissolver.

To summarize, the visual microreactor has been extremely useful in visualizing the behavior of several different types of coal under liquefaction conditions. The observed differences in dissolution behavior among different types of coals made with our microreactor have proven so far to correlate well with the results of our batch reaction studies. Since only a small chip, or particle, of coal is used in the microreactor, the correlation between dissolution behavior observed in the microreactor and that in a 300 cc batch autoclave and in the tremendously larger scale Wilsonville SRC pilot plant is very encouraging. This correlation indicates an unexpected uniformity in behavior of a particular type of coal. The visual microreactor thus appears to be a useful and very inexpensive tool for monitoring dissolution characteristics.

1.E. Effect of Pretreatment on Dissolution Behavior

Objective

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

Summary of Progress

The purpose of most coal liquefaction processes, including the Solvent Refined Coal (SRC) process, is to produce a clean solid or liquid fuel or petrochemical feedstock from coal. Almost all processes rely upon direct or indirect (eg. from a donor solvent) hydrogenation of the coal to accomplish this goal. It may be possible, by some pretreatment of the raw feed coal, prior to liquefaction by hydrogenation, that some advantage might be obtained in the overall coal conversion scheme. Such advantages might include some or all of the following:

(1). Significant organic and/or pyritic sulfur removal in the pretreatment process resulting in better overall sulfur removal in the combined pretreatment - liquefaction process.

(2). Significant mineral matter removal in the pretreatment process resulting in a smaller filtration load for the liquefaction step.

(3). An increase in liquefaction yield, caused perhaps by changes in coal structure and/or incorporation of catalytic agents in the coal matrix from the pretreatment.

(4). A decrease in hydrogen consumption due to removal of oxygen from the coal in the pretreatment step.

(5). An improved desulfurization due to removal of FeS_2 prior to liquefaction with the result that the H_2S partial pressure is lowered thus avoiding undesirable reverse reactions resulting in the formation of organic sulfur species.

Several possible chemical and/or physical pretreatment steps may be postulated; however, many of the effects of these processes, especially when followed by coal liquefaction remain to be evaluated. This is the purpose of the studies being done here, i.e. to evaluate various coal chemical and/or physical pretreatment steps and seek possible process advantages in a combined pretreatment-liquefaction process. Among coal pretreatments currently being considered are:

(1). Oxidative chemical pretreatment and cyclic washings.

(2). Alkali pretreatment to remove oxygen.

(3). Chemical treatment to remove coal minerals, especially pyrite.

(4). Hydrothermal pretreatment.

(5). Physical separation, (eg. screening, magnetic separation, etc.).

(6). Chemo-mechanical pretreatment, (eg. grinding in the presence of selected chemical agents).

(7). Various combinations of the above processes.

While some pretreatments may achieve advantageous results, (eg. removal of mineral matter), there may also be associated side effects which are deleterious to the coal liquefaction process, (eg. a lowering of liquefaction yield). An important objective of the proposed work is to consider and evaluate the overall effect of the proposed pretreatment in light of the overall process objectives, viz. producing a clean fuel product.

One series of experiments has been performed to access the effects of pre-oxidation on the rate of coal liquefaction. Kentucky 9/14 coal, after being oxidized at 100°C in air for varying time periods, was liquefied in tubing bombs (2:1 tetralin/coal, 30 min. 415°C) at 1200 psig hydrogen and 1 atm air pressure respectively. Conversion to cresol soluble material was obtained by ash analysis. The experimental results are shown in Fig. 1.E.1. It was found that oxidation of coal preceding liquefaction was deleterious to dissolution yield. The decreased yield may result because oxygen converts alicyclic hydrogen in the coal to a non-transferable form and the oxygen coal bonds crack readily to form radicals during liquefaction, thus consuming donor hydrogen or, even worse, allowing repolymerization where donor hydrogen was not immediately available. This result was also found by Neavel (8) and the above explanation was offered by him for the decreased yields.

It should be noted here that if the coal is simply dry-ground -- as is standard practice at the Wilsonville SRC pilot plant -- most of the developed

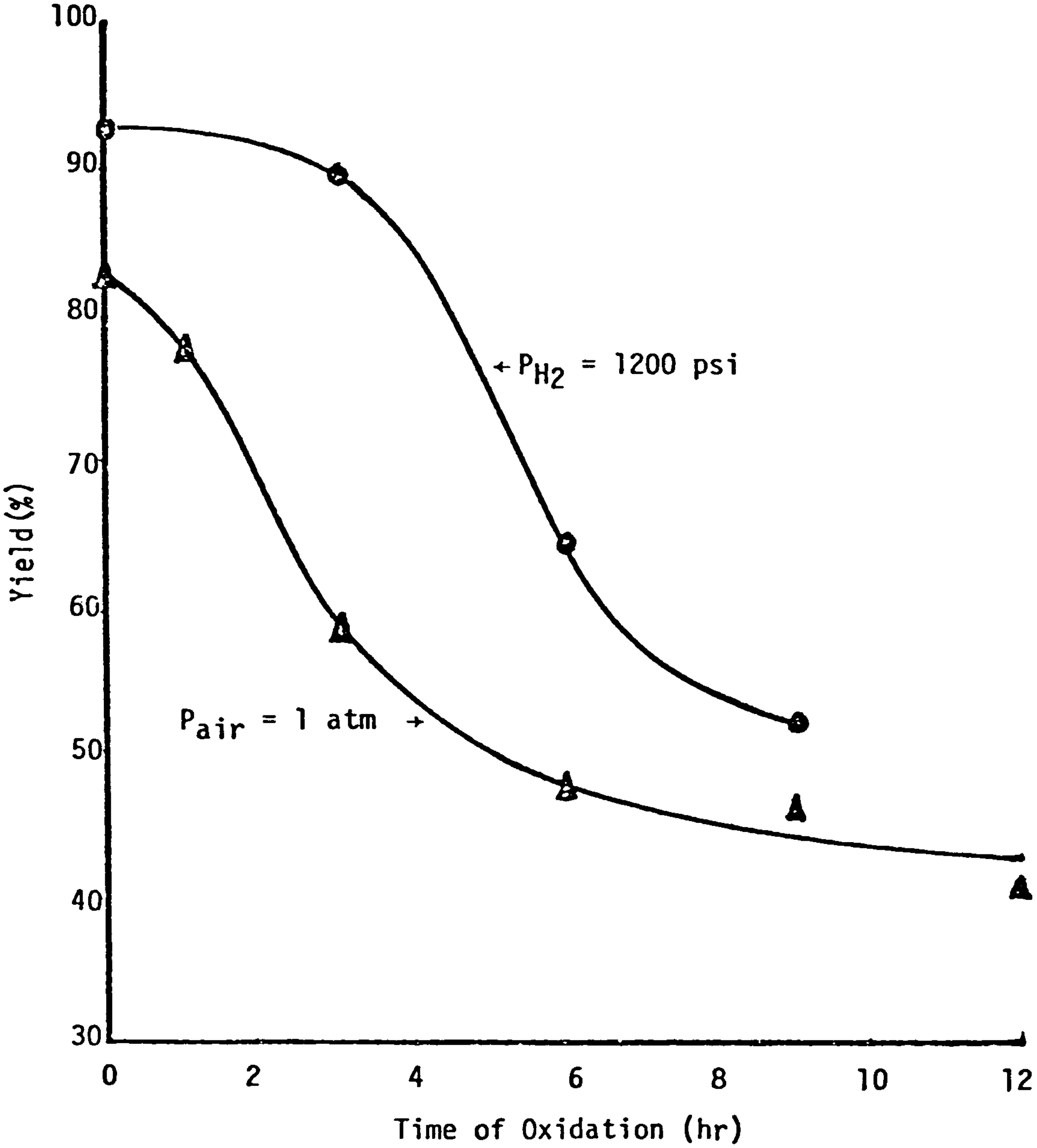


FIGURE 1.E.1. EFFECT OF OXIDATION ON DISSOLUTION (2:1 tetralin/coal, 30 min, 415°C coal particle size -170+325 mesh)

free radicals, due to a rupture of molecular chains by grinding, have a chance to join their physical neighbors to form a carbon bond or to react with oxygen of the air. Since oxidation of coal is deleterious to the dissolution yield, these results suggest that, on the other hand, if the coal is ground in the solvent in which the process of extraction would be done, the oxidation might be prevented, thus, increasing the yield.

Another series of pretreatment experiments has been performed in which NaOH solution was used to pretreat the coal prior to liquefaction. Figure 1.E.2 shows the effect of NaOH extraction time on the sulfur content of the pretreated coal and of the coal slurry after liquefaction. The longer the extraction time, the more the total sulfur removed. For the Kentucky coal used, the total sulfur content was reduced from an original 2.86% to 2.06% after 4.5 hrs. of extraction at room temperature (25°C). The NaOH treated coal was further subjected to a liquefaction reaction with tetralin (solvent/coal = 2/1) at atmospheric pressure for 1/2 hour. The sulfur content in the coal slurry after liquefaction was reduced from 0.47% for coal without any alkali pretreatment to 0.28% for coal with 3.5 hours extraction in 1n NaOH solution. The effect of NaOH concentration on sulfur content is shown in Figure 1.E.3. The coal was treated with different concentrations of NaOH for 1 hour at 300°C. The total sulfur content was lowered from 2.1% for coal pretreated with distilled water to 1.37% for coal pretreated with 1N NaOH solution. The sulfur content in the coal slurry after liquefaction was reduced from 0.449% to 0.355% for coal pretreated with distilled water only and 1N NaOH solution, respectively. The effect of NaOH concentration on coal liquefaction yield and total sulfur removal for the combined processes of pretreatment and liquefaction is also shown in Figure 1.E.4. It may be observed from Figure 1.E.4 that the yield or conversion of daf coal is lowered by about 15% by the NaOH extraction pretreatment. This

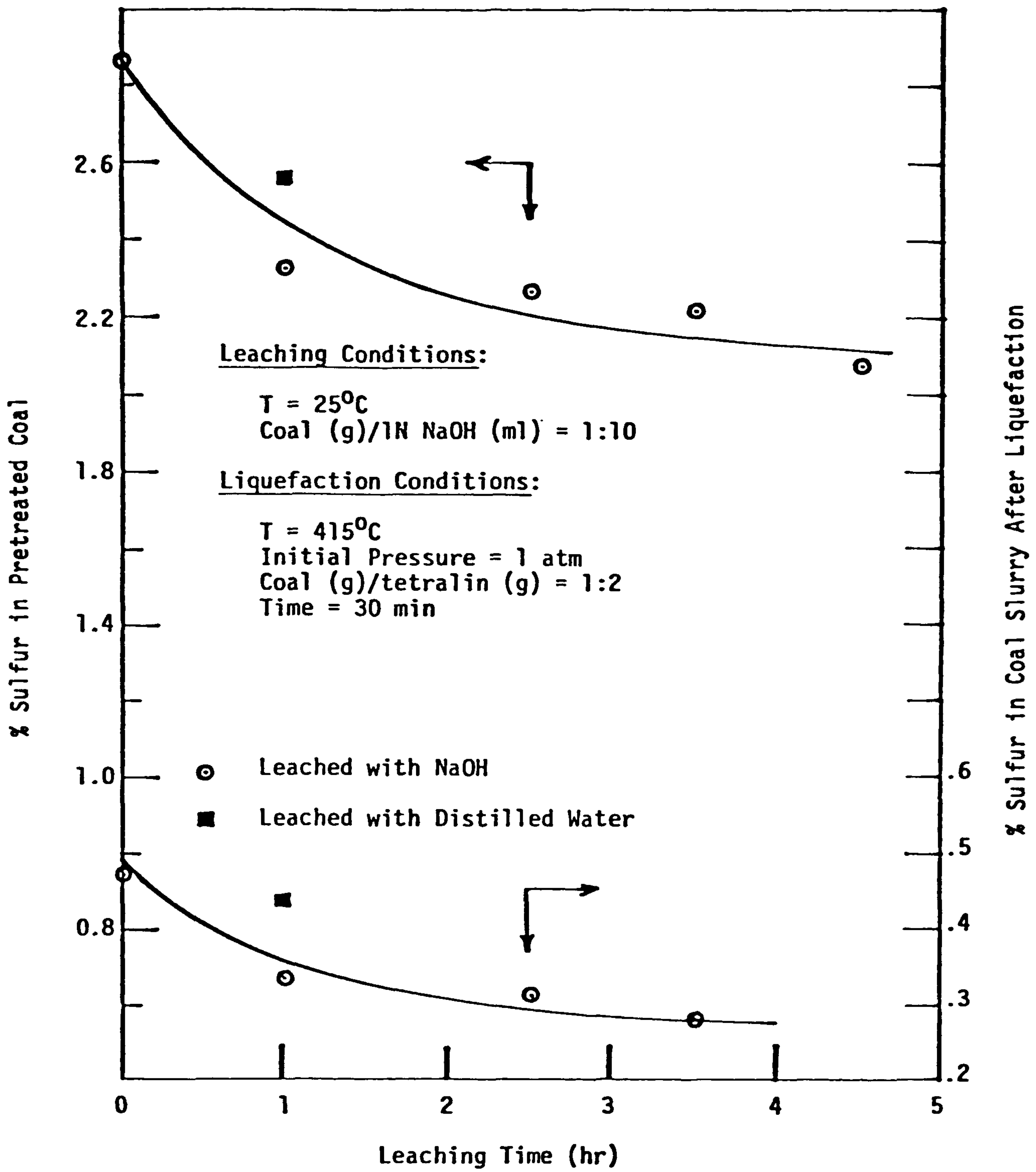


FIGURE 1.E.2. Effect of NaOH Leaching Time on Sulfur Content

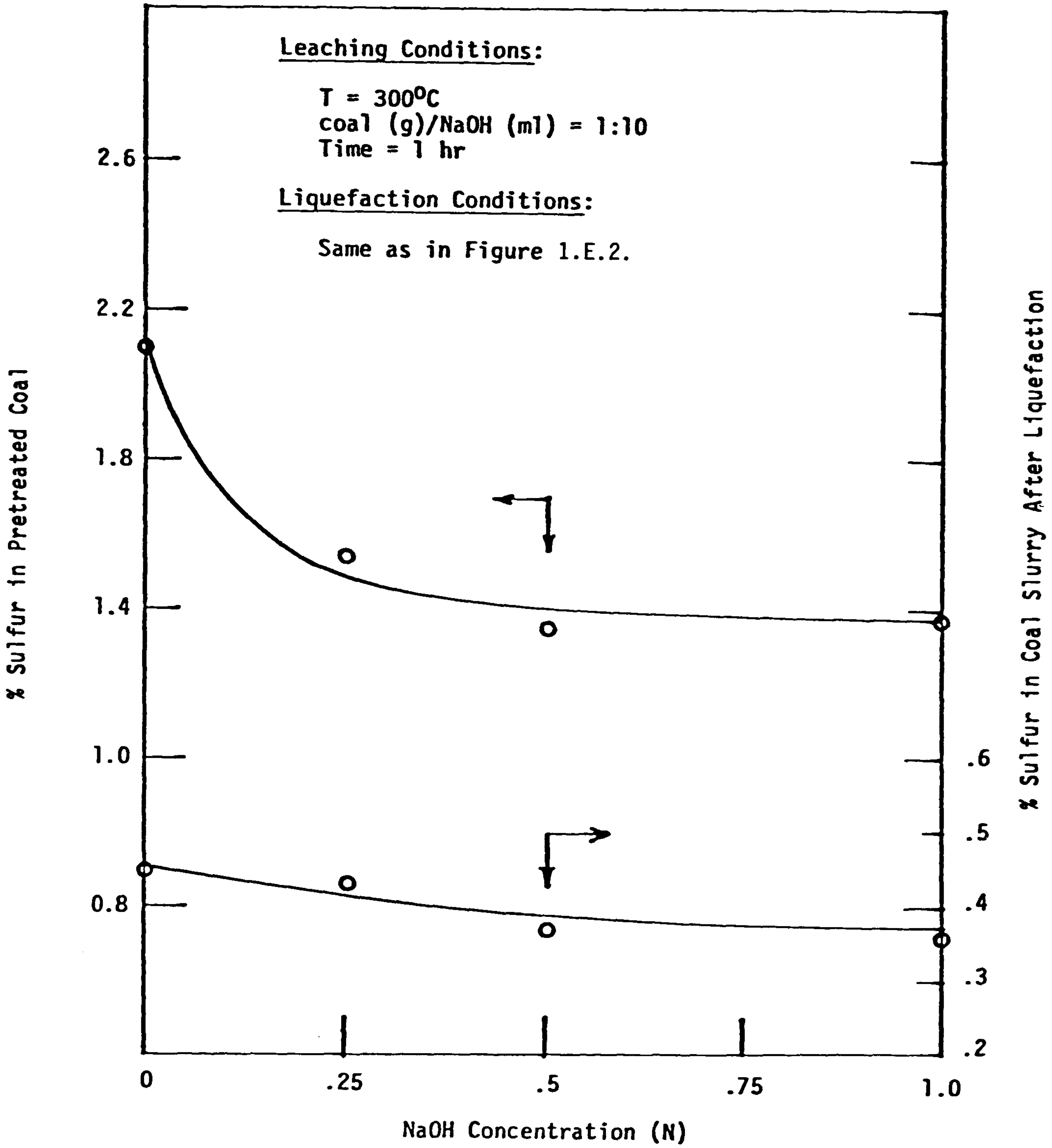


FIGURE 1.E.3. Effect of NaOH Concentration on Sulfur Content

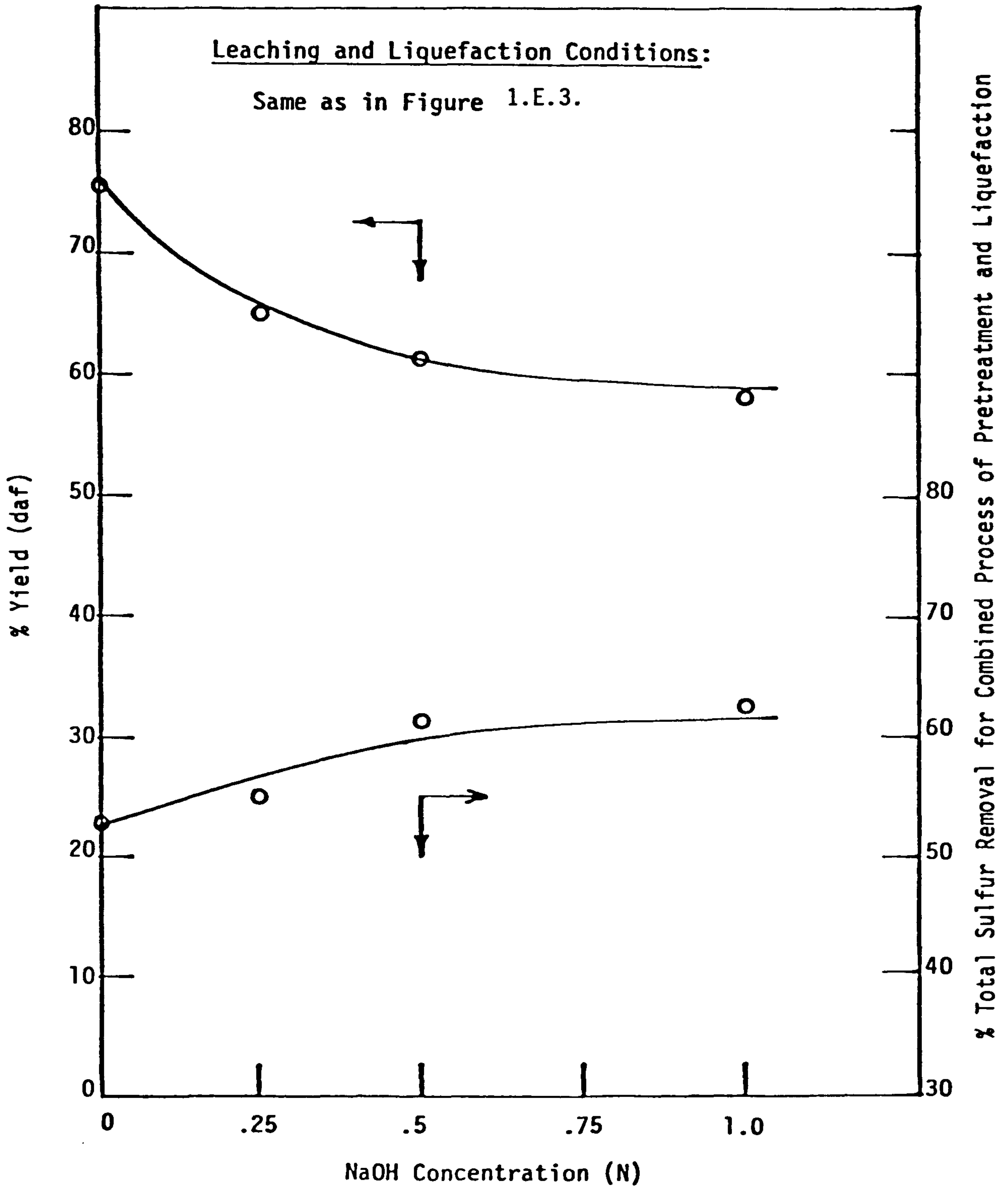


Figure 1.E.4. Effect of NaOH Concentration on Coal Liquefaction

reduction in yield may be due to the fact that some of the alkali soluble organic materials were extracted from the coal in the pretreatment. The higher percentages of organic insolubles existing in the pretreated coal would make liquefaction relatively more difficult. This hypothesis is supported by Kasehagen (9) in the pretreatment of coal with NaOH solution. At 350^{o}C in 1N NaOH solution, he reported that about 16% of the original coal was extracted to produce carbon dioxide, hydrocarbon gases, neutral oil, phenols and acid. Thus at this time it appears that a liquefaction pretreatment of NaOH extraction, while increasing the sulfur removal of the product by almost 10 percent, suffers from the disadvantage of a decrease in daf coal converted of around 15 percent. Other extractive agents are in the process of being investigated for a beneficial coal pretreatment prior to liquefaction. The net reduction of hydrogen consumption resulting from the pretreatment is still being evaluated at this time.

Task 2. Reaction Kinetics and Process Variables Studies

Task 2A. Catalysis by Coal Mineral Matter

Objectives

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.

Summary of Progress

Coal contains various amounts of mineral matter (Si, Al, Fe, Na, K, Ti, Mg, etc.). These coal minerals represent a readily available, abundant, inexpensive source for catalytic agents for use in selectively accelerating liquefaction and desulfurization reactions in coal conversion processes. Experimental evidence for the catalytic effect of coal minerals on coal liquefaction reactions has been reported by our laboratories as well as others (10, 11, 12, 13, 14 and 15). As part of Task 2.A of our ongoing contract we have been studying the catalytic activity and selectivity of coal minerals in the liquefaction, hydrogenation, and desulfurization reactions using high-pressure autoclaves and small tubing-bomb reactors. The results of this work have shown ways by which the SRC process can be easily modified, such that, hydrogen consumption can be reduced by 40 to 50 percent while still achieving the required SRC sulfur level. For this reason we feel that the significance of coal mineral catalysis is no longer questionable. However, many of the results of our work as well as that of others in this area (10-15) are not well understood as yet, and more work is needed before the full benefits of coal mineral catalysis can be realized and before the results will be accepted by practicioners in the area.

Figure 2.1 shows the catalytic effect of the ash of SRC residue on conversion. This effect is small but significant. It has been well established that coal mineral catalyze hydrogenation reactions (Figure 2.2; the reader may refer also to the experimental evidence provided in the following reference 12). In the SRC II process being developed by Gulf at Tacoma, Washington, SRC residue is recycled to enhance the yield of oil from the coal. Untreated SRC residue alone has no appreciable catalytic effect on desulfurization (Table 2.1). As shown in Figure 2.2 the ash of SRC residue, on the other hand, has an appreciable effect on desulfurization. In fact, it acts somewhat selectively in accelerating desulfurization over hydrogenation. For example: After 30 minutes of reaction in the presence of the ash of SRC residue sulfur removal is increased by about 30 percent; whereas hydrogen consumption, by only 11 percent, over that obtained in the absence of a catalyst. Therefore, by ashing SRC residue prior to recycling, unlike Gulf's SRC II process, not only the yield of oil, but also the rate of sulfur removal can be increased.

In the conventional SRC I process a solid boiler fuel is the main product. Some hydrogenation is required to liquefy the coal and allow the remaining solid mineral matter to be separated by physical means; however, minimum hydrogenation is desirable in order to be cost effective. In Figure 2.1 it is apparent that

Figure 2.1. Effect of Reaction Time on Yield of Coal Liquids With and Without SRC Ash Present During Reaction

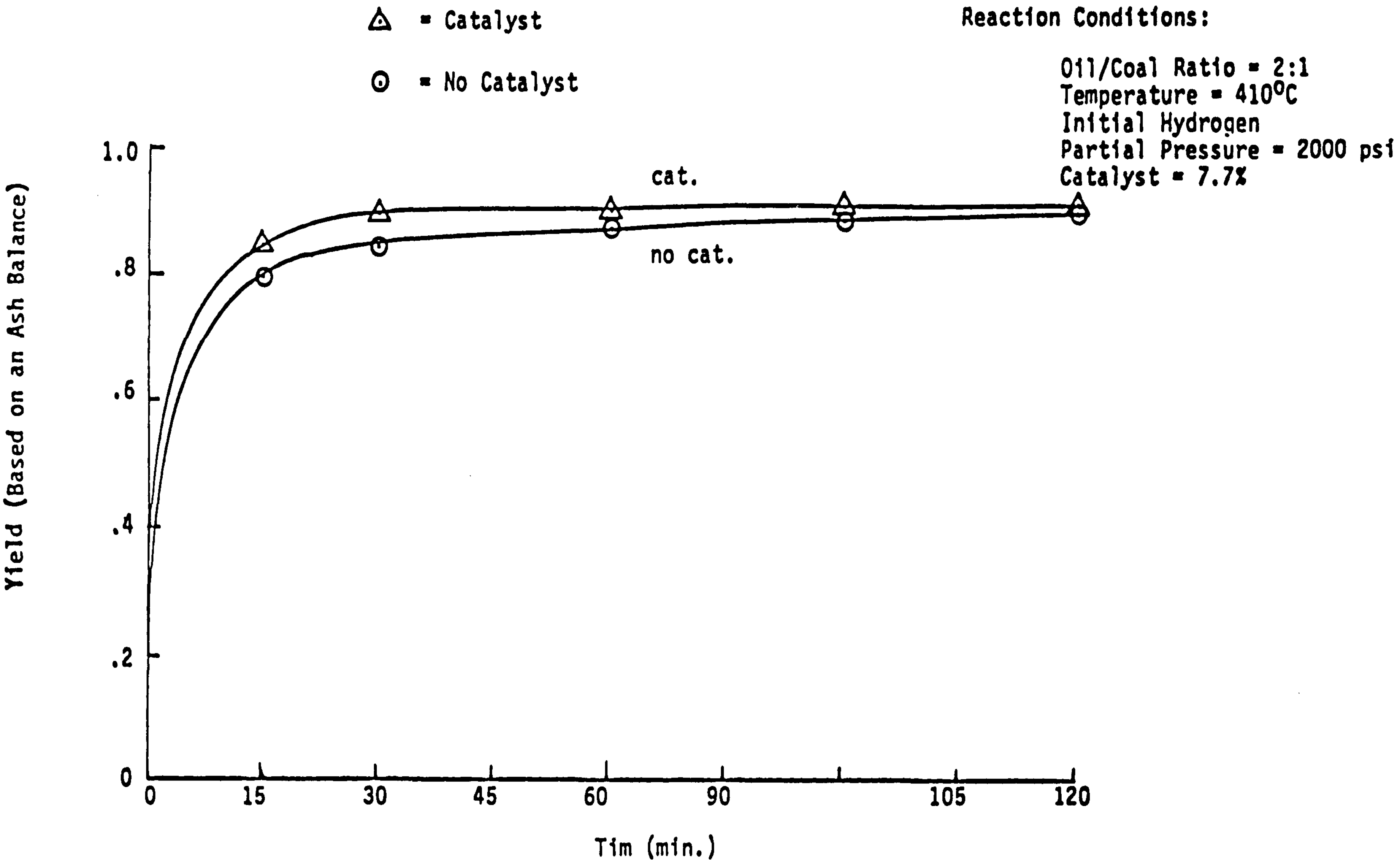


Figure 2.2. **Effect of Reaction Time on Hydrogen Partial Pressure (H_f/H_o) and on Sulfur Content of Liquid Products with and without SRC Ash Present During Reaction**

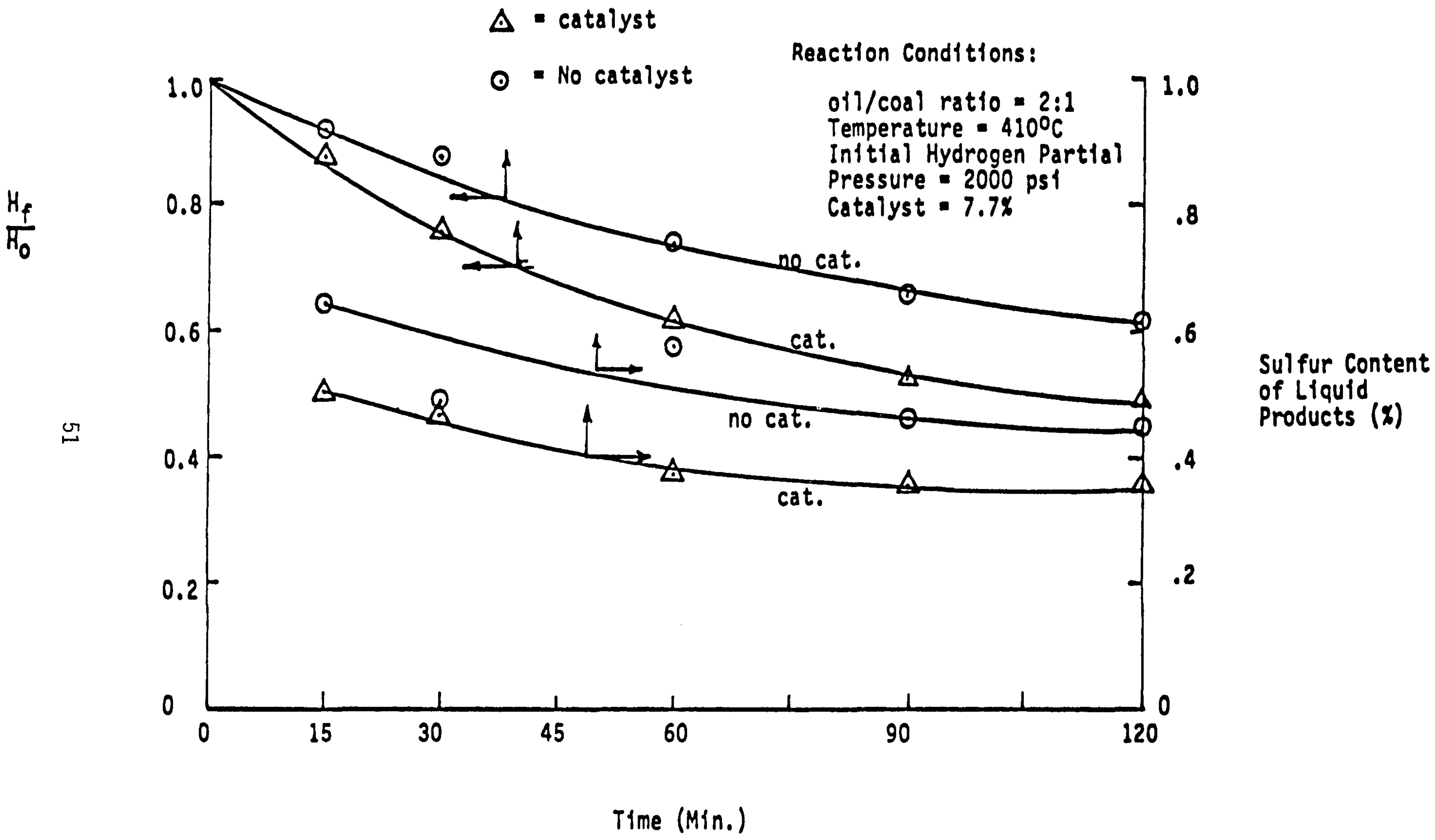


Table 2.1. **Effect of Type of Catalyst on Hydrogen Consumption and Rate of Hydrodesulfurization of a Coal/Oil Slurry**

Solvent (LRO)/coal = 2, T = 410°C, 120 minutes, 1000 rpm, Initial Hydrogen Pressure = 2000 psi

	Partial Pressures (psig)							
Catalyst	H_2 (10^{-3})	H_2S	CO_2	CH_4	C_2-C_5	Sulfur Content Of Liquid Products**	H_f/H_o***	Tetralin/ Napthalene Ratio****
Co-Mo-Al*	0.783	70	48	172	108	0.24	0.42	
- -	0.523	151	97	234	175	0.19	0.28	0.49
SRC Residue	0.842	41	115	244	132	0.38	0.45	
- -	0.739	35	115	206	125	0.37	0.40	
- -	0.834	48	132	219	137	0.39	0.44	0.33
Fly Ash	0.812	23	131	168	106	0.37	0.43	
- -	0.919	25	80	190	127	0.37	0.49	
- -	0.830	11	57	178	104	0.37	0.44	0.29
Fe	1.08	0.0	42	136	87	0.24	0.58	
-	1.01	0.0	45	156	92	0.27	0.55	
-	1.02	0.0	45	157	99	0.24	0.55	0.25
CuO	--	--	--	--	--	0.27	0.62	
-	--	--	--	--	--	0.24	0.64	
CaO (5g)	--	--	--	--	--	0.30	0.83	
None	1.21	35	49	167	114	0.374	0.57	
-	1.11	37	56	155	95	0.417	0.62	0.16
-	1.25	36	44	135	90	0.350	0.64	
-	1.19	48	53	141	83	0.411	0.63	
-		--	--	--	--	0.402	--	

Catalyst = 14.3%

* Presulfided Co-Mo-Al

** Liquid products: those that pass through a Whatman #51 filter paper

*** H_f/H_o: the ratio of the final hydrogen partial pressure to the original

**** The peak height ratio in the gas chromatograph analysis of the liquid products most of the coal is liquefied within the first 30 minutes of reaction, and conversion asymptotically approaches a slightly higher amount with increased reaction time. In the asymptotic region after the first 30 minutes of reaction, hydrogen continues to be consumed (Figure 2.2). It is thus desirable to avoid operation in this asymptotic region. Desulfurization occurs very slowly in the absence of a catalyst as is shown in Figure 2.2, and long reaction times, extending into the asymptotic region, are required to meet new source performance standards (NSPS). However, the selective action of the ash of SRC residue in accelerating desulfurization over hydrogenation allows current requirements set by NSPS to be met without having to operate in the asymptotic region of conversion. After reaction for 30 minutes in the presence of the ash of SRC residue, for example, the same amount of sulfur is removed as that removed after 120 minutes of reaction in the absence of a catalyst. In Table 2.2, this result is shown to have importance in that an SRC having a sulfur content of 0.82 percent can be produced in the presence of the ash of SRC residue while consuming about 46 percent less hydrogen than that required in its absence. In other words, we have shown that the use of the ash of SRC as a catalyst selectively accelerates desulfurization and that an acceptable SRC can be produced without having to operate in the asymptotic region of Figure 2.1. This important finding reduces hydrogen consumption by 40 to 50 percent.

New source performance standards (NSPS) are currently being examined by the Environmental Protection Agency to determine whether guidelines set by the recent legislature are being enforced. The feeling among utilities is that the permissable level of sulfur in SRC is most likely to be reduced to as low as 0.6 to 0.7 percent as opposed to the currently permissable level of 0.9 to 1.0 percent. If this modification in sulfur standards should occur, then the impact of utilizing a catalyst such as the ash of SRC residue would be even greater since it is extremely difficult to meet the NSPS with current SRC technology.

Table 2.2. Comparison of Product Distribution and Sulfur Content of Products for Hydrogenation of a Coal/Oil Slurry in the Presence and in the Absence of the Ash of SRC Residue

Experimental Run	A	B	C	D
Reactions Conditions:				
Solvent/Coal Ratio	2:1	2:1	2:1	2:1
Catalyst	None	10g SRC Ash	10g SRC Ash	None
Pressure (psi)	2000	2000	2000	2000
Reaction Time (min)	120	30	30	30
H_f/H_i	.56	.76	.77	.90
Hydrogen Consumption (%)	44	24	23	9.8
Tetralin/Napthalene Ratio	.24	.37	.32	.29
Distillation: Product Distribution (%)				
Top	57.4	54.5	57.6	58.5
Bottom (SRC)	42.6	45.5	42.4	41.5
Total	100.0	100.0	100.0	100.0
Sulfur Content of Products (%)				
Top	0.23	0.16	0.18	0.24
Bottom (SRC)	0.82	0.83	0.82	1.10
Total	0.44	0.44	0.53	0.64
Detailed Product Distribution (%)				
Oil	39.5	21.9	21.8	9.66
Asphaltene	34.0	35.9	39.4	33.2
Benzene Insolubles	26.5	42.1	38.9	57.1
Pre-asphaltene	22.3	33.7	34.3	41.0
Pyridine Insolubles	4.2	8.4	4.6	16.1
Sulfur Content of Products (%)				
Oil	0.275	0.249	0.260	0.27
Asphaltene	1.03	1.06	1.11	1.02
Pre-asphaltene	0.45	0.41	0.53	0.971
Solid Residue	4.0	4.98	3.85	3.51

Hydrodesulfurization

The selective catalytic activity of coal minerals such as the ash of SRC residue for hydrodesulfurization (HDS) over hydrogenation has been shown (as discussed above) to have importance in producing solvent refined coal. Several mineral additives have been shown to have about the same effect on desulfurization as does the ash of SRC (10) and are just about as selective. For example: In Table 2.1 the presence of each of the mineral additives Fe and CuO has about the same effect on sulfur removal (i.e. sulfur content of the liquid products). Each of these additives reacts with H_2S product from prior desulfurization reactions. The results of our ongoing work (10, 11, 12 and 16) have shown that H_2S inhibits desulfurizaiton. Two possible reasons for the inhibiting effect by H_2S are: 1) the H_2S could be blocking active hydrogenation centers; or 2) the H_2S could actually be involved in reverse reactions. These reasons are only speculative, and much work remains to be done before we can be exact about the mechanism by which H_2S inhibits desulfurization. All of the coal minerals that have been found to be effective catalysts for HDS in our past work act also as sulfur scavengers. For example: In our catalysts screening studies the presence of iron, reduced pyrite (ferrous sulfide), and pyrite had decreasing effects on sulfur removal during hydrogenation/hydrodesulfurization of creosote oil at 425°C. In fact, the apparent catalytic activity of iron was very pronounced; whereas that of pyrite was insignificant. This difference in activity is apparently due to iron scavenging the H_2S--eliminating the H_2S--and pyrite reducing with hydrogenation to produce H_2S--introducing more H_2S. Similarly, the ash of SRC residue and untreated SRC residue, the former being a sulfur scavenger and the latter not, have a very pronounced catalytic activity for HDS reactions and essentially no catalytic activity for HDS reactions, respectively. Table 2.3 shows the results of a set of experiments in which the reactor was spiked with H_2S prior to hydrogenation of a coal/oil mixture.

Table 2.3: Effect of H_2S on Rate of Hydrodesulfurization of Kentucky and Wyodak Coals

Atmosphere	Coal Type	Solvent Type	Solvent-to-Coal Ratio	Cresol Soluble Yield (%)	Total % Sulfur		% Sulfur Liquid Fraction	% Sulfur Solid Fraction
					Before	After		
H_2	Wyodak	Recycle	3:1	76.0	0.52	0.41	0.35	1.15
$H_2 + H_2S$	Wyodak	Recycle	3:1	76.8	0.52	0.72	0.62	2.04
H_2	Kentucky 9/14	Recycle	2:1	86.4	1.10	0.80	0.52	2.86
$H_2 + H_2S$	Kentucky 9/14	Recycle	2:1	88.9	1.10	0.98	0.63	3.58

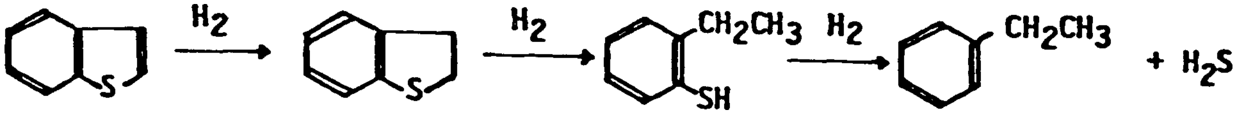
Apparently, the sulfur content of the reaction products was higher when reacted in an H_2S enriched atmosphere. To evaluate the reactivity of H_2S with coal/oil mixtures, SRC recycle solvent obtained from the Wilsonville pilot plant was stirred for an hour at room temperature in the presence of a 30 psi H_2S atmosphere. The sulfur content of the oil actually increased by about 55 percent. Exposure of tetralin to H_2S had about the same effect on its sulfur content, and even after boiling the tetralin under a vacuum of 26 in. Hg for 30 minutes the residual sulfur content was significantly higher than that of the original tetralin(0.12% as opposed to 0.02%). Gas chromatography was used to analyze the tetralin after reaction, and some differences between the chromatograms of the tetralin before and after reaction were detected. But, at this time, no conclusive data can be provided to distinguish whether the increase in sulfur content of the oil and the tetralin after exposure to H_2S is due to chemical or physical bonding.

Table 2.4. Reactivity of H_2S with SRC Recycle Solvent at Room Temperature

Sample	Sulfur Content (%)
SRC Recycle Solvent	
Original Oil	0.272, 0.254
After heating with reflux	0.257, 0.264
Oil after reaction with H_2S	0.207, 0.394 (0.470), 0.407
After heating with reflux	0.409, 0.419, (0.356), (0.341)
Tetralin	
Untreated	0.034, 0.012
After reaction with H_2S	0.255, 0.271
After heating with reflux, 0.5 hr.	0.132, 0.119
After heating with reflux, 1 hr.	0.120, 0.101
After heating with reflux, 2 hr.	0.110, 0.109
Vacuum reflux, 0.5 hr.	0.101, 0.146

The catalytic activity of different mineral additives for the HDS of model compounds--benzothiophene and thiophene--has also been studied to obtain more fundamental information:

1) Hydrodesulfurization of Benzothiophene: Benzothiophene hydrogenolysis has been reported to follow a stepwise reaction course (17, 18):



The results of our reaction studies in which the pure component, benzothiophene, was reacted with hydrogen are summarized in Table 2.5. These data are based on the normalized gas chromatographic peak area or height ratio. Most of the benzothiophene was converted to ethyl benzene when hydrogenated in the presence of Co-Mo-Al catalyst. In the presence of 10% Fe by weight, only about 50% of the benzothiophene was converted to ethyl benzene. The amount of benzothiophene converted to ethyl benzene was directly dependent on the amount of catalyst present. An unidentified product--possibly a reaction intermediate such as dihydrobenzothiophene or thiophenol as suggested in the above reaction sequence--resulted when the benzothiophene was hydrogenated in the presence of pyrite. The reason for this phenomenal effect of pyrite might be speculated to be due to H_2S inhibition--the blocking of active sites for hydrogenolysis reaction by H_2S produced from the hydrogenation of the pyrite. Since this phenomenal effect of pyrite may provide insight on the selectivity of the catalyst as to hydrogenation and hydrogenolysis (desulfurization), further studies including identification of the unknown peak are in progress.

When the benzothiophene was hydrogenated in the presence of the ash of SRC residue, significant amounts of both products, ethyl benzene and the unidentified product, were generated. However, there was a large degree of scatter

Table 2.5 Hydrodesulfurization of Benzothiophene in Dodecane

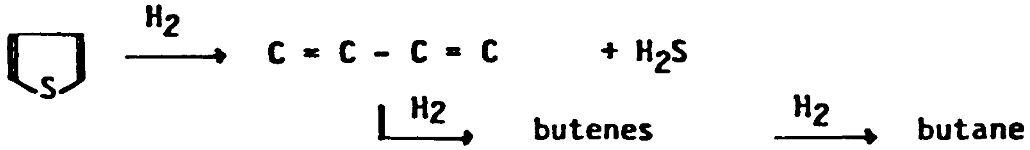
		GC PEAK RATIO ($\times10^3$)		
SAMPLE	CATALYST	BENZOTHIOPHENE TO DODECANE (AREA)*	ETHYL BENZENE TO DODECANE (AREA)*	UNKNOWN TO DODECANE (HEIGHT)*
Untreated 10 wt. % benzothiophene in dodecane	---	74.	0.0	0.0
Treated	None	65.	3.	3.
	Co-Mo-Al (10%)	0.0	79.	0.0
Untreated 8.8 wt. % benzothiophene in dodecane	---	65.	0.0	0.0
Treated	Reduced Pyrite (10%)	55.	0.0	7.
	SRC Residue (10%)	51. ± 2.	4.	4. ± 1.
	CaO (5%)	52.	12.	2.
	CaO (10%)	40.	12.	7.
	CaO (15%)	41.	14.	2.
	Pyrite (10%)	31. ± 3.5	8.	35. ± 2.
	Fe (3%)	50.	10.	2.
	Fe (6%)	42.	18.	3.
	Fe (10%)	30. ± 1.	38. ± 3.	3. ± 1.
	SRC Residue Ash (10%)	30. ± 6.	16. ± 10.	24. ± 14.

$T = 410^{o}C$, $P_i = 1200$ psig H_2, 30 minutes, 1000 cpm

*: normalized GC peak area or height ratio

in the current data obtained while using this catalyst. As a result it is difficult to draw any conclusions at this time. Furthermore refined studies including characterization and sample preparation of this catalyst are necessary. Other catalyst such as reduced pyrite, SRC residue, and CaO show less catalytic activity than that of Fe or the ash of SRC residue, with reduced pyrite having essentially no catalytic effect.

2) Hydrodesulfurization of thiophene. Thiophene hydrodesulfurization has been reported to follow a complicated reaction course (17, 18):



The results of our reaction studies in which the pure component, thiophene, was reacted with hydrogen are summarized in Table 2.6. These data are based on the normalized gas chromatographic peak area ratio. In the presence of Co-Mo-Al catalyst about 85% of the thiophene was converted to gaseous products. In the presence of minerals such as Fe, pyrite, SRC residue and the ash of SRC residue, about 40% of the thiophene was converted to liquid and gaseous products. When the thiophene was hydrogenated in the presence of pyrite an unidentified product (#2) was generated. This phenomenal effect of pyrite might be speculated, as in hydrodesulfurization of benzothiophene, to be due to back-reaction of the H_2S produced from hydrogenation of the pyrite.

Liquefaction

It is generally believed that coal liquefaction follows a coal → preasphaltene → asphaltene → oil route, by breaking C-O, C-S, C-C and possibly C-N bonds and stabilizing coal-derived free radicals by donation of hydrogen atoms or other small entities (7, 19, 20, 21). Our results have shown that

Table 2.6. **Hydrodesulfurization of Thiophene In Dodecane**

Sample	Catalyst	GC Peak Area Ratio* ($x10^3$) Thiophene to Dodecane	Unknown to Dodecane #1	Unknown to Dodecane #2
Untreated	-	53.	0.0	0.0
Treated	None	42. ± 2.8	-	-
	Co-Mo-Al	7.3 ± 0.5	-	-
	Fe	29. ± 2.6	6.3 ± 0.5	-
	SRC residue	30.	-	-
	SRC residue ash	28. ± 2.5	-	-
	Pyrite	32.	2.	9.

T=410°C, Pi=1200 psig H_2, 30 min., 1000 cpm
10 wt.% thiophene in dodecane

* normalized area ratio

the major role of a catalyst (coal minerals or other added catalysts) in liquefaction is the replenishment of the donor solvent in order to maintain the proper level of hydroaromatics (12, 22). As was shown in Figure 2.1 (also refer to reference 25) liquefaction of bituminous coals occurs almost instantaneously upon reaching an advanced reaction temperature while in the presence of a hydrogen-donor solvent.

At a reaction temperature of 410° C and a 2000 psi hydrogen atmosphere, good rates of coal liquefaction in tetralin, or SRC recycle solvent can be readily achieved without the use of a catalyst. An average ash-basis yield of 94.1 percent was obtained, for example, for non-catalyzed runs performed at 410°C and 2000 psig initial hydrogen partial pressure for two hours. Therefore, with regard to liquefaction, the main consequence of catalysis at these conditions would be excess solvent hydrogenation or gas formation with little or no increase in yield. The increased rate of rehydrogenation would affect the composition of the liquid product, with a larger percentage of coal being transformed into oil (10). This may or may not be advantageous, depending upon process objectives.

Earlier it was shown that hydrogen consumption can be reduced by 40 to 50 percent without any significant reduction in liquid yield if the reaction time is reduced and a mineral catalyst (the ash of SRC residue) is used. Our current data indicate that hydrogen consumption can be reduced also by lowering reaction temperature rather than reaction time and using a mineral catalyst. For example, it appears that substantial reductions in hydrogen consumption can be realized by reaction a 2:1 oil/coal slurry at 380°C instead of 410°C, while using the same initial hydrogen partial pressure and reaction time (2000 psig and 2 hours) and using a mineral catalyst (14.3% Fe). As seen in Table 2.7 the catalyzed reaction at 380°C gave a yield of 90.8 percent while the H_f/H_0 ratio (ratio of final hydrogen partial pressure to initial hydrogen partial pressure) was 0.75.

Table 2.7. Effect of Fe Catalyst, Reaction Time, and H_2 Partial Pressure on Yield, Hydrogen Consumption and Rate of Hydrogenation of a Coal/Oil Slurry at a Low Reaction Temperature

Solvent (LRO)/Coal = 2, T = 380°C, 1000 rpm
Coal = 40 g., LRO = 80g

Amount of Catalyst (gm)	Initial H_2 Pressure (1x10^{-3} psig)	Reaction Time(hr)	Yield*	Sulfur Content of Liquid Products**	Hf/Ho***	Tetralin/ Napthalene Ratio****
20	2.00	4	92.6	.348	.56	.409
20	2.00	4	92.4	.319	.57	.34
18	1.00	4	89.0	.361	.45	
20	.50	4	89.5	.375	.53	
20	2.00	2	90.8	.336	.75	
20	1.00	2	91.3	.379	.63	.26
20	.50	2	89.3	.396	.84	.14
5	.50	2	63.4	.410	.88	
2.5	.50	2	43.7	-	.90	

* Based on Ash Balance
** Liquid Products: those that pass through a Whatman #51 filter paper
*** Hf/Ho: the ratio of final hydrogen partial pressure to original
**** The peak height ratio in the gas chromatographic analysis of liquid products

In comparison, the non-catalyzed reaction at 410°C (Table 2.8) gave an average yield of 94.1 percent and an average H_f/H_0 ratio of 0.55. Thus, the catalyzed reaction at reduced temperature (380°C) can give a comparable yield while consuming significantly less hydrogen than the non-catalyzed reaction at 410°C. In addition, desulfurization was better for the catalyzed 380° runs.

At reduced process conditions, liquefaction is difficult to achieve. When both temperature and pressure are lowered ($T = 380°C$, $P_i = 500$ psig H_2), the rate of liquefaction is reduced significanlty. Even when large amounts of catalyst and long reaction times were employed (14.3% Fe, 4 hours), liquid yield remained below 90% (Table 2.7). From the data collected so far, it is questionable whether the use of mineral catalysis will provide adequate yields if both temperature and pressure are substantially reduced.

The data given in Tabel 2.8 indicate, however, that acceptable yields at reduced pressures and temperatures may be possible: When a 2:1 oil/coal mixture was reacted in the presence of Fe (14.3% by weight) at 380°C and in an initial H_2 pressure of 500 psi, a marginally acceptable yield of 89.3 percent was obtained. The data given in Table 2.7 are somewhat discouraging, on the other hand, in that unsatisfactory yields were obtained when Fe was present in smaller amounts. Clearly more work is required before the feasibility of operating at both reduced temperature and pressure can be determined.

Of the two primary reactions involved in the SRC process, liquefaction kinetics seems to be the primary controlling factor when the reaction is performed at lower process conditions. This is just the opposite of what was observed for runs at higher reaction temperatures and pressures. At 410°C and 2000 psig H_2 pressure, for example, it was observed that the kinetics of desulfurization would be the primary limiting process factor in producing SRC--as was discussed earlier with regard to Figures 2.1 and 2.2.

Table 2.8. Effect of Reaction Time on Hydrodesulfurization, Yield, and Hydrogen Consumption of a Coal/Oil Slurry at Low Reaction Temperature and Pressure

Solvent (LRO)/coal = 2, T = 380°C, P_i = 500 psig H_2, 1000 rpm

Catalyst = 14.3% Fe

Reaction Time (hr)	Yield*	Sulfur Content of Liquid Products**	Hf/Ho***
4	89.5	.375	.53
2	89.3	.396	.84
1	80.0	.402	.81
0.5	44.0	.386	.95

Solvent (LRO)/coal = 2, T = 410°C, P_i = 2000 psig, 1000 rpm

No Catalyst

2	95.8	.374	.58
2	91.8	.417	.63
2	94.8	.402	-
2	93.0	.391	.49
2	95.0	.350	.65
2	-	.411	.64

* Based on Ash Balance

** Liquid Products: those that pass through a Whatman #51 filter paper

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

To obtain more fundamental information concerning hydrogenation reactions, several model compound studies were made, as was done in studying hydrodesulfurization reactions. The model compounds used were tetralin and napthalene. Using these model compounds the catalytic activity of commercial Co-Mo-Al and representative coal minerals, such as SRC residue, the ash of SRC residue, Fe, FeS, pyrite, and reduced pyrite, have been examined. The main reactions involved in these studies were:

$$\text{tetralin} \xrightarrow[\text{catalyst}]{} \text{naphthalene} + H_2$$

$$\text{naphthalene} + H_2 \xrightarrow[\text{catalyst}]{} \text{tetralin}$$

The reader may refer to the manuscripts in references 12 and 15 for details concerning these studies and the process variable studies discussed above.

Based on the data given in Tables 2.1, 2.9 and 2.10 a significantly lower amount of hydrogen is consumed when coal/oil mixtures are hydrogenated in the presence of CaO. However, the amount of sulfur removed is greater due to scavenging of inhibiting H_2S by the CaO. Apparently, as shown in Table 2.10, the greater the amount of CaO present during hydrogenation; the lower is the amount of hydrogen consumed. As to be expected, as hydrogen consumption decreases, liquid yield also decreases. Much work needs to be done to show that the inhibiting effect of CaO on hydrogen transfer observed here is real and to develop an understanding as to how this inhibition by CaO occurs.

Solvent Sufficiency

Three process objectives must be met in SRC processing:

(1) The coal must be liquefied at some stage in the process to allow the ash (i.e., the mineral matter in the coal) to be removed.

(2) The sulfur content of the coal must be reduced to some predetermined level.

Table 2.9. **Effect of H_2 Partial Pressure on Rate of Hydrodesulfurization of a Coal/Oil Slurry**

solvent (LRO)/coal = 2, T = 380°C, 1000 rpm, catalyst = 20g Fe (14.3%)

Initial H_2 Pressure ($1x10^{-3}$ psi)	Reaction Time (Hrs)	Sulfur Content of Liquid Products*	H_f/H_0**	Tetralin/Napthalene Ratio***
2.00	4	.334	.57	.41
1.00	4	.361	.45	
0.50	4	.375	.53	
2.00	2	.336	.75	.26
1.00	2	.379	.63	
0.50	2	.396	.84	

solvent (LRO)/coal = 3, T = 385°C, 1000 rpm, catalyst = 5g CaO (4.0%)

2.00	2	.328	.90	
1.00	2	.332	0.91	
0.50	2	.355	0.94	

* Liquid Products: those that pass through a Whatman #51 filter paper

** H_f/H_0: the ratio of the final hydrogen partial pressure to the original

*** The peak height ratio in the gas chromatographic analysis of liquid products

Table 2.10. **Effect of Amount of CaO Present on Hydrogen Consumption and Rate of Hydrodesulfurization**

solvent (LRO)/coal = 3, T = 410°C
1000 rpm, 120 minutes, 1000 psi H_2
coal = 30 g
LRO = 90 g

Amount of Catalyst (g)	Sulfur Content of Liquid Products *	H_f/H_o**	H_2S Partial Pressure (psi)
5	0.295	0.83	1.6
2	0.343	0.79	1.0
2	0.344	0.80	2.5
1	0.387	0.68	15.6
1	0.387	0.69	14.8

* Liquid Products: those that pass through a Whatman #51 filter paper
** H_f/H_o: the ratio of the final hydrogen partial pressure to the original

(3) Solvent sufficiency must be maintained.

We have shown, as discussed earlier, that the critical reactions involved in the SRC process are dependent upon the hydrogen-donor activity of the carrier solvent. Sufficient hydrogen donor species should thus be present in ample proportions in the recycled solvent. One important hydrogen-donor component in SRC process solvent is tetralin, a hydrogenated form of napthalene. A measure which should be roughly indicative of the hydrogen-donor quality of the solvent is the ratio of tetralin to napthalene present (tetralin/napthalene, or T/N ratio). Since the solvent is hydrogenated at the expense of the hydrogen atmosphere, if T/N ratio is representative of total solvent hydrogenation, there should be a strong correlation between T/N ratio of the liquid and hydrogen consumption (as indicated by H_f/H_0). Apparently, based on data given in Figure 2.3, this is indeed the case. The reader may refer to the following references 10 and 12 for details concerning the effect of process variables (reactions temperature, coal particle size or mass transfer, reaction pressure, etc.) on T/N ratio, and its correlation with liquid yield and sulfur removal. T/N ratio is certainly useful only as a rough indicator of solvent sufficiency. The development of more comprehensive indicators of solvent quality are definitely needed. Much work remains to be done in characterizing SRC process solvents (Task 3) and correlating the solvent's characteristics with reaction kinetics and coal mineral catalysis.

2.B. Bench Scale Continuous Reactor Experiments

Objective: The objective of this subtask is to better define the differences in SRC process performance which may occur because of differences in reactor designs, eg. stirred tank versus tubular reactor. Toward this end, a better model will be developed for the SRC continuous reactor.

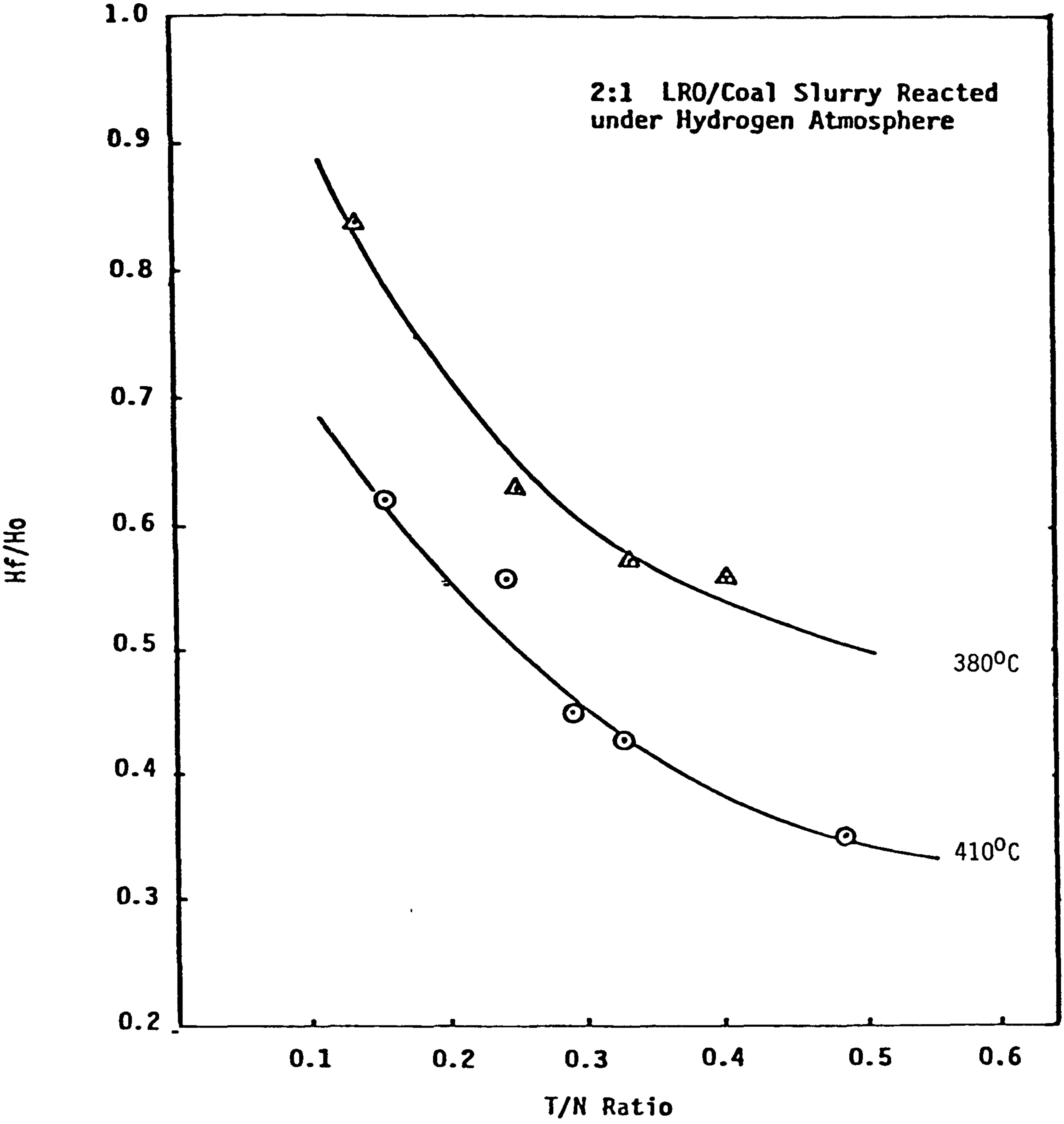


Figure 2.3. Relationship of T/N Ratio with H_f/H_o

Summary of Progress

In the SRC process, pulverized coal is mixed with an internally generated coal-derived solvent. The resulting slurry and hydrogen gas are pumped and preheated to 780-850^{0}F through a gas-fired preheater connected to a dissolver section for further reaction. The SRC pilot plants at Wilsonville, Alabama, and Fort Lewis, Washington, both use continuous tubular reactors (dissolvers) and preheater tubes. Because of heat and mass transfer effects, and the complexities of three phase flow, it is difficult to extrapolate batch autoclave experiments to predict the performance of continuous reactors. Two factors which cause difficulty in the calculation of performance of tubular reactors are (1) the residence time of the liquid and (2) the extent of mixing in the liquid phase. In two-phase vertical tubular flow, such as in Wilsonville and Fort Lewis dissolvers, the gas phase occupies a certain portion of the reactor, thus decreasing the liquid phase residence time as calculated on the basis of the total dissolver volume. In addition, the presence of the multiphase system, particularly the gas bubbles, causes a certain amount of mixing (dispersion) in the reactor. This type of reactor, having multiphase flow, is sometimes referred to as a bubble column, because of the presence of the gas bubbles (largely hydrogen). To date our work has resulted in the development of a comprehensive model, based upon the axial dispersion model, for this type of reactor. The model uses reaction rate expressions obtained from laboratory data and incorporates kinetic rate expressions for desulfurization, hydrogenation, and coal dissolution (conversion). Axial dispersion coefficients are introduced to account for the mixing, which occurs largely in the dissolver section, while the preheater is largely plug flow. In addition mass transfer terms are included in the material balances for each species (eg. hydrogen) to account for the transfer of that species from the gas to the liquid phase. The entire development of the model, together with the kinetics rate expressions used therein is presented in the paper "A Dispersion Model for the Solvent Refined Coal Process" contained in reference 26 and which has been accepted for publication in I & EC Process Design and Development. In summary, the application of the model has resulted in the following conclusions:

1. The mixing and flow pattern of the multi-phase reactor has been taken into account through the axial dispersion term, which has not been previously utilized for SRC reactor modeling.
2. The mass transfer of hydrogen from the gas phase into the liquid phase has also been accounted for in the model, the effect of hydrogen mass transfer rate on the hydrogen consumption and coal dissolution rate can be easily simulated; and the influence and extent of mass transfer control can be assessed. In particular, the Wilsonville SRC reactor is found to operate in a kinetically, rather than a mass transfer limited regime.
3. All of the parameters arising in the model are obtainable independently from literature correlation; these parameters have definite physical meanings based upon the flow conditions, therefore, by changing the relative magnitude of each parameter, the general trend of the effect of each operating variable on the SRC process can be assessed, thus providing a better engineering design basis for simulation and optimization of the SRC process.
4. The hydrogen consumption and organic sulfur removal at the Wilsonville SRC pilot plant are higher than predicted by the

present model, which uses kinetics rate expressions from laboratory experiments. This is believed to be caused by the accumulation of catalytic coal minerals in the Wilsonville reactor, giving higher reaction rates.

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.

Summary of Progress

To date we have successfully employed HPLC and GPC in the following three areas of analysis: 1) characterization of coal oils by HPLC, 2) preliminary separation of SRC and coal liquids by HPLC, and 3) determination of molecular size/weight distributions of SRC by GPC.

Creosote and recycle oils have been successfully separated by reverse phase HPLC using bondapak/C_{18} columns with a 45:55 volume-to-volume acetonitrile-water solvent (reference 38). Preparatory scale columns were used to collect sufficient amounts of twelve major components to permit their positive identification by infrared spectroscopy. These identified major constituents are listed in Table 3.A.1 and compose about 50.3% by weight of the original creosote oil. The components fall into basically two categories: polynuclear aromatics and heteroatom compounds. Polynuclear aromatics are considered to play an important role in hydrogen transfer reactions occurring during coal liquefaction, as in the

TABLE 3.A.1.

HPLC Analysis of Treated Creosote Oil

Compound	Wt. %					
	A	B	C	D	E	F
1 and 2-naphthanitrile	0.611	0.458	0.243	trace	0.046	trace
carbazole	0.423	0.386	0.418	0.386	0.443	0.526
naphthalene	8.92	7.49	6.55	4.16	4.01	4.17
2-methylcarbazole	0.106	0.084	0.059	0.067	0.102	trace
1-methylnaphthalene	5.23	4.55	3.14	3.13	2.33	2.08
2-methylnapthalene	8.00	6.21	7.63	5.42	4.61	4.37
acenaphthene	6.28	4.75	1.56	2.38	2.24	2.08
fluorene	5.22	5.02	3.78	3.62	3.64	4.55
dibenzothiophene	1.27	0.888	0.720	trace	0.576	0.622
phenanthrene	12.4	9.10	7.95	8.05	7.11	5.96
anthracene	1.86	1.88	1.31	2.17	1.50	1.53
Total	50.32	40.23	33.36	29.39	26.61	25.89

A - original oil
B - oil heated with hydrogen, no catalyst
C - oil heated with hydrogen and pyrite
D - oil heated with hydrogen and cobalt molybdate
E - oil heated with hydrogen and coal ash
F - oil heated with hydrogen and SRC solids

Three runs were made for each treatment with a relative standard deviation between runs of ± 8% of the determined mean weight per cent.

SRC process. The heteroatom compounds containing atoms such as N, O, and S are of great interest since during combustion these constituents form pollutants, SO_2 and NO_x.

The characterized creosote oil whose analysis is given in column A of Table 3.A.1, was subjected to hydrogenation and hydrodesulfurization at 425°C in the presence of an initial hydrogen partial pressure of 3000 psig. The hydrogenation of the oil reduced the weight percent of the analyzed compounds by 20%. HPLC analysis of the reaction product is listed in Table 3.A.1. When the creosote oil was hydrogenated in the presence of various catalysts, the weight percentage of the analyzed compounds was even further reduced (34%, when pyrite was present, to 49% when SRC mineral residue was present). Table 3.A.1 gives a complete tabulation of the effect of mineral matter on the individual components in creosote oil.

As shown in Table 3.A.1 HPLC offers sufficient specificity to detect differences in the final concentration of major constituents of the oil when hydrogenated in the presence of the various catalytic agents. For example: assuming that the disappearance of the major constituents is due to hydrogenation, then Co-Mo-Al, coal ash, and SRC mineral residue show a decisive preference for accelerating hydrogenation of naphthalene, 1-methylnaphthalene, and 2-methylnaphthalene; whereas pyrite favors hydrogenation of acenaphthene and, to a lesser extent, anthracene. Also, in the presence of a commercial Co-Mo-Al catalyst, the concentration of dibenzothiophene, a major organic sulfur component, is reduced to a much greater extent than when the other catalysts were present. In fact, the concentration of dibenzothiophene was reduced essentially to zero when Co-Mo-Al was present. Since Co-Mo-Al is an excellent catalyst for hydrodesulfurization reactions, these results are not surprising. Most interestingly, however, the trend in dibenzothiophene removal is exactly the same as that found by analysis of the total sulfur content: namely, Co-Mo-Al >> coal ash >> SRC mineral residue > pyrite > H_2 only. Carbazole, on the other hand, has essentially the same concentration as that in the original oil, despite the catalyst used; whereas the naphthonitriles are completely removed when either Co-Mo-Al, coal ash, or SRC mineral residue is present. Chromatograms of untreated creosote oil, hydrogenated creosote oil, and hydrogenated creosote oil treated with pyrite and Co-Mo-Al catalyst are shown in Figure 3.A.1.

To better characterize coal liquids and SRC product, these substances were initially separated into four well-defined fractions - pyridine solubles, pyridine insolubles, benzene solubles and pentane solubles. The pentane solubles - the oil fractions - from several autoclave experiments were analyzed by HPLC using μbondapak columns and the acetonitrile-water system. A summary of the results is given in Table 3.A.2. It can be seen from Table 3.A.2 that there is little change in the composition of this oil fraction. Of the sixteen compounds determined, most show little change after contact with coal, hydrogen and iron at 400°C with the possible exception of dibenzofuran and biphenyl. This observation is most readily seen in the total weight percent of these sixteen compounds, 38.43, 33.33, and 35.51% when treated with solvent + coal + hydrogen, solvent + coal + hydrogen + iron, and starting solvent respectively.

Even though some oil fraction is produced from the coal itself, it appears that the overall composition is not changed significantly. However, it should be remembered that the starting ratio of coal to solvent of 1:2 makes detection of slight changes in the oil fraction difficult because of masking by the oil originally present; only about 10% of the oil fraction comes from the coal.

To delve into the chemical nature of SRC, particularly the pyridine solubles and insolubles - the asphaltenes and preasphaltene fractions - molecular size/weight distributions have been investigated by gel permeation chromatography.

Figure 3.A.1.

Chromatograms of creosote oil which show the effect of the various treatments. Positively identified components in order of elution are:

a. internal standard (benzofuran)

b. 1 and 2-naphthonitrile

c. carbazole

d. naphthalene

e. 2-methylcarbazole

f. 1-methylnaphthalene

g. 2-methylnaphthalene

h. dibenzofuran

i. biphenyl

j. acenaphthene

k. fluorene

l. dibenzothiophene

m. phenanthrene

n. anthracene

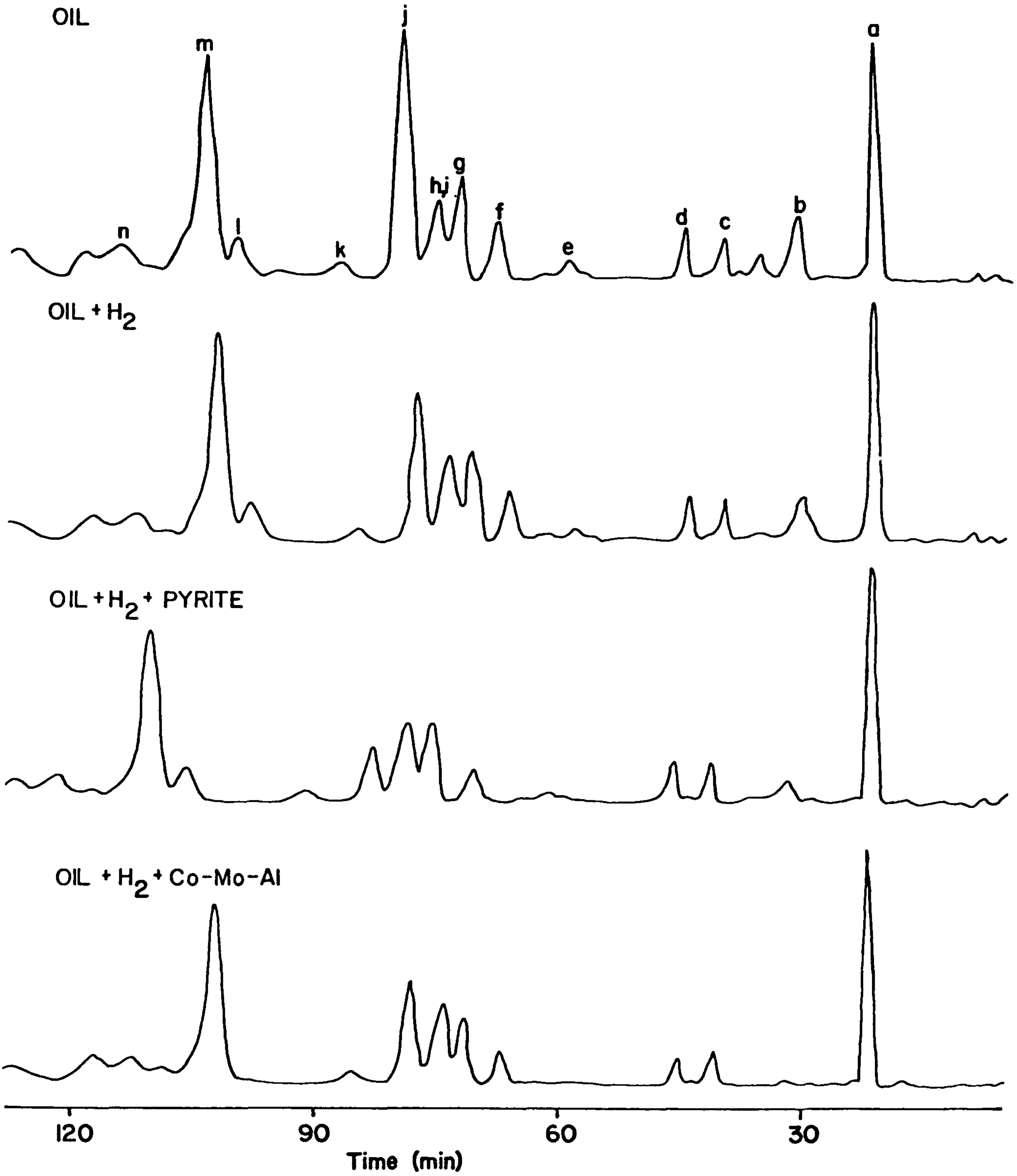

OIL
j
m
a
g
hj
f
n
l
d
c
b
k
e
OIL + H_2
OIL + H_2 + PYRITE
OIL + H_2 + Co-Mo-Al
120
90
60
30
Time (min)

TABLE 3.A.2.

Composition of Hexane Solubles from Batch Autoclave Reaction

		WT%	
Compound	A*	B*	C*
naphthonitriles	0.04	0.04	0.04
carbazole	0.22	0.20	0.22
naphthalene	6.65	5.92	6.96
2-methylcarbazole	0.10	0.05	0.17
1-methylnaphthalene	1.32	1.15	1.37
2-methylnaphthalene	5.44	4.43	3.47
dibenzofuran	1.58	1.86	4.27
biphenyl	4.59	3.92	2.41
acenaphthene	0.96	0.88	1.18
fluorene	1.13	1.31	1.62
dibenzothiophene	0.33	0.28	0.28
phenanthrene	5.19	4.55	4.78
anthracene	0.48	0.34	0.53
9,10-dihydrophenanthrene	4.85	3.92	4.02
fluoranthene	4.54	3.57	3.23
pyrene	1.01	0.91	0.96
TOTAL	38.43	33.33	35.51

A* - Oil fraction from reaction of solvent, hydrogen and coal.

B* - Oil fraction from reaction of solvent, hydrogen, coal and iron catalyst.

C* - Original solvent only (unreacted).

To determine the approximate molecular weight range studied in the GPC of SRC, calibration standards of polynuclear aromatics and polyethylene glycol were chromatographed using the following conditions:

Solvent: tetrahydrofuran
Flow Rate: 1 ml/min
Temperature: ambient
Columns: two 30 cm 100 Å μ-styragel
one 30 cm 500 Å μ-styragel
Detector: refractive index (64 attenuation)

The retention times of the various molecular weight polyethylene glycols are:

Molecular Weight	t_R (minutes)
285-315	27.9
380-415	21.0
570-630	19.1
950-1050	17.6
1300-1600	16.8

Five standard aromatic compounds were analyzed by GPC and their retention times (t_r) at the above given conditions are as follows:

Compound	Molecular Weight	t_R (minutes)
Benzene	78	30.1
Anthracene	178	28.7
Phenanthrene	178	28.8
1,1-Bi-2-Naphathol	236	23.0
Rubrene	532	23.0

In Figure 3.A.2 the molecular weights of both the polyethylene glycols and the polynuclear aromatics are plotted versus their retention times. In GPC analysis molecular size and shape as well as molecular weight play an important role in the elution time of compounds from the GPC. Consequently, some poly-

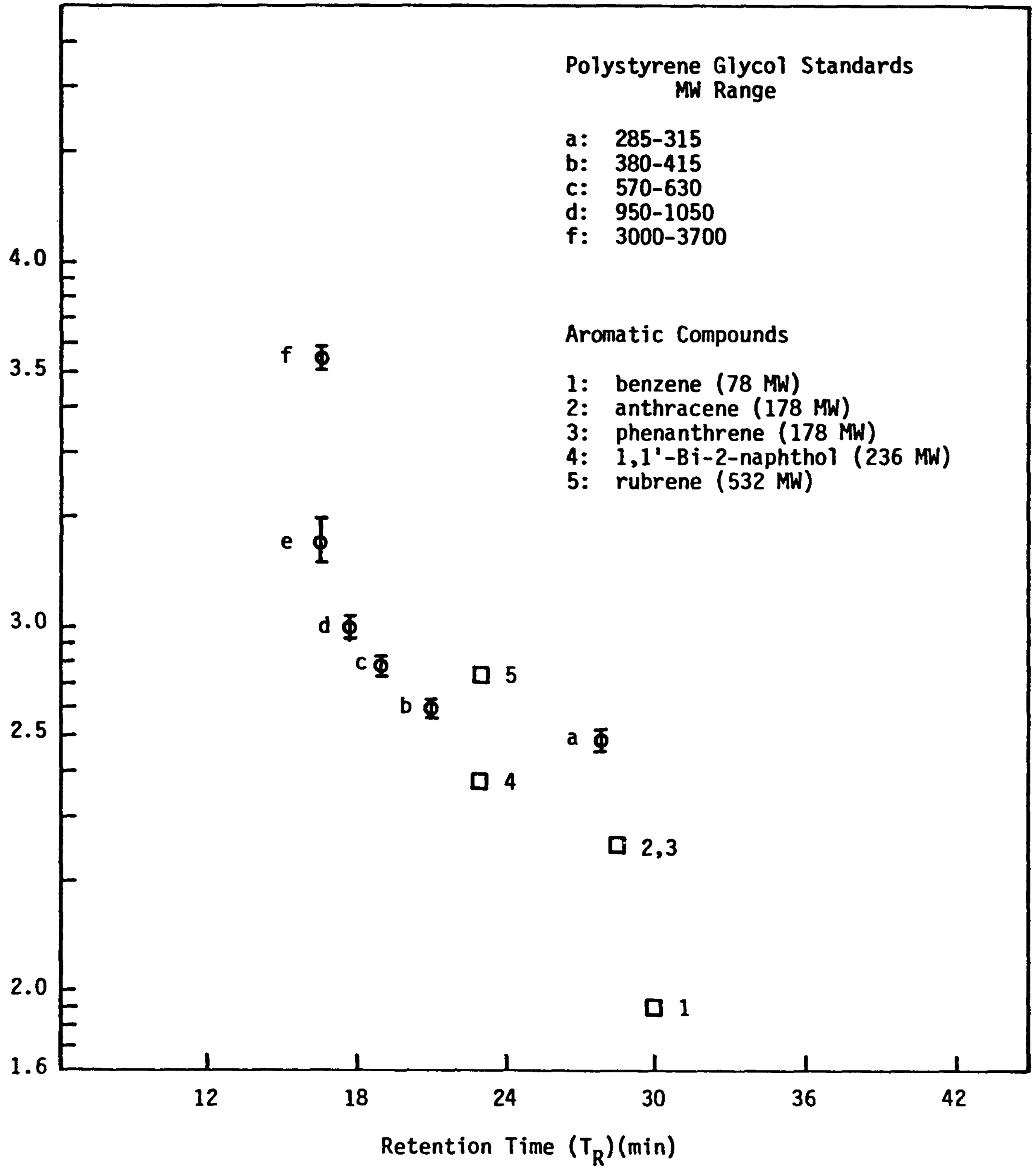


Figure 3.A.2.

Gel Permeation Chromatography Calibration of Polynuclear Aromatics and Polyethylene Glycols nuclear aromatic compounds of different molecular weights elute at the same time as in the case of rubrene and 1,1-Bi-2-naphthol. Some of the polynuclear aromatics tend to be retained on the column packing giving spurious retention times for some compounds.

When SRC is analyzed using GPC at the conditions previously given and at a concentration of 100 mg/ml with a one milliliter injection, SRC beings to elute at a retention time of fifteen minutes and is essentially complete at thirty-three minutes. In Figure 3.A.3 the molecular size distributions for Amax, Monterey, and Illinois No. 6 SRC are given. Currently, in the analysis we are taking six fractional cuts at three minute intervals from the beginning of the SRC elution. Each of these fractions will be analyzed using Fourier transform infrared spectroscopy, ultraviolet spectroscopy, nuclear magnetic resonance, elemental analysis and thermal analysis. As a part of our current program, solvent properties of common HPLC solvents have been assessed in terms of satisfactory analysis of coal liquids and SRC products. Different solvent systems were rated according to 1) molar absorptivity at the wavelength used in ultraviolet detection of the chromatographic eluents; 2) column pressure at a reasonable flow rate, 1 ml/min; 3) sensitivity of column pressure and resolution to increases in column temperature; and 4) most importantly, percent solubility of the complex coal-derived mixtures.

In reverse phase HPLC using an acetonitrile-water solvent mixture for oils, the best wavelength for total absorptivity on a weight or number of peaks observed basis is 232 nm. Almost any functional group which absorbs in the ultraviolet will absorb at 232 nm; therefore, the ultraviolet detector set at 232 nm sees almost every compound that absorbs in the ultraviolet which elutes from the column. At 232 nm no interference is observed from the solvent since the UV cutoff for acetonitrile is 210 nm. In gel permeation chromatography the wavelength of choice is 300 nm. To choose the best wavelength for GPC analysis of SRC, SRC was

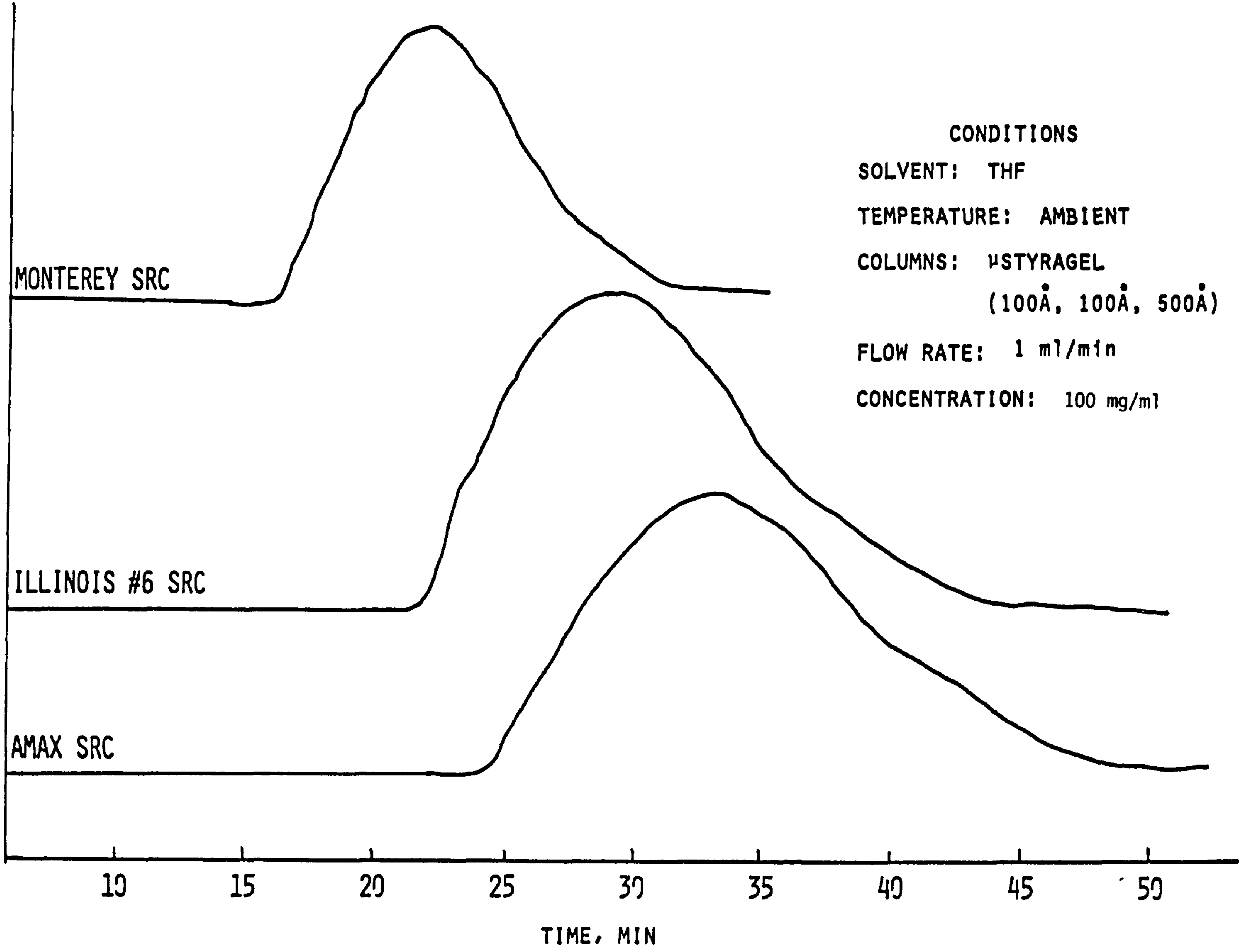


Figure 3.A.3. GPC Chromatogram of SRC

dissolved in THF at 100 mg/ml and then chromatographed at wavelengths ranging from 224 to 316 nm at 10 nm intervals; 300 nm appeared to be as sensitive as the lower wavelength but at 300 nm the SRC chromatogram did show some structure. It should be noted that at the lower wavelengths the SRC absorbed so strongly that essentially a total block absorption was observed. At wavelengths greater than 300 nm the sensitivity of UV absorption rapidly declined. The UV cutoff for unstablized THF is 211 nm.

A solubility study of solvent refined coal is currently under investigation in our laboratory. The solubility of SRC in a wide variety of solvents at three concentration levels is being studied and the results to date are shown in Table 3.A.3. The question arises after performing this initial solubility work if the SRC is truly dissolved in the solvents at the percentage level indicated or if SRC particles are present in a colloidal suspension. Further experiments on selected solvents are using centrifuging as a preliminary clarification technique. From the results of the centrifuge experiments shown in Table 3.A.4, it appears that the SRC is in a colloidal type suspension in many solvents. In order to perform HPLC experiments this colloidal suspension of SRC must be eliminated. This suspension is most likely the cause of clogging of the filters and 0.009 stainless steel tubing in the liquid chromatograph which has caused break-downs and delays. A reliable method of determining the solubility of start-up and steady-state solvents and reaction coal/oil slurries has not yet been developed. When dealing with mixtures such as creosote or recycle oil which are universal organic solvents in themselves, it is difficult to determine their solubility in other solvents. It is possible, however, to keep the creosote and recycle oils in solution in a 45:55 acetonitrile-water solution and to separate their constituents using reverse phase HPLC.

In the HPLC investigation of SRC product, it became immediately apparent that some preanalysis or preseparation step was necessary. Direct HPLC analysis

TABLE 3.A.3.

Solubility of SRC at Three Concentration Levels

Solvent	% Insoluble - Concentration (mg/ml) 4	20	100
Tetrahydrofuran	23.7 ± 0.5	17.6 ± 1.4	13.0 ± 1.2
Dimethylformamide	20.0 ± 1.0	20.4 ± 1.3	28.6 ± 6.7
Chloroform	42.1 ± 1.6	48.0 ± 1.2	49.2 ± 1.2
Benzene	51.4 ± 3.0	59.4 ± 1.4	40.6 ± 3.5
2-Propanol	71.3 ± 5.9	49.0 ± 3.1	75.1 ± 7.8
Heptane	82.6 ± 2.2	94.2 ± 0.6	97.6 ± 1.1
Ethanol	65.9 ± 1.9	77.9 ± 1.3	58.1 ± 1.4
Hexane	80.6 ± 1.2	95.1 ± 3.4	98.1 ± 0.4
Xylene	50.2 ± 1.8	63.5 ± 0.4	75.1 ± 1.2
Toluene	51.3 ± 4.6	63.0 ± 2.3	75.1 ± 1.2
Methylene Chloride	38.4 ± 3.2	54.3 ± 1.3	58.4 ± 0.64
Cresol	2.9 ± 0.4	5.1 ± 1.0	--------
Carbon Disulfide	54.5 ± 2.0	58.3 ± 0.6	61.1 ± 0.5
Carbon Tetrachloride	79.5 ± 3.9	78.5 ± 2.3	92.6 ± 0.6
Petroleum Ether	90.5 ± 2.8	94.6 ± 1.3	98.2 ± 0.8
Acetonitrile	79.6 ± 2.9	89.7 ± 3.4	91.6 ± 0.3
Pyridine	63.9 ± 2.7	81.9 ± 0.6	70.9 ± 1.4

of SRC particularly by reverse phase chromatography resulted in no separation, poisoning of the packing and precipitation of the SRC during HPLC analysis. Preseparation is currently underway using gel permeation chromatography. Initial experiments using a preparatory scale HPLC for preliminary separation have been begun.

TABLE 3.A.4.

Solubility of SRC at Three Concentration

Levels Using Centrifuging

	% Insoluble - Concentration (mg/ml)		
Solvent	4	20	100
Tetrahydrofuran	74.5 ± 1.2	86.1 ± 2.7	101.4 ± 4.0
Acetonitrile	60.3 ± 8.2	90.7 ± 1.4	97.5 ± 0.2
Hexane	90.9 ± 2.1	101.7 ± 0.6	98.5 ± 1.4
Dichloromethane	36.8 ± 2.6	98.8 ± 4.6	96.8 ± 1.2
Cresol	132.4 ± 16.4	191.0 ± 14.1	211.0 ± 9.0

3.B. Gas Chromatography of Coal Liquids and Other 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 detectors (FID and TD). Through the development of these gas chromatographic techniques, the determination of a solvent quality index and the characterization of coal and SRC by GC chromatogram of their products be achieved.

Summary of Progress

Separation techniques employing gas chromatography now have advanced to the stage where meaningful and reproducible separation of coal generated gases and coal liquids is possible. Gas analyses are being performed using a Porapak Q and R column and a thermal conductivity detector. An example of a typical gas chromatogram is shown in Figure 3.B.1. Coal liquids are separated by using methyl phenyl silicon columns and are detected in nanogram quantities by flame ionization detectors. Spiking with a known compound has been the only feasible method in the past for identification of coal liquids: that is, if a peak in the sample increases in height with addition of a known compound then the peak is said to be identified through spiking. In Figures 3.B.2 and 3.B.3 chromatograms of recycle and creosote oil are shown with the individual peaks that have been tentatively identified through spiking.

Using gas chromatography the molecular composition of untreated creosote oil and creosote oils treated under a hydrogen atmosphere and in the presence of various catalytic agents has been investigated. Using known weights of creosote oil samples, the oils were dissolved in a constant amount of tetrahydrofuran, and a given weight of an internal standard was added. A noticeable difference was observed when the peak heights of the major components of the untreated creosote oil were compared to those of the treated oil. The ratio of the peak area of the major components to that of the internal standard for each creosote oil normalized to the untreated creosote oil sample weight is shown in Table 3.B.1 (a corresponding

Figure 3.B.1.

Gas Chromatogram of Gas Evolved during an Autoclave Reaction

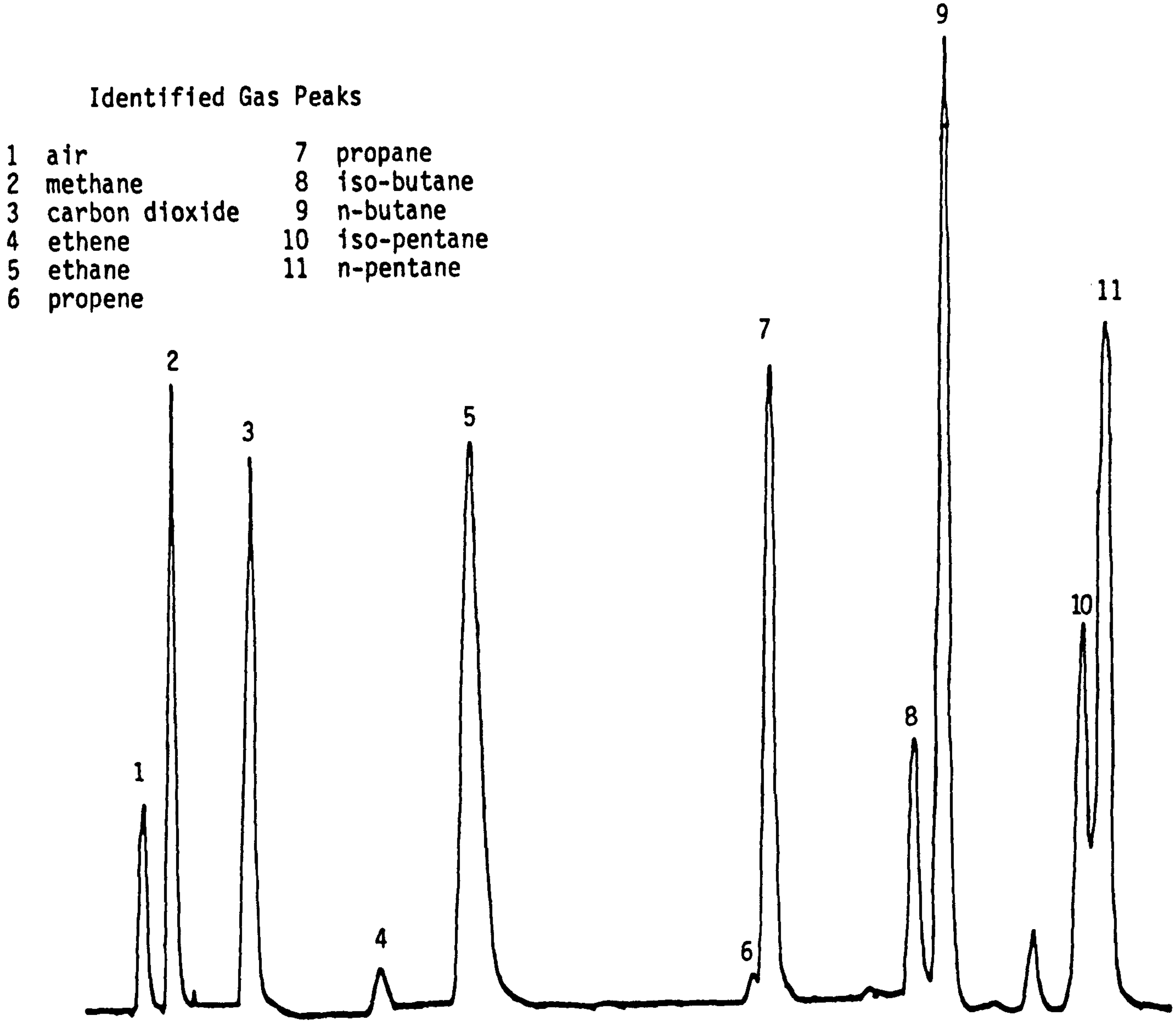
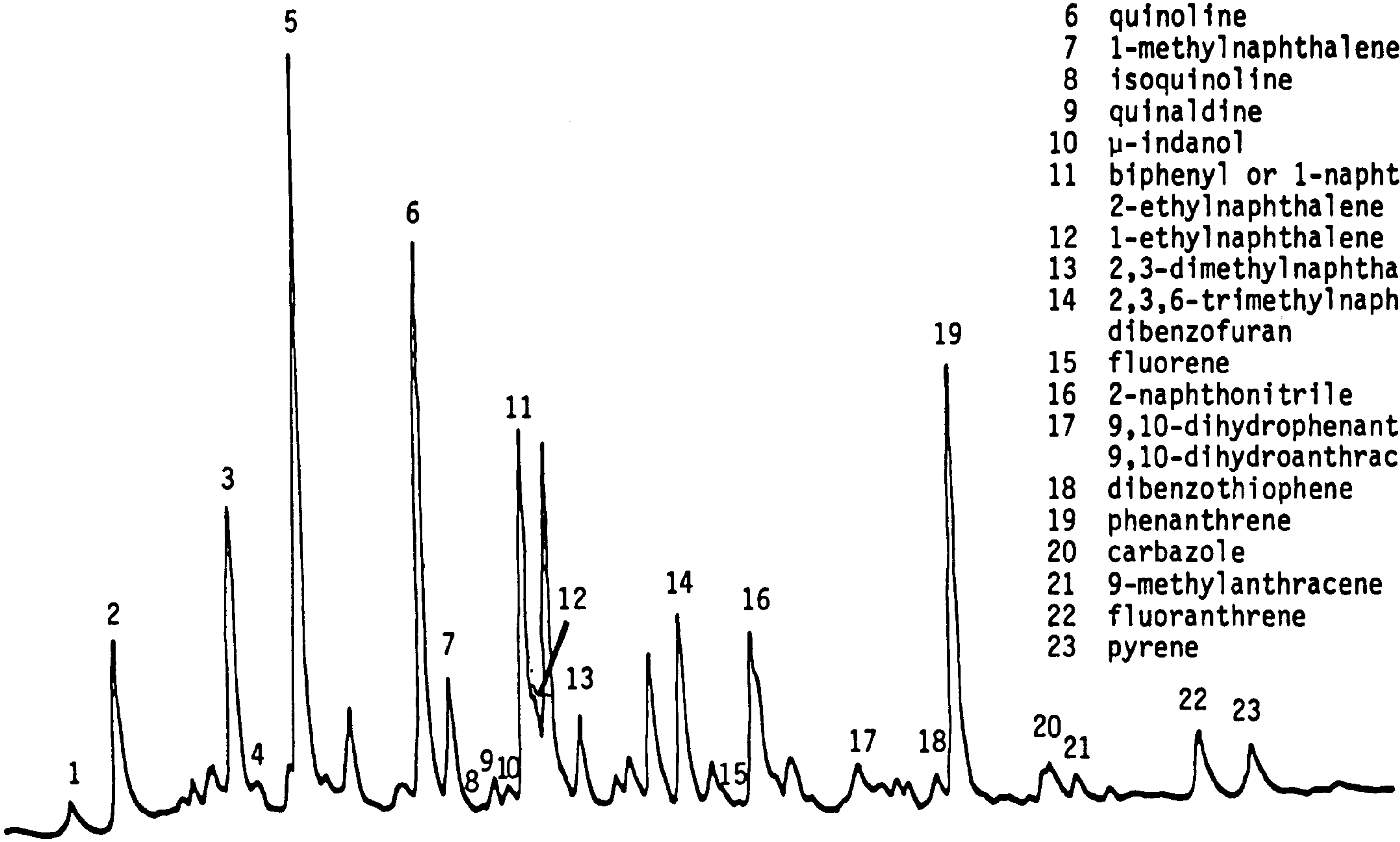


Figure 3.B.2.

Gas Chromatogram of Light Recycle Oil

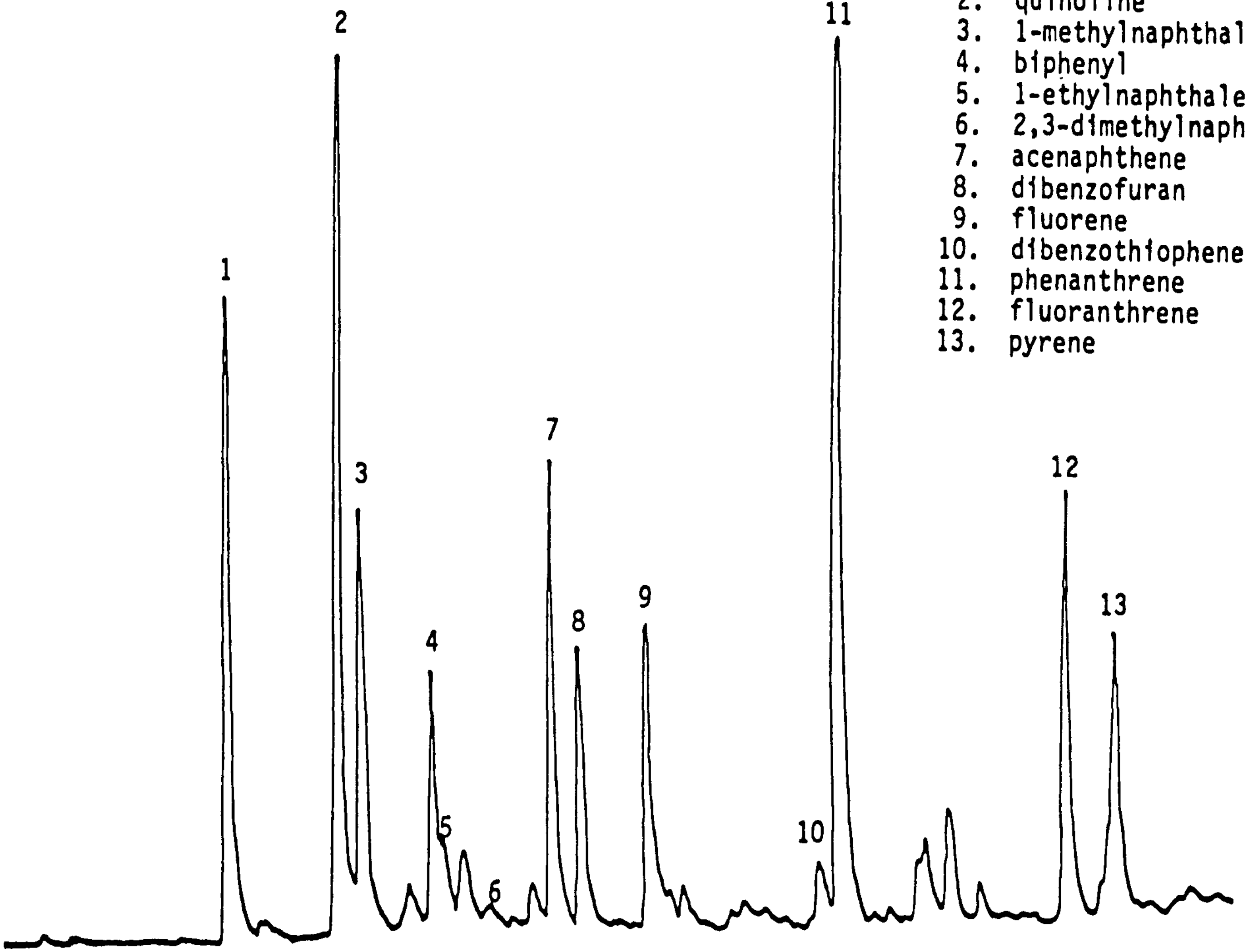


Tentatively Identified Peaks

1	decalin
2	indan
3	tetralin or 1,2 dihydronaphthalene
4	1,2-dimethylnaphthalene
5	naphthalene
6	quinoline
7	1-methylnaphthalene
8	isoquinoline
9	quinaldine
10	μ-indanol
11	biphenyl or 1-naphthonitrile or 2-ethylnaphthalene
12	1-ethylnaphthalene
13	2,3-dimethylnaphthalene
14	2,3,6-trimethylnaphthalene or dibenzofuran
15	fluorene
16	2-naphthonitrile
17	9,10-dihydrophenanthrene or 9,10-dihydroanthracene
18	dibenzothiophene
19	phenanthrene
20	carbazole
21	9-methylanthracene
22	fluoranthrene
23	pyrene

Figure 3.B.3.

Gas Chromatogram of Creosote Oil



Tentatively Identified Peaks:

1. naphthalene
2. quinoline
3. 1-methylnaphthalene
4. biphenyl
5. 1-ethylnaphthalene
6. 2,3-dimethylnaphthalene
7. acenaphthene
8. dibenzofuran
9. fluorene
10. dibenzothiophene
11. phenanthrene
12. fluoranthrene
13. pyrene

TABLE 3.B.1.

Comparison of Major G.C. Peaks of Untreated and Treated Creosote Oil

GC Peak	Original Creosote Oil Untreated	Creosote Oil Hydrogen No Catalyst	Creosote Oil Hydrogen Co Mo Al	Creosote Oil Hydrogen Fe, Pyrite	Creosote Oil Hydrogen S.R.C.Solids	Creosote Oil Hydrogen Coal Ash
3	------	.114 ± .039	.495 ± .022	.606 ± .026	.261 ± .032	.302 ± .041
4	1.727 ± .138	1.344 ± .094	.945 ± .047	1.158 ± .064	.961 ± .082	1.108 ± .084
7	1.492 ± .276	1.100 ± .053	1.074 ± .054	.976 ± .066	.807 ± .061	.952 ± .042
8	.553 ± .037	.394 ± .047	.530 ± .023	.383 ± .044	.229 ± .045	.444 ± .019
10	.279 ± .021	.407 ± .039	.759 ± .031	.504 ± .039	.440 ± .041	.651 ± .034
17	1.832 ± .146	.992 ± .066	1.403 ± .079	.399 ± .047	.511 ± .049	.849 ± .039
18	.896 ± .069	.866 ± .038	1.009 ± .084	.839 ± .056	.634 ± .059	.789 ± .059
20	.824 ± .067	.779 ± .025	.843 ± .073	.752 ± .045	.585 ± .046	.717 ± .019
28	.179 ± .027	.364 ± .059	.666 ± .071	.485 ± .040	.321 ± .042	.406 ± .027
29	3.016 ± .234	2.829 ± .050	2.659 ± .237	2.176 ± .116	2.016 ± .120	2.140 ± .166
37	1.558 ± .156	1.484 ± .052	1.616 ± .114	1.239 ± .059	.978 ± .061	1.040 ± .058
38	1.213 ± .156	1.065 ± .064	1.242 ± .068	.964 ± .035	.773 ± .037	.868 ± .066

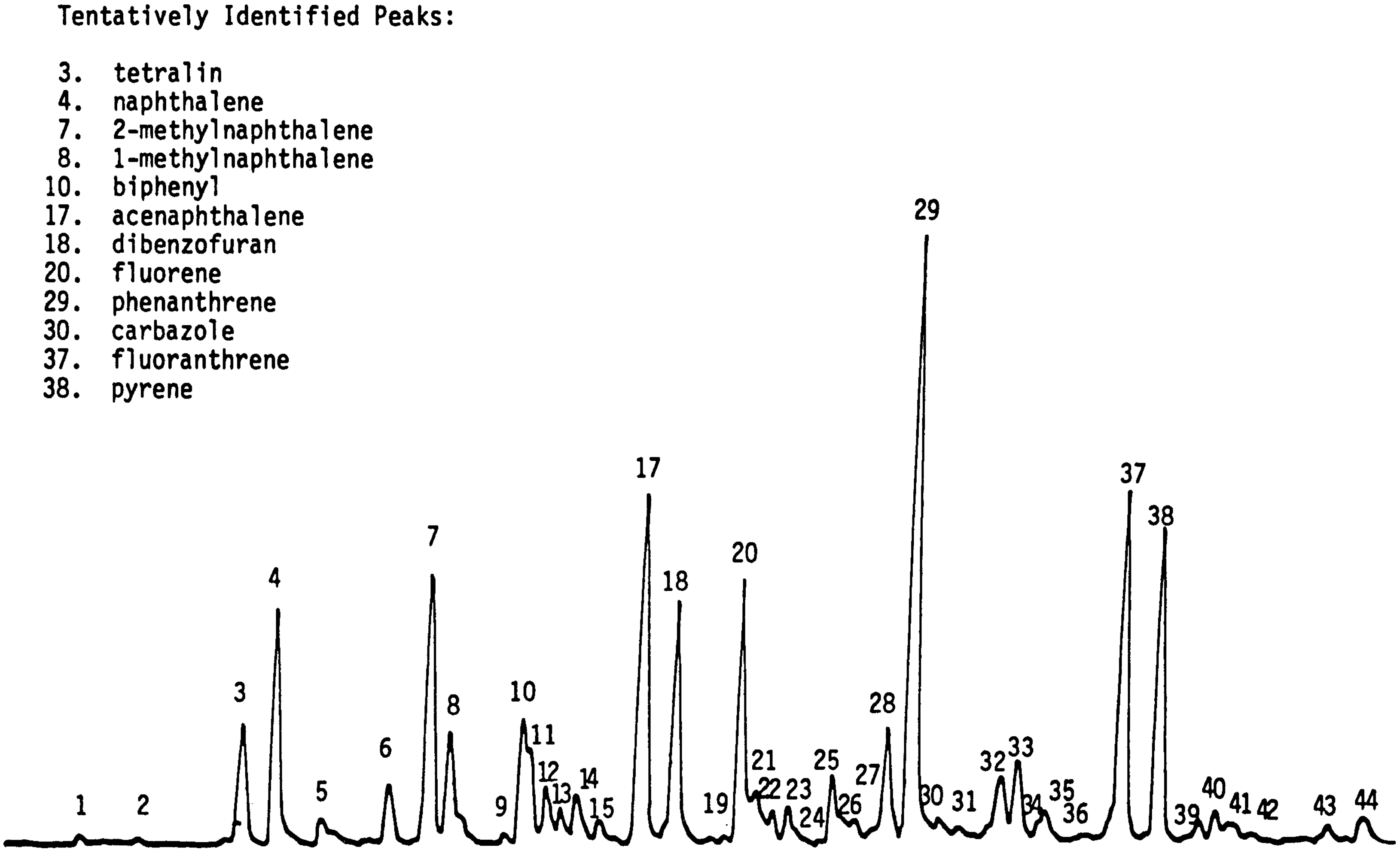
chromatogram is shown in Figure 3.B.4). A difference in the peak areas of the creosote oils can definitely be seen. In Table 3.B.2, a tentative identification of the major sample peaks is given along with a comparison of the increase or decrease of the major peaks of the treated oils with the peaks of the untreated oil. An examination of Tables 3.B.1 and 3.B.2 reveals several interesting phenomena. Since the untreated creosote oil contains no tetralin (a good hydrogen donor), any increase in the amount of this compound must be at the expense of some other (probably hydrogen deficient) species. This is most likely why there is a decrease in the naphthalenic content (peaks 4, 7, and 8); they are being hydrogenated to tetralin. Iron pyrite is particularly effective in producing tetralin, as seen in the first row of Table 3.B.2. Other hydrogen deficient condensed aromatics such as phenanthrene (peak 29) and pyrene (peak 38) also decrease, most likely because of hydrogenation to hydroaromatic donor species; however, we have not yet identified any of these hydrogenated species. The increase in biphenyl (peak 10) concentration is probably due to a cracking reaction, although this also has not yet been proven.

Although spiking is the commonly used method for identification of coal liquid components, inconclusive results often occur. Compounds used in spiking often overlap (having the same retention times) making it difficult to conclude which compound or mixture of compounds actually is present in the the sample. In order to perform meaningful kinetic studies involving coal liquids, absolute identification of the reaction solvent components and the subsequent reaction products will be necessary.

Catalysis experiments have employed gas chromatographic analyses in determining the effect of different catalysts upon the hydrogen donating capability of the solvent. The recycle oil from catalytically treated autoclave reaction mixtures has been analyzed by gas chromatography and the ratio of the peak heights of the resulting tetralin and naphthalene peaks have been determined.

Figure 3.B.4.

Gas Chromatogram of Hydrogenated Creosote Oil



Tentatively Identified Peaks:

3. tetralin
4. naphthalene
7. 2-methylnaphthalene
8. 1-methylnaphthalene
10. biphenyl
17. acenaphthalene
18. dibenzofuran
20. fluorene
29. phenanthrene
30. carbazole
37. fluoranthrene
38. pyrene

TABLE 3.B.2.

Comparison of Creosote Oils Reacted Under Hydrogen and Various Catalytic Conditions With Untreated Creosote Oil

I - Increase D - Decrease S - Same

Tentative Identification of G.C. Peak	Creosote Oil Hydrogen No Catalyst	Hydrogen Co-Mo-Al	Hydrogen Fe, Pyrite	Hydrogen SRC Solids	Hydrogen Coal Ash
3 Tetralin*	I	I	I	I	I
4 Naphthalene	D 22.2%	D 45.3%	D 32.9%	D 44.4%	D 35.8%
7 2-methyl-naphthalene	D 26.3%	D 28.0%	D 34.6%	D 45.9%	D 36.2%
8 1-methyl-Naphthalene	D 28.8%	S	D 30.8%	D 58.6%	D 19.7%
10 Biphenyl	I 45.9%	I 172.0%	I 80.6%	I 57.7%	I 133.3%
17 Acenaphthene	D 45.9%	D 23.4%	D 78.2%	D 72.1%	D 53.7%
18 Dibenzofuran	S	I 12.6%	S	D 29.2%	D 11.9%
20 Fluorene	S	S	D 8.7%	D 29.0%	D 12.9%
28 Unidentified	I 103.4%	I 272.0%	I 170.9%	I 79.3%	I 126.8%
29 Phenathrene	S	D 11.8%	D 27.9%	D 33.2%	D 29.0%
37 Unidentified	S	S	D 20.5%	D 37.2%	D 33.2%
38 Pyrene	D 12.2%	S	D 20.5%	D 36.3%	D 28.4%

*No tetralin is present in standard creosote oil

The tetralin to napthalene ratio provided an indication of the hydrogen donating capability of the solvent.

Gas chromatography has been used extensively to analyze reaction generated products and to monitor changes in concentration of model compounds during reaction. The effect of catalyst on the dehydrogenation of tetralin to napthalene was determined by ratioing their peak areas. Likewise, the hydrogenation of tetralin to naphthalene in dodecane under catalytic action was examined by comparison of the peak height of tetralin to the peak height of dodecane. The hydrodesulfurization of benzothiophene to ethyl benzene under Co-Mo-Al and Fe catalyst was verified by spiking and quantitated by peak area ratioing (10,11 and 12).

3.C. Fourier Transform Infrared Spectroscopy of Coal, SRC, and Coal Liquids

Objective

The objective of this work is to conduct infrared spectroscopic experiments: 1) to determine the chemical nature of solvent refined coals and their respective feed coals, 2) to determine the mineral constituents in coal, 3) to separate by matrix isolation unchromatographable coal liquid mixtures, and 4) to develop the technique of infrared emission of coal and SRC and determine its feasibility and benefit in coal research.

Summary of Progress

The ability to make process improvements in SRC and related coal liquefaction processes hinges upon obtaining a detailed analysis and characterization of SRC products and recycle solvents. Discerning the compositional variations in these coal derived products as a function of various mineral matter catalysts, process variables, and coal types is essential to improving the SRC process. Up to the present time considerable progress has been attained in the characterization of SRC recycle solvents by gas and liquid chromatography. However, the inability to postively identify any compound eluting from the chromatographs without an elaborate cold trapping/isolation procedure has until recently greatly hindered our progress in coal liquids characterization. To overcome this difficulty a Fourier transform infrared spectrometer with the capability of on-the-fly infrared analysis of gas chromatographic effluent has been purchased. Besides its on-the-fly capability, the Fourier transform spectrometer offers high sensitivity, signal averaging capabilities, and computer manipulation of data which makes infrared spectroscopy of routine samples, easy, and of difficult or minute samples, possible.

Complete installation of the Digilab FTS-10, System I, should be accomplished in February 1978. The spectrometer and data system have been installed for approximately five months; whereas, the GC/IR accessory and magnetic tape have been just received. Repeated instrument breakdown and lack of auxiliary data storage have plagued and impeded the progress of coal research on the spectrometer. In the meantime, training of personnel on the System I has proceeded. A senior investigator and a research associate have attended the instrument manufacturer's training school in September 1977. Training of more research personnel is currently in progress.

Auxiliary equipment has been ordered and installed to insure proper and trouble-free operation of the FTS 10 spectrometer. Air conditioning and dehumidifying equipment have been added to the laboratory to provide a proper environment for the FTIR instrument. One important effect of the air conditioning is to stabilize the temperature of the instrument so that small temperature induced variations in critical dimensions of the optical path do not occur. Another important aspect of the ambient air condition is the humidity. Excessive humidity makes it very difficult to keep the interior of the instrument purged sufficiently to eliminate absorption bands due to atmospheric water. Water absorbs very strongly in the infrared and failure to remove it or at least to keep its concentration constant between sample and reference can lead to major errors in the acquired spectrum.

The purging system used in single beam FTIR instruments is conventionally the use of nitrogen gas from the boil-off of liquid nitrogen. This gas is the driest and most hydrocarbon-free which can be conveniently obtained. Unfortunately, liquid nitrogen boil-off is rather expensive if used on a 24-hour basis. Accordingly, we have constructed an air-drying system which removes moisture from the ambient air which is then used as a purge gas. In addition to the spectral errors resulting from atmospheric composition fluctuations, serious hazard to the instrument results when no purge is used.

During the FTS 10 spectrometer installation, modification was made to the basic System I to make the instrument capable of infrared emission measurements. A special source assembly incorporating a selectable mirror for optionally accepting radiation from another direction was obtained as a gift from the instrument manufacturer. Auburn University's instrument technicians installed a new optical port at the proper position. It is not yet practical to measure infrared emission since a high sensitivity detector is needed. One of these detectors will be installed in January, 1978, as a portion of the gas chromatography accessory. Meanwhile, a very strong emission source has been used to verify that the optical portion of this modification is working correctly.

Other research efforts have included initiation of a design for a suitable link between the FTS 10 data system and Auburn University's IBM 370 computer. Such a link will enormously enhance the power of the FTIR as an analytical instrument since the library of stored reference spectra which can be maintained in the IBM's 370 memory is very large. This capability will enable immediate comparison of spectra of unknown materials with those of known compounds whose standard spectra are stored in the reference library. Again, the instrument manufacturer has made a gift of an accessory which makes this link possible. We will, however, need to write our own software for this search and comparison routine.

3.D. 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.

Summary of Progress

Investigation of trace metals in the SRC product and feed coals is being actively pursued in our laboratory using Energy Dispersive X-Ray Fluorescence (EDXRF). EDXRF yields both qualitative and quantitative information concerning trace metals. As a result of recent improvements in the design of solid state detectors for X-ray fluorescence, it is possible to do very rapid simultaneous quantitative analysis of a large number of elements.

The content of trace metals in SRC and in the feed coal is important for a variety of process, environmental, and utilization reasons. Certain metals, such as iron, catalyze the hydrogenation and hydrodesulfurization reactions that occur in the SRC process. If the SRC product is to be used to fire a gas turbine, trace metals such as calcium, sodium and vanadium present potential corrosion or fouling problems. When a feed coal has a high oxygen and a low sulfur content - like many western, sub-bituminous coals - calcium, a trace metal in the coal, tends to react with CO_2 formed in the SRC dissolver and then collect in the dissolver, eventually resulting in plugging problems. Trace metals such as arsenic in SRC product present potential environmental problems.

EDXRF has been directly applied to analyses on trace metals in SRC and their feed coals. Quantitative EDXRF analysis of sulfur and iron in a number of coals has been compared with two other analytical techniques, atomic absorption and Leco sulfur analysis, commonly used in our laboratory. In Table 3.D.1., the comparison is shown and in all cases EDXRF gave the best accuracy for the standards used.

With information of this type it is possible to make an element by element comparison of the various coals and SRC's and thereby to obtain insight into the influence of various elements upon SRC processability. On the other hand, Figure 3.D.1 gives an interesting correlation between ash content of moisture free coal and cumulative weight percent of 15 elements (Si, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, As, Br, and Sr) as determined by EDXRF. Least Squares analysis of the data gave a straight line correlation factor (r) of 0.92 at the 95% confidence level. An r value of 0.92 indicates a reasonable fit was obtained and that the resulting correlation can be used to compute the approximate percent ash in feed coals. Most importantly, these data demonstrate that the ash content of a feed coal can be approximated very rapidly in this manner (reference 28).

EDXRF is a rapid, semi-automated technique for trace metals analysis which does not required highly skilled operators. Unfortunately, our progress of the X-ray fluorescence determination of trace metals in coal and SRC has been impeded by instrumental and computer malfunctions and the lack of readily available coal and high quality metal standards. As soon as the computer hardware problems are solved, the EDXRF software controlling the quantitative manipulation of the raw data will be thoroughly examined to assure reproducible and reliable data.

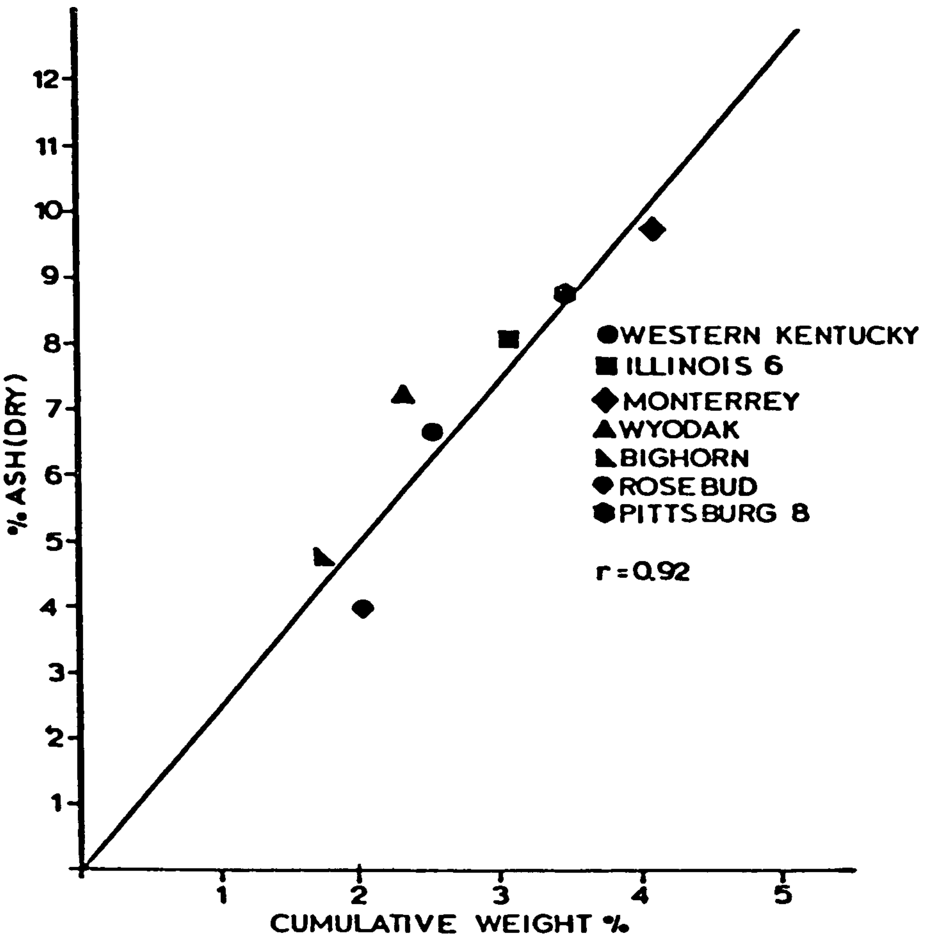
TABLE 3.D.1.

Comparison of EDXRF to Atomic Absorption and Leco Sulfur

Coal	XRF	A.A.	Leco	Known Value
Western Kentucky				
Fe	0.697	0.800		
S	2.24		2.56	
Wyodak				
Fe	0.265	0.247		
S	0.637		0.764	
Illinois #6				
Fe	0.629	0.526		
S	2.76		2.45	
Pittsburgh #8				
Fe	0.561	0.615		
S	2.22		2.87	
Monterey				
Fe	1.165	0.732		
S	3.07		3.24	
Rosebud				
Fe	0.466	0.270		
S	0.976		1.04	
Bighorn				
Fe	0.267	0.216		
S	0.582		0.620	
Standards				
Fe	0.1072	0.937		0.1000
S	1.995		2.22	2.02
S	0.301		0.278	0.31

Figure 3.D.1.

Correlation Between Ash Content of Moisture Free Coal and Cumulative Weight Percent of Fifteen Elements



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