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

Quarterly Report for the
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James A. Guin
Arthur R. Tarrer

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

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J. W. Prather
J. M. Lee
C. W. Curtis
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D. Garg
B. M. Adkison
T. E. Smith
D. N. Bush
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C. D. Hathaway
G. A. Thomas
R. D. Wilson
F. A. Brewer
L. C. Davis
W. Glass
D. M. Dyer
D. D. Adams

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ABSTRACT

This report describes work performed during the third quarter in a program designed to further understand and improve the Solvent Refined Coal and related liquefaction processes. Considerable progress was made during the quarter as four papers were finished for presentation at the Chicago meeting of the ACS Fuel Chemistry Division in August, 1977. These papers give the results of a Coulter Counter particle size analysis method for the SRC process, the effects of mineral matter on the hydrogenation/desulfurization reactions in the SRC process, a comprehensive model for the continuous SRC reactor/dissolver, and an X-ray fluorescence technique for SRC analysis. Other results include a detailed study of the effect of initial particle size on four coals used in the SRC process, an evaluation of additional coals in the visual reactor for SRC processability, experimental data showing the viscosity peaks present in the SRC preheater/dissolver and solubility of CO_2 and CH_4 in SRC recycle solvent.

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

EXECUTIVE SUMMARY

As the milestone chart indicates, the program is on schedule in all tasks.

Major Accomplishments this Quarter:

1. Preparation of four papers for the August 1977 meeting of the ACS Fuel Chemistry Division (see Appendix).
2. A detailed study of the effect and importance of initial particle size on four coals used in the SRC process.
3. Experimental data for the viscosity peaks occurring in the preheater/dissolver of the SRC process for two types of solvents.
4. Solubility data for CO_2 and CH_4 in SRC recycle solvent at process temperatures and pressures.

Papers and Presentations

This quarter four papers were finished for presentation at the ACS Liquid Fuels from Coal Symposium to be held in Chicago in August, 1977. These are:

1. "A Dispersion Reaction Model for the Solvent Refined Coal Process"
2. "The Selectivity of Coal Minerals as Catalysts in Liquefaction"
3. "X-Ray Emission Fluorescence of Trace Metals in Solvent Refined Coal"
4. "Particle Size Analysis in the SRC Process by Coulter Counter"

They are contained in the Appendix of this report.

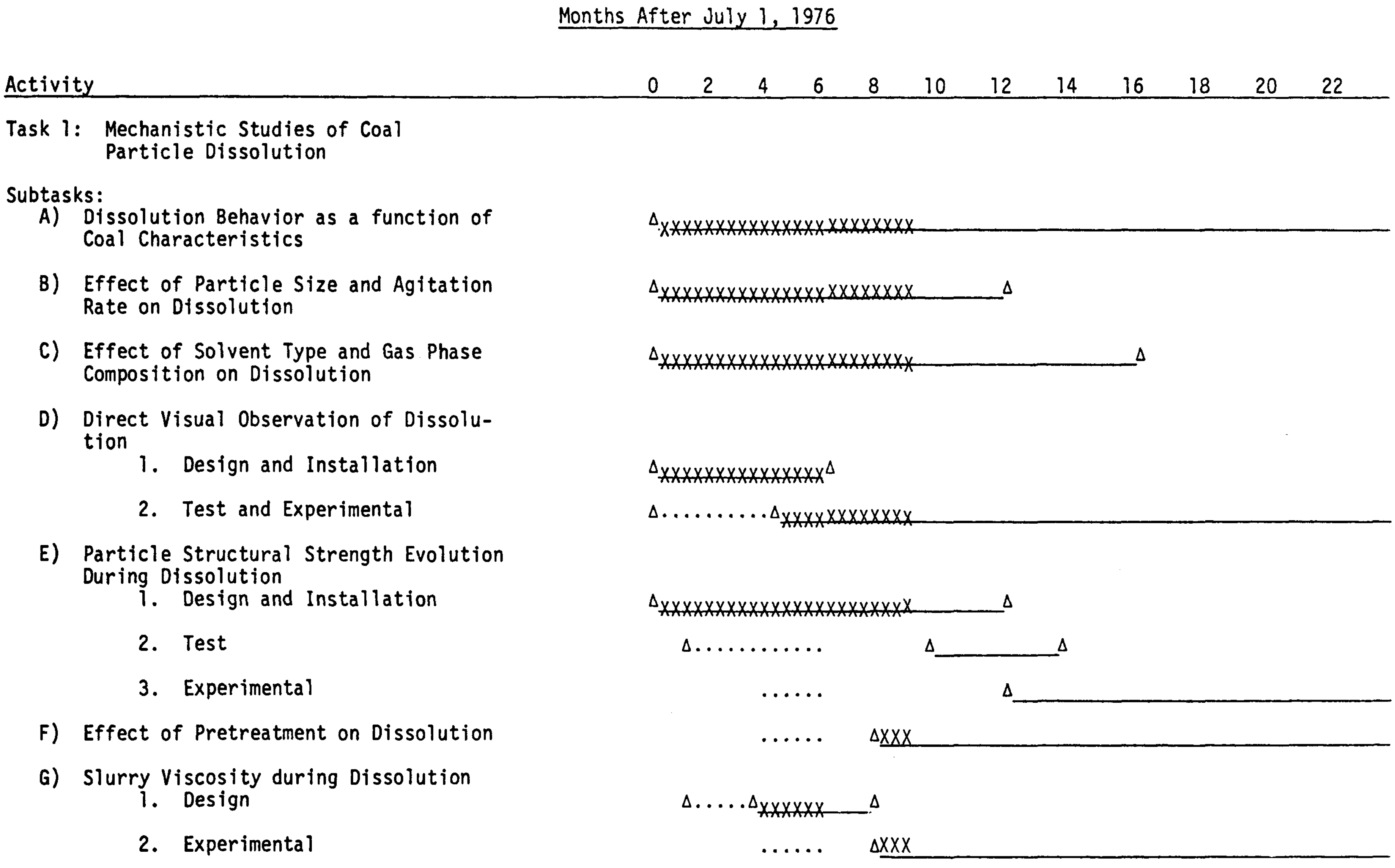


Figure 1. Work Schedule

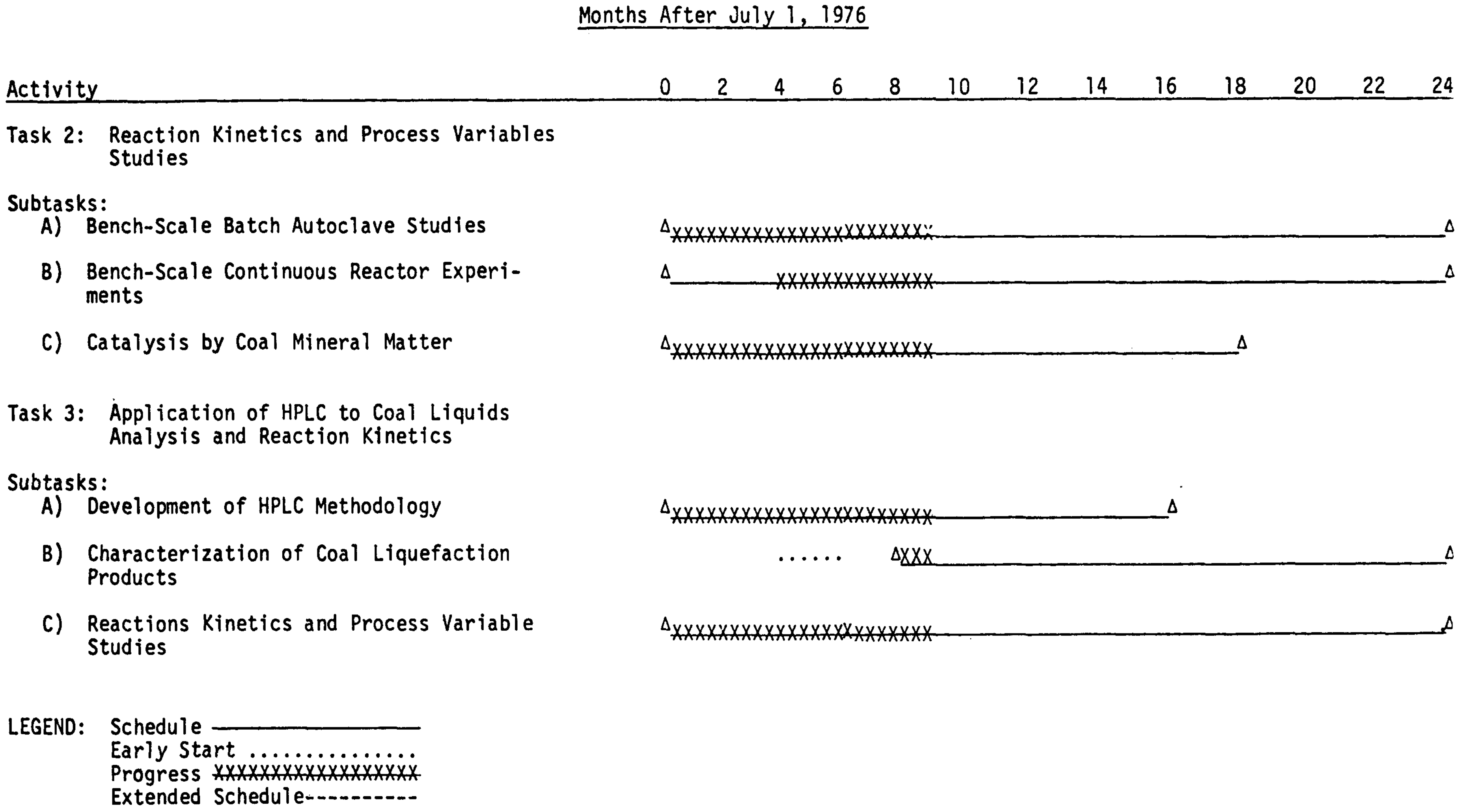


Figure 1 (continued)

TECHNICAL PROGRESS BY TASKS

Task 1. Mechanistic Studies of Coal Particle Dissolution

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

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

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

Progress: Particle size measurements have now been made for several types of coals during dissolution in the SRC process. These coal types include Amax, Western Kentucky, Pittsburgh, and Illinois Montery Coal, all obtained from Wilsonville. The results of this work are presented in the paper "Particle Size Analysis in the SRC Process by Coulter Counter" contained in the Appendix. This paper is to be presented at the ACS Fuel Chemistry Division Meeting in Chicago in August, 1977.

Planned Work: We shall continue to use the Coulter Counter technique to monitor evolutionary changes in particle size distribution of residual coal particles under different reaction conditions. These particle size data shall be correlated, in turn, with filterability data collected at the Wilsonville SRC pilot plant to determine if on-line monitoring of particle size by electronic techniques is a feasible possibility.

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

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

Progress: This quarter a series of experiments was performed, using four coal types, to assess the effect of particle size upon dissolution rate in the SRC process.

Materials Used

Four samples of different types of lump coal, weighing 6-7 pounds each, were furnished by the Wilsonville SRC Pilot Plant. The four types were Amax, Pittsburgh No. 8, Illinois No. 6, and a mixture of Kentucky No. 9 and No. 14 Coal. Their analyses of these types of coal are shown in Table 1.B.1. The solvent used was practical grade tetralin (Eastman Kodak Company). Nitrogen gas tanks were supplied by Liquid Air, Inc.

Experimental Apparatus

A 300 cc magnedrive stainless steel autoclave from Autoclave Engineers, Inc., was used.

Experimental Procedure

The lump coal was crushed and sized by screening using a Ro-Tap Testing Sieve Shaker (The W. S. Tyler Company). Several fractions were selected for use. They were dried overnight at 100°C and 25 inches Hg vacuum. It was observed that for the same type of coal each size fraction had a different original percent ash. For example, the two fractions -7 +8 mesh and -200 +270 mesh of Kentucky

TABLE 1.B.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%

No. 9/14 coal had an original percent ash of 7.83 and 18.90, respectively. To overcome this problem, the following procedure was used. For each type of coal, a large mesh size fraction was used for at least one autoclave run and, to demonstrate good reproducibility of the results, a duplicate run was made. The remainder of the large mesh size fraction was then ground using a micro mill followed by a mortar and pestle until the entire fraction passed a certain small mesh size. The small mesh size particles were then used to make duplicate autoclave runs. This method provided an adequate means for producing various mesh size fractions with the same ash content and chemical composition.

For each run, 30 grams of coal and 90 grams of tetralin were mixed then poured into the autoclave. The reaction conditions and the procedure for sealing and heating the autoclave are given in detail by Stino(1977). After the reaction time was over (15 minutes) no liquid samples were withdrawn; instead, the autoclave was quenched and the electric furnace was removed. It took about 2 minutes for the autoclave to cool down to 300°C. When the temperature had reached 30°C (about 40-60 minutes), the autoclave was vented and opened. The entire contents were then removed by suction into a clean vacuum flask.

Cresol extraction and ash analysis were carried out on the reaction mixture liquid samples. It should be noted here that during cresol extraction, Amax, Illinois No. 6, and Kentucky No. 9/14 reaction mixture liquid samples were filtered through Whatman No. 50 paper but Pittsburgh No. 8 reaction mixture liquid samples were extremely difficult to filter through those papers. Whatman

No. 54 filter papers, which filters 98% of 20-25 micron particles at a rapid flow rate, were used instead. It seems that during the liquefaction of Pittsburgh No. 8 coal, disintegration appears to produce smaller particle sizes than the other three types of coal used here.

Figure 1.B.1. shows the variation in temperature during heat-up, reaction, and cool-down for a typical autoclave run where Amax coal was used.

Results and Discussion

The experimental results are presented in Tables 1.B.2.-1.B.5. Each table shows the initial particle size, the fraction ash in dry feed coal, the fraction ash in cresol insoluble residue, and the percent yield based on ash content of the cresol insoluble residue.

From these results, one can notice that the percent yield was not affected 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.

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 2 grams of paraffin oil were absorbed. The particles were then mixed with 90 grams tetralin and the mixture was used to make a run similar to those which have been performed earlier in this chapter. The resulting yield was found to be the same as that obtained when the

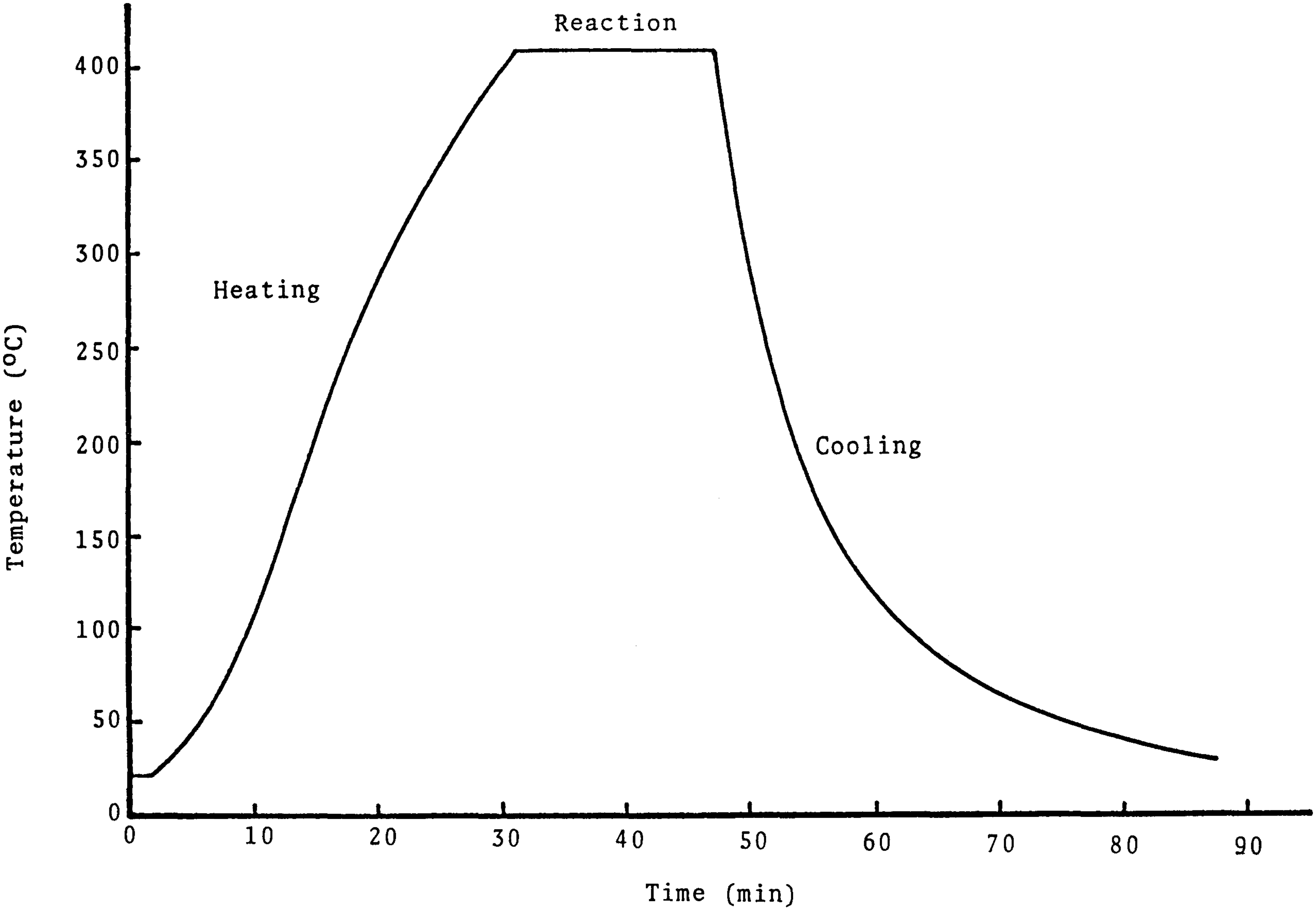


FIGURE 1.B.1 TEMPERATURE VARIATION FOR A TYPICAL AUTOCLAVE RUN WHERE AMAX COAL WAS USED

TABLE 1.B.2

EFFECT OF INITIAL PARTICLE SIZE OF AMAX COAL ON YIELD

Initial Particle Size (mesh)	Fraction Ash in Dry Feed Coal	Fraction Ash in Cresol Insoluble Residue	Yield* (%)
-3½ +4	0.0698	0.1766	65.73
-3½ +4	0.0698	0.1753	65.42
-150	0.0698	0.1704	64.17
-150	0.0698	0.1648	62.66

*Based on 8% mineral matter in dry feed coal.

TABLE 1.B.3

EFFECT OF INITIAL PARTICLE SIZE OF PITTSBURGH NO. 8 COAL ON YIELD

Initial Particle Size (mesh)	Fraction Ash in Dry Feed Coal	Fraction Ash in Cresol Insoluble Residue	Yield* (%)
-3½ +4	0.0785	0.3839	87.42
-3½ +4	0.0785	0.3682	86.46
-150	0.0785	0.3727	86.74
-150	0.0785	0.3551	85.60

*Based on 9% mineral matter in dry feed coal.

TABLE 1.B.4

EFFECT OF INITIAL PARTICLE SIZE OF ILLINOIS NO. 6 COAL ON YIELD

Initial Particle Size (mesh)	Fraction Ash in Dry Feed Coal	Fraction Ash in Cresol Insoluble Residue	Yield* (%)
-3½ +4	0.1033	0.3834	83.02
-3½ +4	0.1033	0.3621	81.22
-150	0.1033	0.3745	82.29
-150	0.1033	0.3570	80.76

*Based on 12% mineral matter in dry feed coal.

TABLE 1.B.5

EFFECT OF INITIAL PARTICLE SIZE OF KENTUCKY NO. 9/14 COAL ON YIELD

Initial Particle Size (mesh)	Fraction Ash in Dry Feed Coal	Fraction Ash in Cresol Insoluble Residue	Yield* (%)
-7 +8	0.0783	0.3608	88.89
-7 +8	0.0783	0.3559	88.64
-200	0.0783	0.3332	86.93
-200	0.0783	0.3329	86.91

*Based on 12% mineral matter in dry feed coal.

coal particles were not soaked in paraffin oil. It is believed that during the heat-up period, while the tetralin-coal slurry is 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 further evidence that intraparticle diffusion and absorption mechanisms are not significant variables in the SRC process. Thus the process design can proceed without consideration of these phenomenon. Furthermore, a substantial economic savings in grinding cost can be realized by using larger coal feed particles without a decrease in SRC yield.

Planned Work: Research to assess the effect of coal particle size upon the rate and extent of coal dissolution shall be continued. A continued evaluation of agitation rate and particle size in all liquefaction experiments shall be made.

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

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

Progress: As shown in the previous quarterly, there is general agreement that the effectiveness of a solvent for coal liquefaction depends, in large measure, upon its ability to donote 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 heteroatom species. The effectiveness of this "artificial" solvent will be determined under a variety of conditions. In paricular the tetralin/napthalene ratio should yield information about the amount of hydrogen donated. Also the new FTIR instrument, just received under the contract modification, should be very helpful in determining liquid compositions.

Planned Work: Work will be continued toward establishing a "quality" index for SRC type solvents and an index of their effectiveness under various liquefaction conditions.

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

Objective: The objective of this task is to design, construct, and employ a sight glass aparatus suitable for direct visual observation of particle dissolution at temperatures to a maximum of 450°C and pressures to 1000 psig.

Progress: Several runs were carried out to evaluate the liquefaction suitability for Emery coal. Run conditions were 650 psig at 400°C and solvents were either tetralin or SRC recycle solvent. The results of this evaluation were as follows:

Tetralin Runs - Coal Breakdown Characteristics and Observations:

1. Encountered swelling of the coal particle in the capillary tube at about 300°C.
2. After swelling there was a slight discoloration of the solvent indicating slight superficial breakdown or reaction of the coal. This breakdown or reaction was very slight and occured around 350°C.
3. When residence time in the reactor was completed a hard intact coal particle was left behind.
4. When the penetrator (physical crush testor)(see next subtask) was applied to the remaining coal particle, very little crushing occured. Many times the reactor could not be flushed because of lack of coal dissolution.

5. The heat up time and residence time were varied both by lengthening and shortening and the results were similar. The diffcult flushing and no breakdown of the coal was noted.
6. With tetralin as solvent Emery coal was the most difficult to process in all criteria mentioned above as compared to Kentucky, Amax, Pittsburgh, and Illinois coals.

Recycle Solvent Runs - Observations:

1. Coal swells at about 365°C to fill the tube.
2. Some superficial reaction of the coal at 400°C. Not significant compared to softer coals.
3. When residence time was completed there was usually a very hard single intact coal particle in reaction chamber.
4. When penetrator (next subtask) was applied to the remaining coal particle (after completed residence time) the coal would not breakdown with very strong pressure.
5. Heat up time and residence time were varied by lengthening and shortening; this produced no difference in processing.
6. With recycle solvent this coal was extremely difficult to process as compared to others.

Emery Coal - Conclusions From Above Observations:

This coal was the most difficult to dissolve coal that has been processed in the visual reactor since even the extreme physical force of the penetrator could not break down the coal particle. The second most difficult coal, from the Amax mine, would show some signs of breakdown as the penetrator was applied and thus could be flushed from reactor, but the Emery coal would not break down at all. Thus it was concluded that the Emery coal would not be suitable for liquefaction processing.

Planned Work: The transparent wall microreactor will remain an integral part of our coal evaluation procedures and shall be utilized whenever it is advantageous. Efforts shall be continued to improve upon its design and experimental techniques employed in its utilization.

1.E. Particle Structural Strength Evolution During Dissolution

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

Progress: As shown in the previous section (1.D.), the high temperature penetrometer is a valuable tool in determining the liquefaction processability of various coals. In addition to the Emery coal tested in subtask 1.D., a series of experiments was performed here to examine the structural strength of Kentucky 9/14 coal under liquefaction processing conditions. The results of these experiments were as follows:

300°C 600 psig

Solvent showed no significant discoloration. No apparent reaction.

325°C 600 psig

Solvent showed no significant discoloration. No apparent reaction. However, when penetrator was applied, coal was softening, almost tarlike.

350°C 600 psig

Same as before except coal very soft and mushy.

360°C 600 psig

Solvent very dark, much coal dissolution, soft coal flushed easily from reactor. (3 runs made)

360°C 650 psig

More gradual dissolution of the coal it "eroded" away leaving small residue.

360°C 700 psig

Coal "eroded" away but the reaction chamber burst, causing emergency shutdown.

From the above observations, several conclusions may be drawn. First, the Kentucky coal is a much more viable candidate for liquefaction than the Emery coal tested in subtask 1.D. At low pressure and 360°C, the Kentucky coal shows definite signs of softening. At higher pressures this softness is accompanied by a more pronounced erosion of the coal particle. Although some solvent discoloration occurs at lower temperatures (around 325°C), the consistency of the coal particle under penetrometer application seems to be a better indication of liquefaction suitability.

Planned Work: Developmental work shall continue using the penetrometer to characterize the liquefaction suitability of various coal/solvent systems for SRC processing.

1.F. Effect of Pretreatment on Dissolution Behavior

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

Progress: During the quarter several tubing bomb experiments were performed to assess the effect of oxidation upon the rate and extent of coal dissolution. Samples of Kentucky 9/14 coal were air-oxidized at 175°C for varying periods of time. The oxidized samples were then reacted 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.F.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 (1976) and the above explanation was offered by him for the decreased yields.

It was mentioned in the previous quarterly report that if the coal is simply dry-ground -- as is standard practice at the Wilsonville SRC pilot plant -- most of the developed 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, this suggests that, on the other hand, if the coal is ground in the solvent in which the process of extraction would be done, the oxidation could be prevented, thus, increasing the yield.

<u>Planned Work</u>: Chemical pretreatments specifically designed to remove sulfur and mineral matter as in the Meyers and Battelle processes and the extraction of coal with acid and alkali will be conducted and the enhancement and/or retardation of these pretreatments on the dissolution yield and sulfur removal will be assessed.

1.G. Slurry Viscosity During Particle Dissolution

Objective: The objective of this subtask is to investigate slurry viscosity

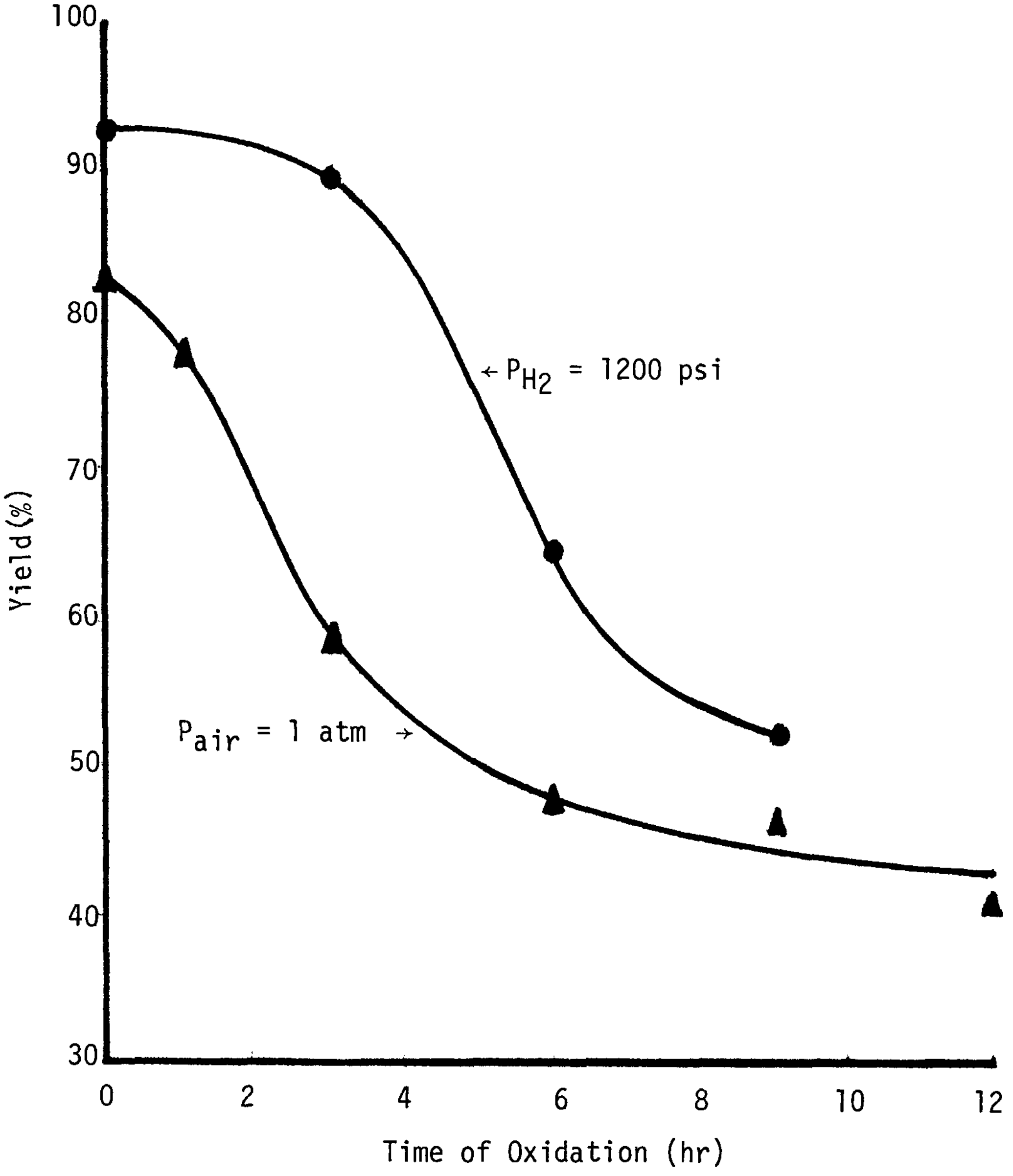


FIGURE 1.F.1. EFFECT OF OXIDATION ON DISSOLUTION (2:1 tetralin/coal, 30 min, 415°C coal particle size -170+325 mesh)

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

Progress: Several experiments were performed during this quarter to determine the viscosity of the coal/solvent slurry during the early dissolution period. Two different solvent, recycle oil and cresote oil, were studied. Kentucky 9/14 coal (80% - 325 mesh) was used. The coal was dried in a vacuum oven overnight at 110°C before it was used.

A coal slurry (3:1 solvent to coal ratio by weight) was loaded into a 1 liter magnedrive autoclave. The autoclave was purged two or three times with nitrogen gas to remove all air. It was then pressurized to 250 psig with nitrogen. After testing for the absence of leakage, the sample was heated. When the required temperature was reached, it was maintained for 5 minutes. The autoclave then was quenched to about 90°C and a gas sample was then taken for gas chromatograph analysis. A liquid sample was obtained for viscosity determination. The same procedure was repeated for different temperatures and different solvents.

Since it was not possible to measure the variation of viscosity of the coal slurry in-situ at the actual conditions of the autoclave, an alternative approach was used. A series of autoclave runs was made at various autoclave temperatures (say 100,200,250°C etc.). The viscosities of the liquid samples obtained from these runs were measured at lower temperatures using a variable speed Synchro-lectric Brookfield Viscometer. Figures 1.G.1a and 1.G.1b show the variation of viscosity with temperature with the autoclave operating temperature

Fig. 1.G.1a

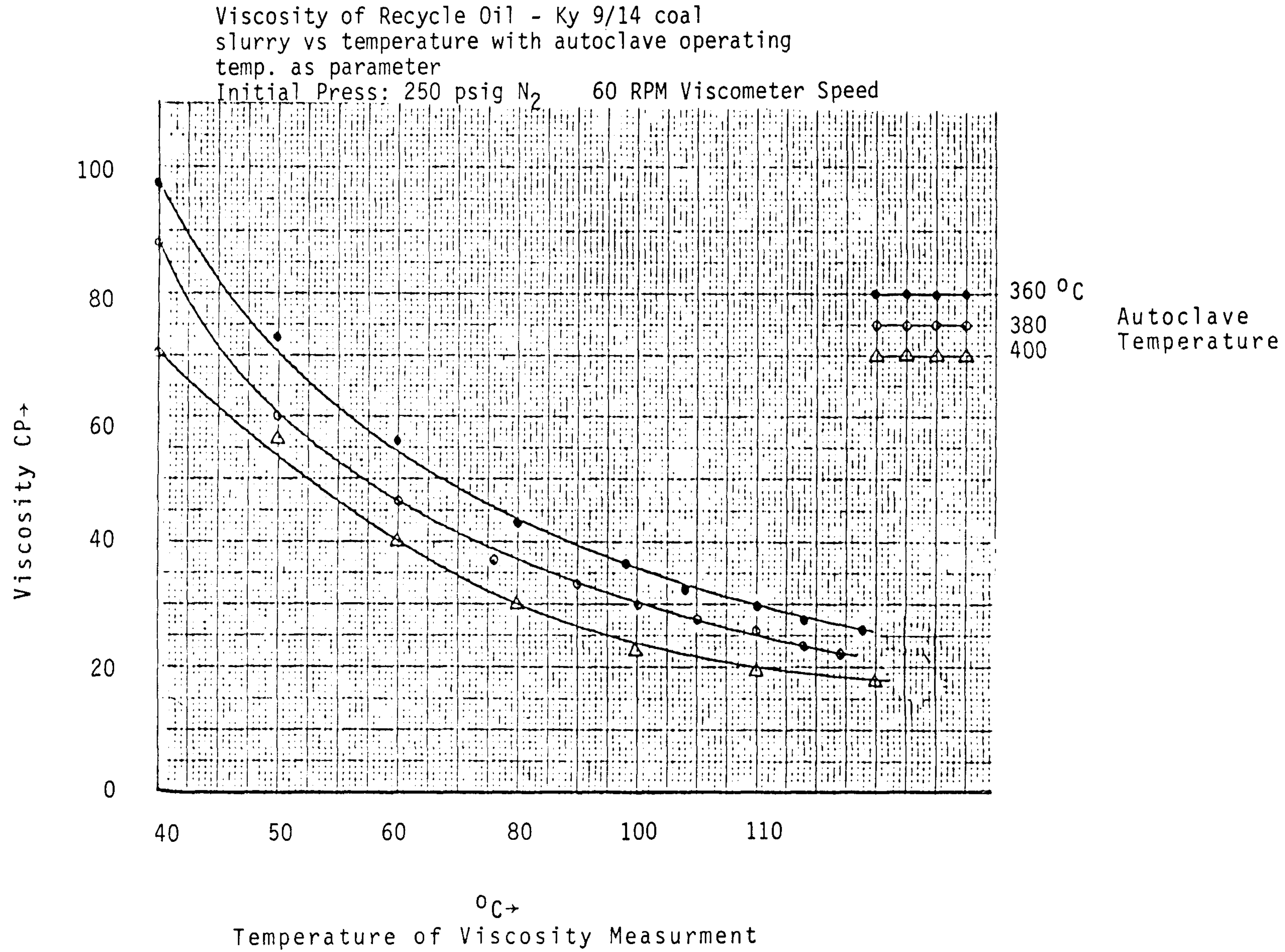
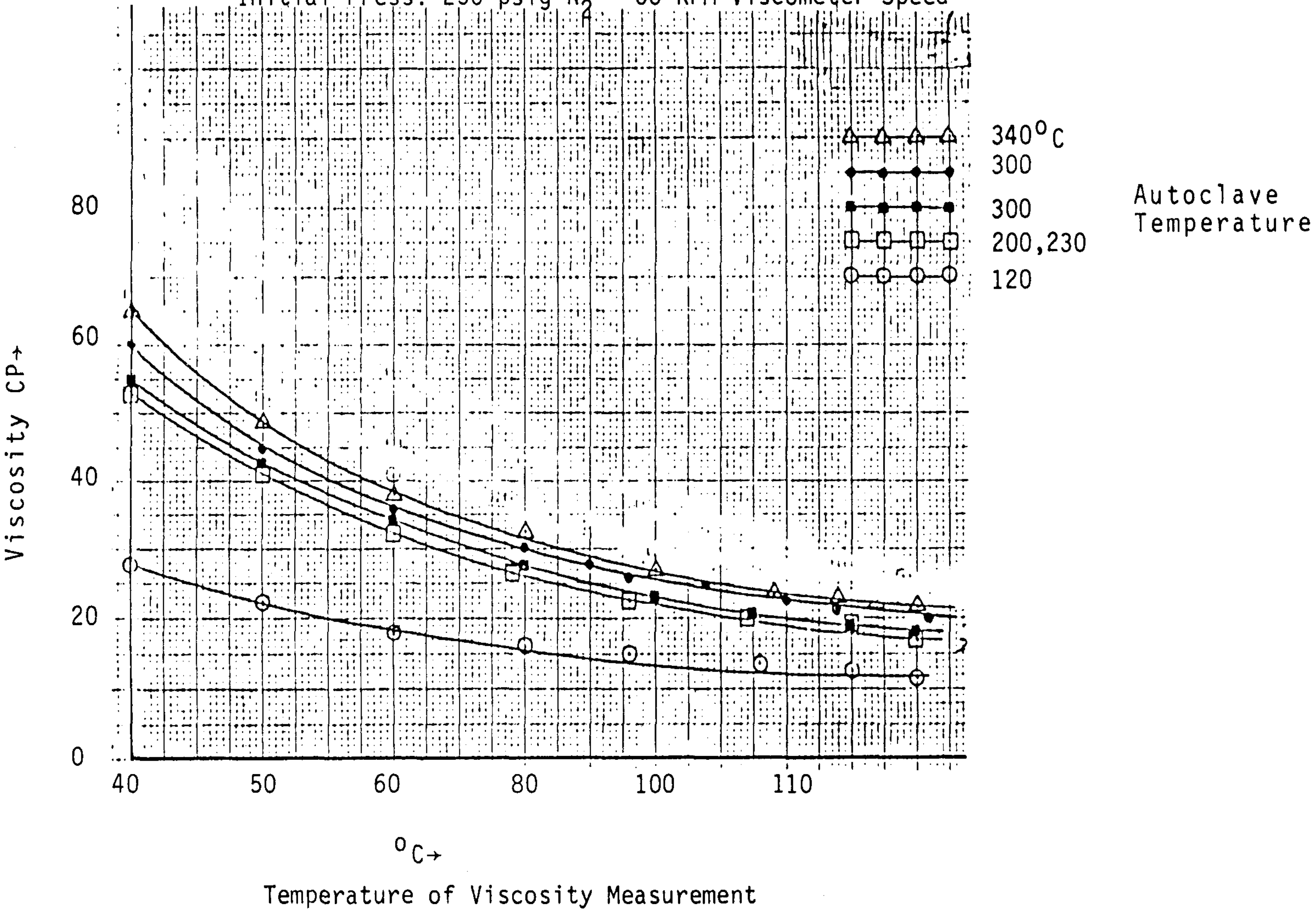

Viscosity of Recycle Oil - Ky 9/14 coal
slurry vs temperature with autoclave operating
temp. as parameter
Initial Press: 250 psig N2 60 RPM Viscometer Speed
Viscosity CP→
100
80
60
40
20
0
40
50
60
80
100
110
°C→
Temperature of Viscosity Measurment
360 °C
380
400
Autoclave
Temperature

Figure 1.G.1b

Viscosity of Recycle Oil - Ky 9/14 coal
slurry vs temperature with autoclave operating
temp. as parameter
Initial Press: 250 psig N_2 60 RPM Viscometer Speed



as an additional parameter. From Figures 1.G.1a and 1.G.1b we observe that the autoclave mixture reacted at 360°C has the highest viscosity of those samples run, thus indicating a viscosity peak in the heated slurry around 360°C with the recycle oil. A cross plot of the data as pictured in Figure 1.G.2 reveals a viscosity peak for the Kentucky 9/14 coal-recycle solvent system at about 360°C. Similar plots for the same coal with a cresote oil solvent are shown in Figures 1.G.3a, 1.G.3b, and 1.G.4. It is extremely interesting to note that a much sharper viscosity peak occurs with cresote oil and at a much higher temperature of about 390°C, as contrasted with 360°C for the recycle solvent system. One explanation for this is that the recycle solvent, with more donatable hydrogen than the creosote oil, is able to depolymerize the coal into smaller fragments much more readily and these smaller fragments result in a less viscous solution. The fact that the phenomenon occurs at a lower temperature with recycle solvent indicates the increased reactivity of this solvent as opposed to cresote oil.

In order to detect whether the reacted coal slurry behaves as an Newtonian or non-Newtonian fluid, we measured viscosities of the slurry at different speeds of spindle rotation. The nature of the viscometer dial reading (proportional to viscosity) was found to increase with decreasing speed of rotation of the spindle. This indicates a dependence of the viscosity on the rate of shear, which is characteristic of pseudo-plastic behavior. Figures 1.G.5 and 1.G.6 represent the changes in viscosity at two different speeds of spindle rotation for recycle oil - coal and cresote oil - coal slurries, respectively. As reported in the last report, untreated coal-oil slurries behave as Newtonian fluids, but as found this quarter, the

Fig. 1.G.2

Recycle Oil - Ky 9/14 Sample viscosity measured at various temperatures vs autoclave treatment temperature. Spindle Speed: 60 RPM 250 psig N_2

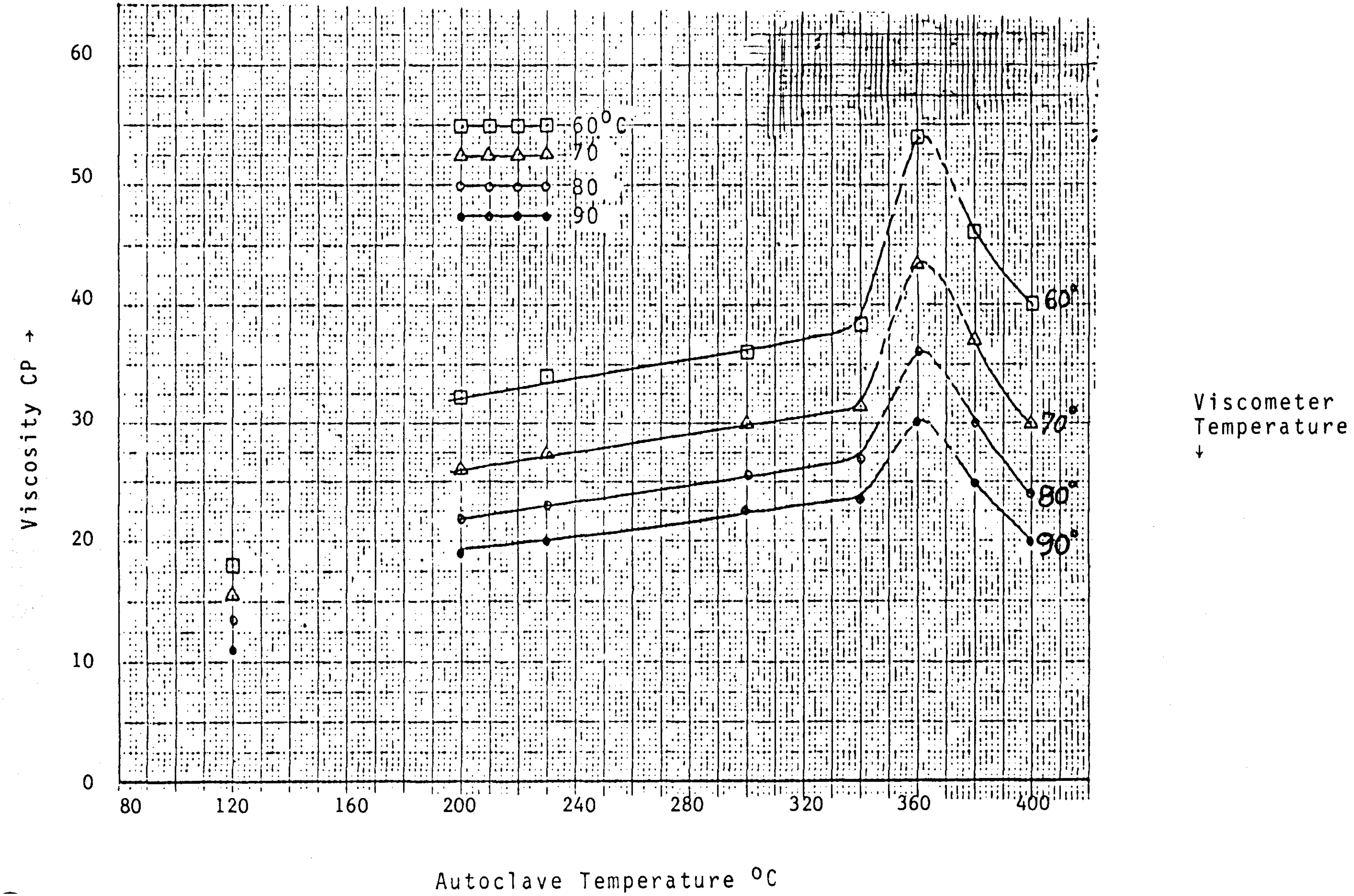


Figure 1.G.3a

Viscosity of Cresote Oil
Ky 9/14 coal slurry vs
temperature with autoclave
operating temp. as parameter
Initial press. 250 psig N_2
60 RPM Spindle Speed

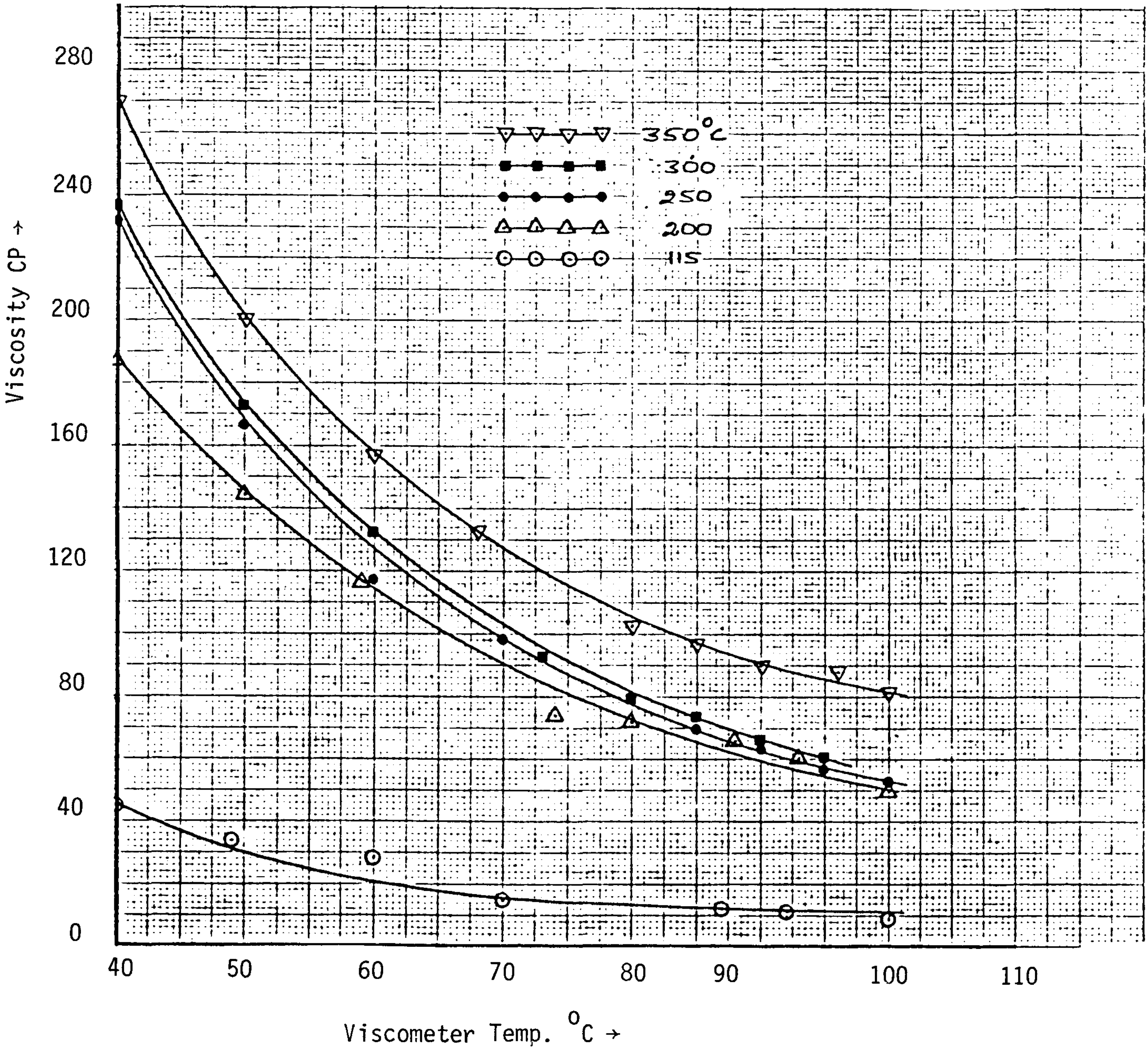
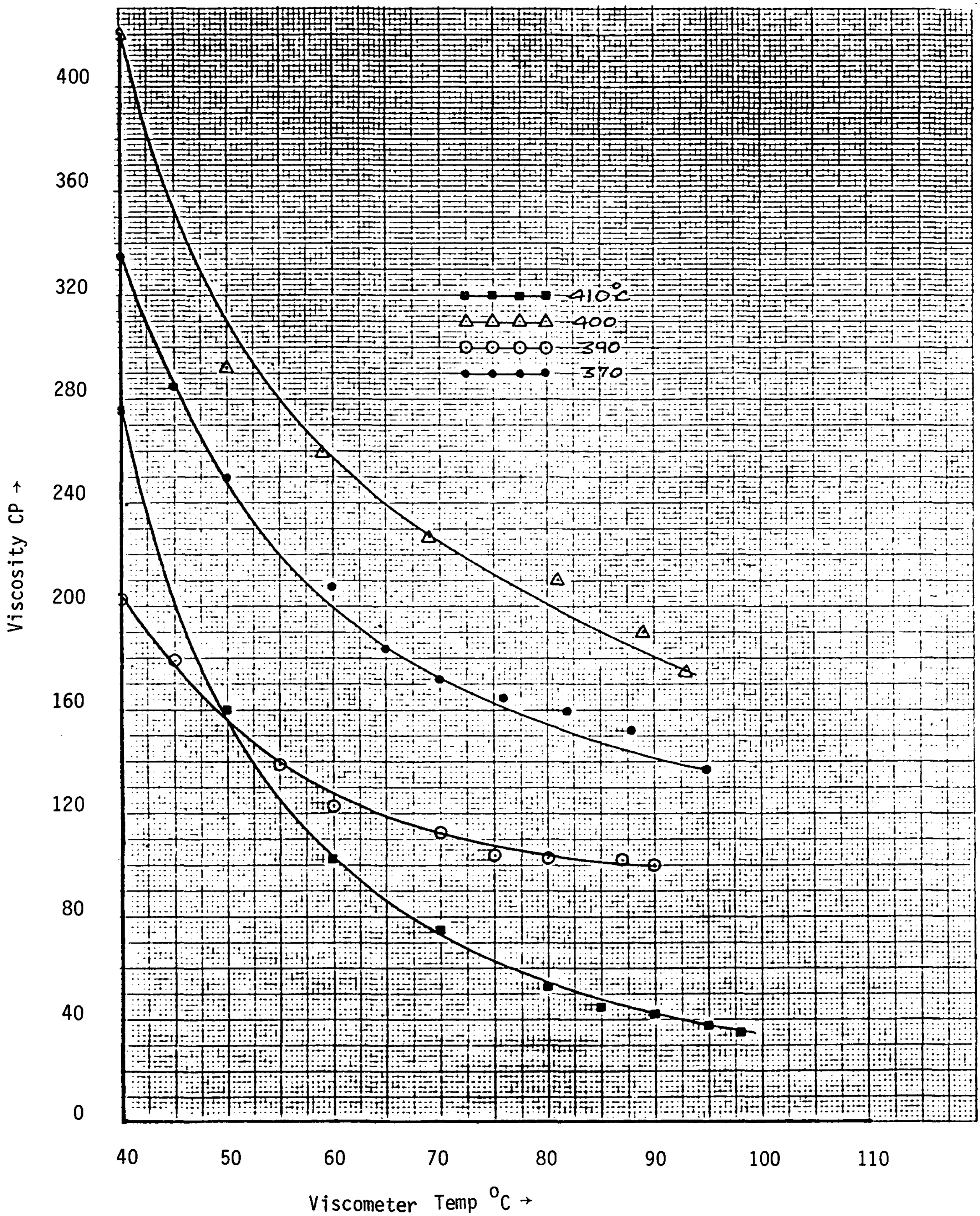


Figure 1.G.3b

Viscosity of Cresote Oil - Ky 9/14 coal slurry vs temp.
with autoclave operating temp. as parameter
Initial press: 250 psig N_2 60 RPM Spindle Speed



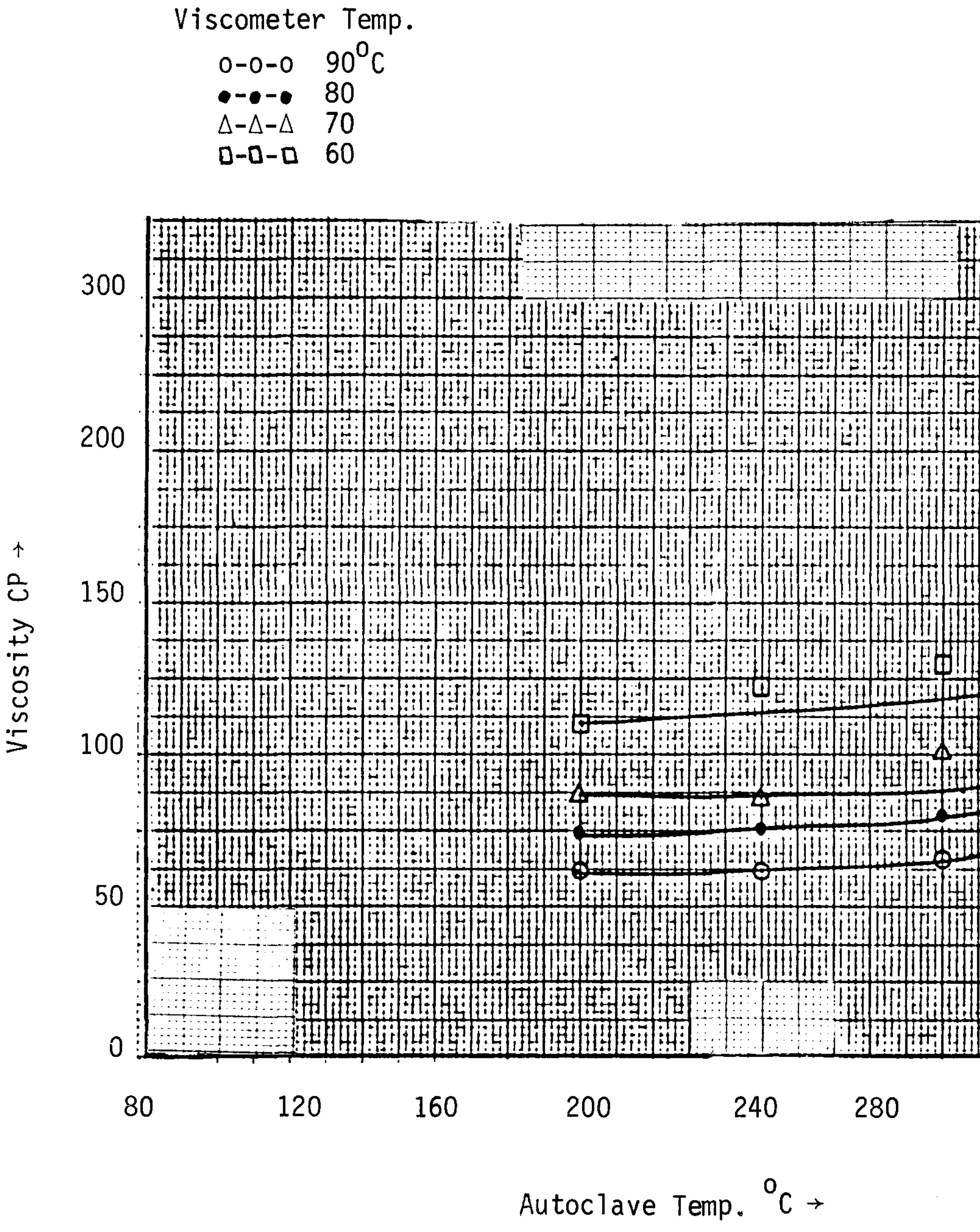


Figure 1.G.4
Cresote Oil - Ky 9/14 coal slurry viscosity measured at a fix temp. vs actual autoclave temp.
60 RPM, 250 psi N_2

Figure 1.G.5

Viscosity vs Temp. plot for
Recycle Oil-Coal slurry treated
at 200°C in autoclave.

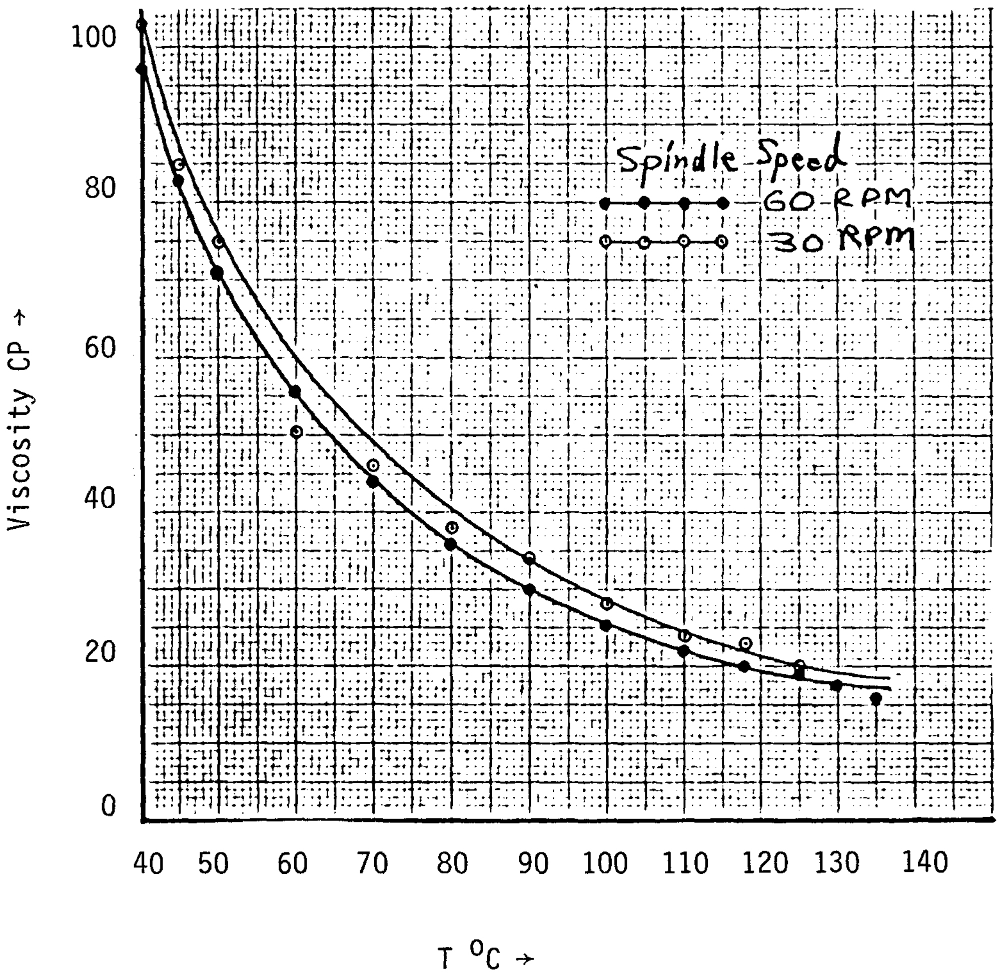
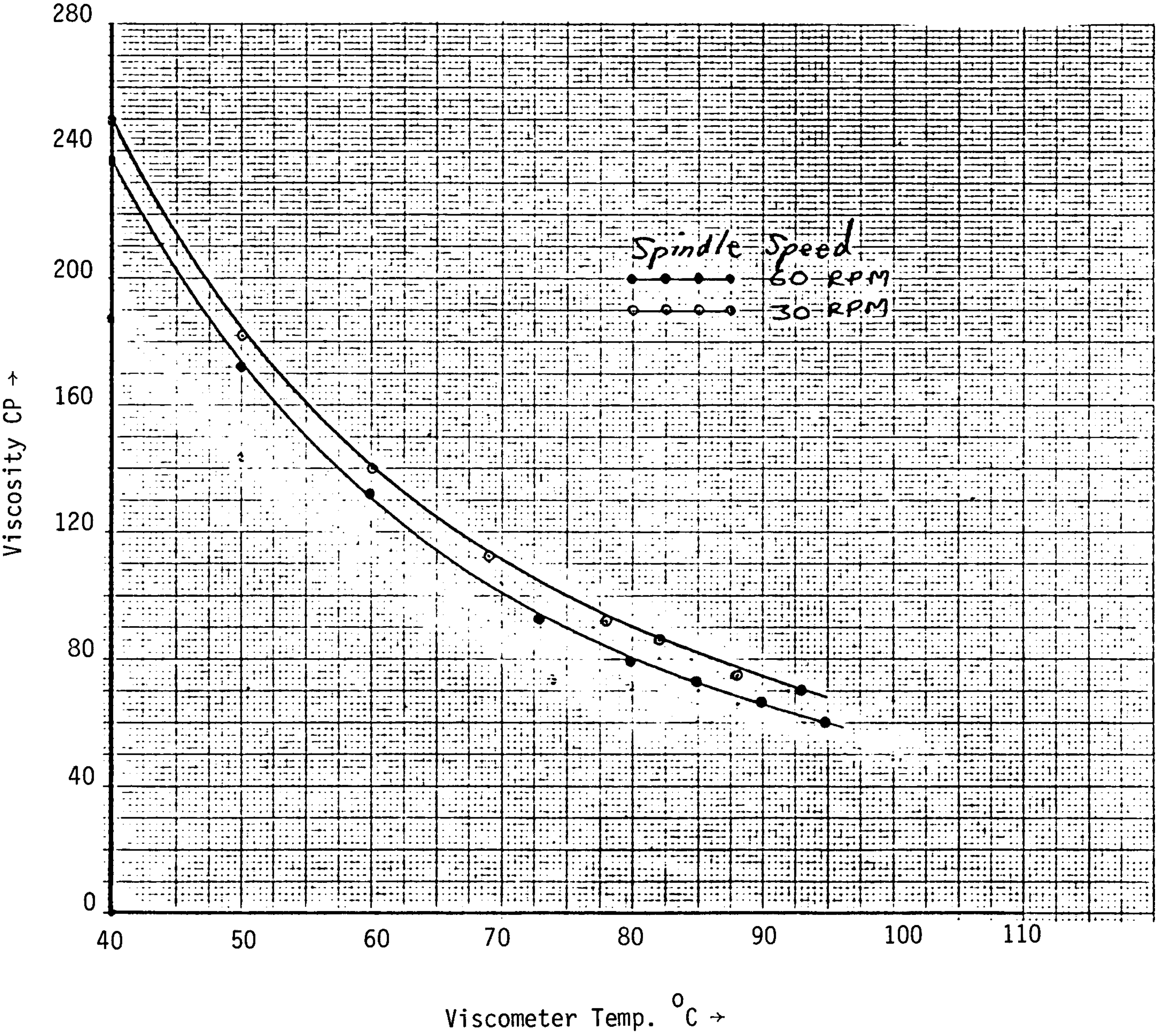


Figure 1.G.6

Viscosity Vs Temp. plot for
Cresote Oil - coal slurry
treated at 300°C in autoclave.



treated coal slurries behave as non-Newtonian fluids.

Planned Work: The investigation of coal slurry viscosity variations during dissolution shall be maintained with emphasis on a wide variety of processing conditions and different types of coals and solvents. General correlations for the observed behavior shall be sought.

Task 2. Reaction Kinetics and Process Variables Studies

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

2.A. Bench-Scale Batch Autoclave Experiments

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

Progress: A number of batch autoclave experiments were performed during the quarter to determine the solubility of methane and carbon dioxide in SRC recycle solvent. The rate of formation of these two gases is related to the kinetics of several reactions occurring in the SRC process. For example, carbon dioxide in production is related to the accumulation of carbonate minerals in the SRC dissolver, a problem which has caused some concern at the Wilsonville SRC pilot plant. Likewise, methane, while possibly recoverable as a fuel source for the process, is responsible for a major amount of hydrogen consumption. Thus information on the kinetics and solubilities of these two gases in SRC process solvent is of considerable interest and use to engineers and others attempting to scale-up the SRC process to demonstration and commercial levels.

Of the gases produced in the SRC process methane and carbon dioxide represent 30-50 weight percent of the total gaseous products. The balance of the gas produced is made up of n-alkanes water, hydrogen sulfide and ammonia. The other n-alkanes can probably be expected to conform to solubility data obtained here for methane. Therefore, by using the data obtained here and gas composition information obtained at the plant, it should be possible to determine the amounts of these gases at any point in the system, allowing for a more accurate process design.

Experimental Detail

Methane used in these experiments was 3500 psi grade gas of 99% purity and was obtained from Matheson, Inc., Morrow, Georgia. Carbon Dioxide used in this work was 1500 psi grade of 99.9% purity and was obtained from Alabama Oxygen, Inc., Opelika, Alabama.

The procedures used in these experiments are essentially the same as those reported in the earlier hydrogen solubility work (Guin, et al, 1976).

Experimental Results

Experimental data for the solubility of methane in SRC process solvent were obtained at temperatures of 200°, 300°, and 400°C at partial pressures of methane ranging from 500 to 3000 psia; the resulting data is shown in Figure 2.A.1. Experimental data for the solubility of carbon dioxide in SRC process solvent were obtained at temperatures of 100°, 200°, 300°, and 400°C at partial pressures of carbon dioxide ranging from 100 to 650 psia; the resulting data are shown in Figure 2.A.2.

As shown in Figure 2.A.1, methane exhibits an interesting inverse

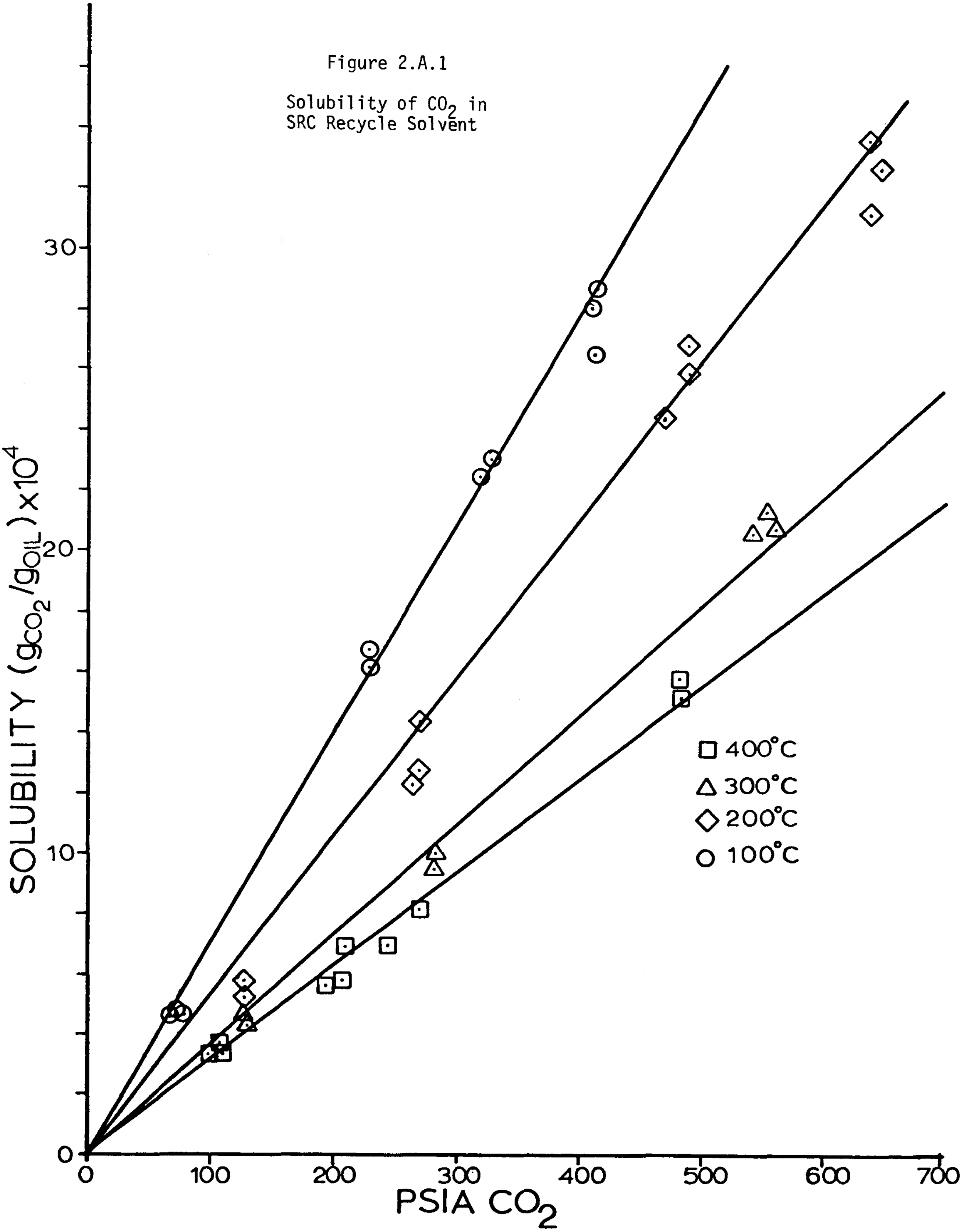


Figure 2.A.1

Solubility of CO_2 in SRC Recycle Solvent

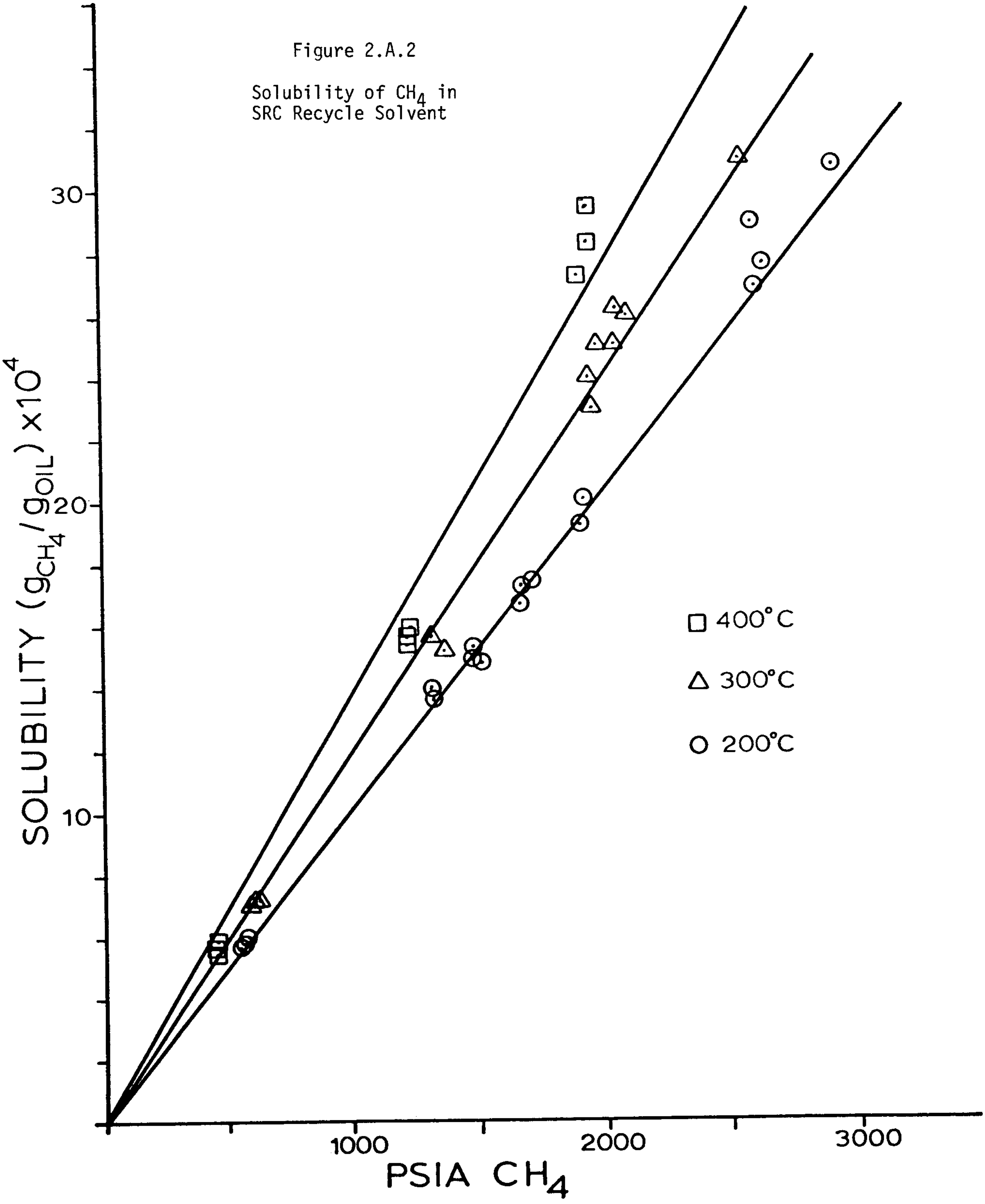


Figure 2.A.2

Solubility of CH_4 in SRC Recycle Solvent temperature behavior, with solubility at 400°C being greater than values at 200°C at the same pressure. This design data may indicate the best point in the coal processing train for removal of methane; i.e., the coolest point in the stream would be the best place to recover methane. The carbon dioxide data exhibits the normal temperature behavior with solubility at 400°C being less than values at 100°C for the same pressure.

Planned Work: Batch autoclave experiments shall be continued to assess the effects of process variables and coal/solvent type upon performance in the SRC process. As new instrumentation, particularly the FTIR, is brought on line, emphasis will be on monitoring the changes in concentration of individual species.

2.B. Bench Scale Continuous Reactor

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

Progress: The continuous reactor modeling work culminated this quarter in a comprehensive computerized model for the SRC preheater-dissolver system. The model, based on axial dispersion in a two phase system, uses kinetics rate expressions to predict the rate and extent of hydrodesulfurization, hydrogenation, and coal conversion under various processing conditions in the SRC process. The model and results are presented in the attached paper, "A Dispersion Model for the Solvent Refined Coal Process," to be presented at the ACS Fuel Chemistry Division Meeting in Chicago in August, 1977.

Planned Work: Using our mathematical model, several computer runs shall be performed for the Rust Engineering Company to evaluate several alternative designs for the SRC preheater-dissolver train. Our model will be used to determine the efficiency of several schemes and to recommend any changes and/or modifications in the design of the SRC demonstration plant.

2.C. Catalysis by Coal Mineral Matter

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

Progress: The results of the work on catalysis by coal minerals are presented in the manuscript "The Selectivity of Coal Minerals as Catalysts in Coal Liquefaction and Hydrodesulfurization contained in the Appendix. This manuscript has been accepted for presentation at the ACS Fuel Chemistry Division meeting in Chicago in August, 1977.

Planned Work: The experiments to determine the effects of coal minerals on product distribution selectivity and on hydrodesulfurization will be continued. The reaction products from the high pressure autoclave reactor and the short-residence time tubing-bomb reactor will be characterized by using conventional methods of product separation with solvent extraction, elemental analysis, and gas chromatography analysis. Various ranks of coal and demineralized coal (using magnetic separation and acid extraction) will be examined. Iron-containing catalysts such as Fe metal, FeS, FeS_2, and Fe_2O_3 in addition to other minerals in coal will be tested. Hydrogen-donor and non-hydrogen-donor solvents (tetralin, dodecane, or naphthalene) will be also used in addition to complex donor solvent mixtures such as SRC recycle solvent from the solvent refining process.

Task 3: Development and Application of Techniques and Methodology for Coal Liquids Analysis and Reaction Kinetic Studies

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

3.A. Development of HPLC Methodology

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

Progress: Based on work during the previous quarter, it was decided that to determine the chemical nature of Solvent Refined Coal (SRC), particularly the asphaltene and preasphaltene fractions, gel permeation chromatography (GPC) needed to be developed. Gel permeation chromatography (GPC) provides distribution of the SRC components by molecular size. In order to perform GPC the solubility of SRC must first be established. Table 3.A.1 shows the solubility of SRC in five solvents. Considering the HPLC system and the delicate gel permeation columns,tetrahydrofuran and benzene were the two solvents of choice.

A technique for analyzing autoclave reaction mixtures dissolved in tetrahydrofuran into three fractions,(preasphaltene, asphaltene and oil fractions)by GPC is being developed. Presently, the differential refractive index dectector shows some separation of these three major types of compounds; however, for verification and clarification of this separation, ultraviolet detection is also necessary.

TABLE 3.A.1 Solubility of Western Kentucky 9/14 SRC

Western Kentucky 9/14 SRC from Wilsonville Pilot Plant (made in 1974)

Solvent	% insoluble
Tetrahydrofuran	2.64% ± 1.71%
Benzene	58.4% ± 4.5%
Acetone	87.0%
Dimethylformamide	3.7%
Cresol	1 to 2%

Western Kentucky 9/14 SRC from Wilsonville Pilot Plant (made in 1976)

Solvent	% insoluble
Benzene	65.7% ± 6.4%

Stability of SRC at High Temperature

The effect of temperature at increasing time spans on SRC must be determined to ascertain if SRC is a chemically inert species or if subjection to elevated temperatures causes a major or minor change in its chemical nature. To evaluate this question, SRC was heated in an evacuated glass tube encased in a stainless steel tubing bomb and heated in a fluidized bed for varying lengths of time. After reaction the solubility of the reacted SRC was determined by Soxhlet extraction and gravimetric analysis of the dried SRC insolubles.

Initially the solubility experiments were conducted at 225°C with tetrahydrofuran (THF) as solvent. But, as can be seen in Table 3.A.2 tetrahydrofuran essentially solublized all of the SRC reacted at 225° for times ranging from 15 to 120 minutes. After four hours, however, the solubility of SRC in THF substantially decreased. At this point in the experiment it was difficult to determine if the temperature was too low to produce repolymerization or if tetrahydrofuran was too strong a solvent. Possibly repolymerization was occurring but tetrahydrofuran was so powerful as a solvent that it essentially broke all the newly formed bonds. In order to determine if repolymerization was actually occurring, a less potent solvent, benzene, and higher temperature, 425°C were used in the experiments. Table 3.A.2 shows that for two different batches of Western Kentucky SRC a definite increase in the percent of benzene insolubles occurs as reaction time increases. For 120 minutes the percent benzene insolubles is over 90% compared to 65% in the original SRC.

This increase in benzene insolubles indicates that the organic constituents - most likely aromatic - are shifting to higher molecular

TABLE 3.A.2 Temperature and Temporal Effects on the Solubility of Western Kentucky 9/14 SRC in Tetrahydrofuran and Benzene

Solvent: Tetrahydrofuran
Temperature: 225°C
SRC: Western Kentucky 9/14 (made 1974)

Reaction Time (minutes)	% Insolubles
zero	2.64% ± 1.71%
15	3.74% ± 1.74%
30	2.76% ± 0.56%
60	3.06% ± 1.09%
120	1.92% ± 0.51%
240	22.9% ± 9.23%

Solvent: Benzene
Temperature: 425°C
SRC: Western Kentucky 9/14

Reaction Time (minutes)	% Insolubles SRC (made in 1974)	% Insolubles SRC (made in 1976)
zero	58.4% ± 4.5%	65.7% ± 6.4%
15	60.2% ± 1.2%	65.8% ± 14.5%
30	63.2% ± 6.3%	76.3% ± 14.8%
60	67.5% ± .42%	74.1% ± 1.8%
120	86.4% ± 10.8%	92.4% ± 2.0%
240	>96%	

weight compounds or polymer chains. To test this premise a gel permeation chromatographic technique is being developed to determine the molecular size - weight constituents of the benzene soluble portion of SRC. Calibration of the system using commonly occurring aromatic constituents in coal such as naphthalene, dibenzofuran, rubrene, etc., is nearly complete. Preliminary experiments on the benzene soluble Soxhlet extract indicate that molecular weight distributions and shifts can indeed be determined by GPC. Quantitative analysis of the molecular weight distribution is planned.

In conjunction with the compound molecular size (molecular weight) distribution of SRC, the chemical nature and mechanism of reaction of SRC also are being studied through solubility studies and gel permeation chromatography. The impetus for this investigation lies in the recurring problem of agglomeration of organic material in SRC reactors. An outline of the background and possible reaction mechanism of SRC repolymerization follows which will show the basis for our interest in the solubility of SRC after being subjected to heat for increasing periods of time.

Studies on Repolymerization and Stability of Solvent Refined Coal

Background of the Problem of SRC Stability: It is frequently necessary to keep SRC in a molten condition for extended periods of time when it is to be used in the molten state as fuel. After such holding, the SRC frequently becomes "insoluble" and aggregates into a mass which is not fluid at the temperatures used. This behavior is commonly called repolymerization although little is actually known of its origin. An excellent review by Neavel (1976) discusses much of what is known about the complex reactions of coal with SRC solvents. Relevant aspects of these are summarized in the following paragraph. Our own work, aimed at developing a sufficient understanding of the repolymerization process to be able to control it, will be described in subsequent sections.

It is known that the dissolution of coal in the SRC process leads to the creation of a number of free radicals at the sites of bond cleavage which occur upon breakup of the original coal molecule into component subunits. Some of these radicals are "capped" by hydrogen which is either abstracted from the solvent or is possibly directly added from dissolved hydrogen. In either event, a number of the free radicals escape hydrogenation and remain highly reactive. A certain amount of repolymerization is known to occur in the process stream as the radicals on adjacent small units react to form large insoluble structures. It appears to us that this free radical polymerization, which is effectively halted when the SRC is quenched to the solid state, can resume when the SRC is melted and kept at high temperatures. This polymerized material being of high molecular weight would be expected to be of higher melting point that the original SRC and to be insoluble in ordinary SRC solvents.

Experimental Approaches

A. Degree of Repolymerization: The conventional measure of the extent of SRC repolymerization is taken to be the percent of "cresol insolubles" as determined by simple extraction with hot cresol. This procedure is far from ideal and an improved method based on Soxhlet extraction with benzene has been undertaken. This work is discussed in more detail later. At this point it is sufficient to say that this method is very effective and provides an excellent working method for determining the gross degree of repolymerization. Thus, measurements of free radical content and other molecular parameters can be related directly to known degrees of repolymerization.

B. Free Radical Measurements: Testing of the free radical hypothesis of repolymerization requires some means for determining the concentration and nature of the radicals. Electron Spin Resonance (ESR) is such a method.

ESR monitors the behavior of an unpaired electron subjected to a magnetic field. An electron has a spin angular momentum quantum number corresponding to + or - ½. When a field is applied the electron will align with the field (-½ lower energy level) or against the field (+½ higher energy level).

Radiation in the microfrequencey range of 9,000 mc sec^{-1} can be absorbed by the molecule containing an unpaired electrons. The energy of this absorption is given by $E=hv=BgH_0$. In the equation h represents Planck's constant, v is the frequency, B is the Bohr magneton which relates the magnetic moment of an electron due to the contribution of its angular momentum, g (spectroscopic splitting factor) relates the orientation of the molecule containing the unpaired electron with the magnetic field, and H_0 is the field strength. For a free electron, g = 2.00023; this is the approximate value for most free radicals.

It is easily seen that the above considerations lead to the fact that, all other factors being equal, the absorption of microwave radiation of the proper frequency is directly proportional to the concentration of the absorbing radicals. This is the basis of this simplest analytical application of ESR.

In this preliminary work we will attempt to use ESR as a tool for the measurement of radical concentration in SRC and in reploymerized SRC. If the radical concentration in the repolymerized material is lower than that of the original material, it would support the possibility that repolymerization is a free radical process in which the SRC "monomer", which carries the radical ends, polymerizes to yield insoluble material having few or no radicals. Such a process would be favored at high temperatures since the decreased viscosity would permit sufficient molecular motion to bring about radical-radical contacts.

We have completed the first measurement, that of determining the radical content of original SRC. Using a Varian EM-500 ESR spectrometer, we have found approximately 10^{17} spins per 100 mg of sample. Because ESR is an absolute measurement technique, its accuracy depends on the stability of the system and on accurate calibration using known standards. Thus, the forgoing data could be somewhat in error but at the present point some error can be tolerated. Subsequent work aimed at obtaining quantitative correlations between the amount of insoluble matter and decreases in free radical content, require more sophisticated instrumentation.

Planned Work: From the forgoing discussion it can be seen that a reasonably good test of the proposed SRC free radical repolymerization hypothesis can be made using fairly simple techniques. We plan to proceed with the following steps:

1. Quantitative ESR studies of the radical contents of original and repolymerized SRC will be performed. Major decreases in the free radical content of the repolymerized material relative to the original SRC will indicate proof

of the free radical hypothesis of repolymerization.

Assuming that this first step is successful in clearly showing the free radical nature of the repolymerization we will proceed to the following:

2. ESR studies of the free radical concentration of SRC samples anealed at various temperatures and times will be conducted. From these, the kinetics and activation energy of the repolymerization reaction will be determined.
3. Concurrent studies of the solubilities of the SRC samples will be conducted to help quantify the relation between radical content and observed insolubilization. A search will be begun for various free radical scavengers which might be used immediately to slow the repolymerization reaction.
4. In addition to these directly usable aspects of the repolymerization problem, we plan to eventually explore more thoroughly the fundamental nature of the free radical(s) which are likely to be present. Such information may provide a better basis for selection of useful scavenging agents than mere broad spectrum trial of randomly chosen quenching agents.
5. The effect of temperature level on the SRC stability will be studied further with the next series of experiments at 225^{o}C using benzene as a solvent.
6. Further work will continue on the GPC technique development as soon as the ordered unstablized tetrahydrofuran (without UV interference) arrives. Calibration of this technique to directly correlates molecular size distributions to molecular weight distributions is being explored.

3.B. Characterization of Coal Liquefaction Products

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

Progress: During the quarter work continued on the quantitative analysis of trace elements in both feed coal and SRC product from the Wilsonville pilot plant. A correlation was developed between the ash content of mf coal and the cumulative weight percent of fifteen elements as measured by X-ray. A similar correlation is being sought for SRC product. Thus far it has been determined that the Energy Dispersive X-ray fluoresence method is capable of simultaneously determining several important elements; namely, sulfur, iron and calcium, as well as approximately the ash content of coals and SRC products with an analysis time of approximately two hours. Also during the quarter the X-ray flourescence technique was developed to the point where a paper could be finalized for presentation at the ACS Fuel Chemistry Division meeting in Chicago in August, 1977. The remainder of the progress under this task is thus presented in this paper which is contained in the Appendix.

Planned Work: Quantification and identification of compounds in coal liquids and SRC product shall be continued. The new FTIR system, purchased under the recent contract modification shall be installed and calibrated. Further, a new G.C. sulfur specific detection system expected to arrive soon should prove very valuable for identification of sulfur species in SRC process streams.

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

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

Progress: Gas chromatographic investigation of the molecular composition of coal liquids has continued this quarter. The major-thrust of this work has been the spiking of creosote and recycle oils with known compounds. Tables 3.C.1 and 3.C.2 list compounds identified in the oils by spiking. Although spiking is the commonly used method for identification of coal liquid components, inconclusive results often occur. Tables 3.C.1 and 3.C.2 show that compounds used in spiking often overlap making it difficult to conclude which compound or mixture of compounds actually is present in the sample. In order to perform meaningful kinetic studies involving coal liquids, absolute identification of the reaction solvent components and the subsequent reaction products is necessary. This is discussed under planned work.

Catalysis experiments (Section 2.C.) 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 was analyzed by gas chromatography and the ratio of the peak heights of the resulting tetralin and naphthalene peaks were determined. The tetralin to naphthalene ratio provided one indication of the hydrogen donating capability of the solvent.

Planned Work: To facilitate the use of gas chromatography for identification of the more volatile constituents of coal liquids such as SRC recycle solvents, we plan to use a direct analysis of the effluent gases

Table 3.C.1

Analysis of Creosote Oil Using the Spiking Method

Column: 10% SP 2100, 10ft

Peaks tentatively identified

indan

cis and trans decalin

tetralin

naphthalene

1-methyl naphthalene

biphenyl

2-ethyl naphthalene

2,3-dimethyl naphthalene

acenaphthene and 1-naphthonitrile

dibenzofuran and 2-naphthonitrile

2,3,6-trimethyl naphthalene

fluorene

9,10 dihydroanthracene

dibenzothiophene

phenanthrene

carbazole

fluoranthene

pyrene

Table 3.C.2

Analysis of Recycle Oil
Using the Spiking Method

Column: 3% SP 2250, 12ft

Peaks tentatively indentified

cis and trans decalin

indan

* tetralin and 1,2 dihydronaphthalene

1,2 dimethylnaphthalene

naphthalene

1-methyl naphthalene

* 2-ethyl naphthalene and 1-naphthonitrile and biphenyl

1-ethyl naphthalene

2,3-dimethyl naphthalene

* 2,3,6-trimethyl naphthalene and dibenzofuran

2-naphthonitrile

* 9,10-dihydroanthracene and 9,10-dihydrophenanthrene

dibenzathiophene

phenanthrene

anthracene

carbazole

fluoranthrene

pyrene

* Overlapped peaks: possible that both peaks are present

via Fourier Transform infrared spectrometry. Its principle of operation is completely different from conventional prism or grating instruments. FTIR depends upon high speed computer treatment of optical data produced by an interferometer. This treatment is done by an internal dedicated computer. Thus, the output of the spectrometer can be delivered in a form suitable for immediate analog recording like conventional spectrometers or compared with spectra of known compounds. It is possible in this way to make unambigious assignments of infrared spectra in a few seconds which would require hours or days of hand-searching and visual comparisons using conventional printed standard spectra. Visual comparison and identification would be practically impossible for complex coal liquefaction streams.

The interferometric scanning system provides a complete scan of the normal infrared region (4000 cm^{-1} to 400 cm^{-1}) in about 0.5 sec. This rapidity permits multiple scans to be made in even the short time a gas chromatographic sample would be present in a flow cell. These spectra are summed and averaged by the dedicated computer to effectively average out the noise and enhance the signals. It is this ability combined with the expected benefits of Fellgett's Advantage which permits the high sensitivity of FTIR.

FTIR with the GC capability will enable the Auburn Coal Con-Version Laboratory to more completely evaluate the heteroatoms (S,N,O) present in the SRC process. FTIR provides a direct method of spectroscopic identification of these heteroatoms. FTIR/GC is especially powerful in determining organic sulfur when coupled to a gas chromatograph equipped with a flame photometric detector which specifically detects sulfur, an element of major interest in the SRC process.

A Digilab FTIR/GC, System 10, will be delivered and installed in the next two quarters. A Varian 3700 gas chromatograph equipped with a flame photometric is also ordered and will be installed in the same time frame. The preliminary spiking experiments done so far provide an excellent means of determining column performance and will provide a good foundation for more extensive and conclusive analyses of the SRC solvents through FTIR/GC.

CONCLUSIONS

1. An evaluation of Emery coal as a potential feed coal for the SRC process showed it to be completely unsuitable and thus its consideration as a viable liquefaction candidate was not recommended.
2. Results of Coulter Counter measurements of dissolved coal particle size correlated well with filterability behavior at the Wilsonville Pilot Plant.
3. The initial coal particle size was found to be unimportant in the SRC processing of four coals, thus indicating the possibility of significantly relaxing current grinding requirements and lowering costs.
4. Large viscosity "peaks" were found to occur in the preheating period of the SRC process; however, the "peak" using SRC recycle solvent was rather smaller and occurred at a lower temperature as compared to the "peak" when a creosote oil solvent was used.
5. The solubilities of methane and carbon dioxide in SRC recycle solvent have been determined at process temperatures and pressures, with methane exhibiting an inverse type solubility behavior.
6. The two-phase axial dispersion SRC reactor model correlates reasonably well with observed performance of the Wilsonville SRC pilot plant, if allowances are made for the mineral matter accumulation (catalytic effect) in the Wilsonville dissolver.
7. Iron is more effective in promoting desulfurization than hydrogenation in the SRC process - a potential advantage.

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2. Neavel, R.C., Fuel 55 237 (1976).

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APPENDIX

Papers to be presented at the August, 1977 meeting of the ACS Division of Fuel Chemistry, Chicago, Illinois.

The Selectivity of Coal Minerals as Catalysts in Coal Liquefaction and Hydrodesulfurization

J. M. Lee, A. R. Tarrer, J. A. Guin and J. W. Prather

Chemical Engineering Department
Auburn University
Auburn, Alabama 36830

Introduction

Certain coal minerals are well-known to catalyze liquefaction and hydrodesulfurization in coal conversion processes (1,2,3,4). It is generally understood in connection with liquefaction processes that heating coal to temperatures in the range of 350°C and higher produces free radicals by thermal bond rupture. These free radicals are then stabilized by abstracting a small entity such as a hydrogen atom from some source. The source may be hydrogen chemically interacted with the catalyst (coal minerals or other added catalysts), hydrogen on the hydroaromatic portion of a hydrogen donor solvent or perhaps hydrogen on the hydroaromatic portion of coal (5,6,7). Some studies of catalytic hydrodesulfurization of coal-solvent slurry systems have been done with various commercial catalysts (8,9, 10). Instead of voluminous work with good hydrogenation and hydrodesulfurization catalysts, little attention has been paid to coal mineral catalysis. Coal mineral catalysis might be important in the Solvent Refined Coal (SRC) process, in which solid boiler fuel is produced through mild or little hydrogenation of coal - probably mainly through dissolution of coal.

To better understand the importance of coal mineral catalysis in the SRC process, this work presents comparative results of the rates of hydrogenation and hydrodesulfurization of coal/oil slurries under different reaction conditions and in the presence of different coal minerals. The selectivity of coal minerals such as reduced iron and SRC residue (Wilsonville SRC pilot plant) for hydrodesulfurization as opposed to hydrogenation has been determined based on product distribution (oil, asphaltene and preasphaltene), sulfur content of each product and analyses of liquid products. The rate limiting steps, or the reaction step most affected by catalytic activity of coal minerals have also been examined.

Experimental

Equipment

All autoclave studies were performed in a commercial 300 cc magnedrive autoclave (Autoclave Engineers). The autoclave was equipped with a stirrer, thermowell, furnace, cooling coil, gas inlet and sampling lines. Coal-tetralin systems were studied in a small tubing-bomb reactor (½" O.D. stainless steel tube with 0.035" wall thickness). Under air atmosphere about 16 ml reactors were used with Swagelock caps on both ends. Hydrogen gas was introduced into a smaller tubing-bomb reactor (about 13 ml), sealed with Swagelock cap on one end, through 1/16" tube which was connected to the pressure indicator to read pressure change during reaction. Varian gas chromatographs (Model 1800) were used for analysis of oil fraction. A Leco sulfur determinator (Model 532) was used for analysis of sulfur in each product.

Materials

Creosote oil (Allied Chemical Company) and light recycle oil (LRO) used in this study were obtained from Southern Services, Inc. The creosote oil has a carbon-to hydrogen ratio of 1.25 (90.72% C and 6.05% H), a specific gravity of 1.10 at 25°C, and a boiling point range of 175 to 350°C. The creosote oil consists of 96.1% oil, 3.5% asphaltene, 0.2% preasphaltene and 0.3% pyridine insolubles. The light recycle oil (LRO) contains mainly oil (99.4%) and a little asphaltene (0.6%). The values were obtained following the solvent extraction scheme, which will be described in the experimental procedure section. The sulfur content is 0.64% in the creosote oil and 0.26% in the light recycle oil (LRO).

Kentucky No. 9/14 mixture (-150+325 mesh, a high volatile bituminous coal) was used in all experiments (67.8% C, 4.9% H, 2.69% S and 12% mineral matter). All coal samples were dried overnight at 100°C and 25 inches Hg vacuum before use.

Co-Mo-Al and representative coal minerals (iron and SRC residue) were obtained and studied as catalysts for the reactions of hydrogenation and hydrodesulfurization. Co-Mo-Al is a commercial catalyst from Laporte Industries, Inc. (Comox 451). Iron is a reagent grade hydrogen reduced iron from Mallinckrodt, Inc. SRC residue was obtained from filter cake from Wilsonville SRC pilot plant (2.48% S). All catalysts were screened to -325 mesh before use. Presulfided Co-Mo-Al was prepared by collection of solid residue after reaction of creosote oil with Co-Mo-Al in the autoclave reactor. Sulfur content is about 2.76%.

Hydrogen and nitrogen gas cylinders (6000 psi grade) were supplied by Linde. The following chemicals were used: benzene (Mallinckrodt, nanograde or Fisher Certified A.C.S.), pentane (Mallinckrodt, nanograde), hexane (Fisher Certified), pyridine (Fisher Certified A.C.S.) and tetralin (J.T. Baker, practical grade).

Procedures

A 2:1 solvent-to-coal weight ratio (40 grams of coal, 80 grams of solvent-LRO or creosote oil) was charged to the autoclave. In some cases, a 3:1 solvent-to-coal weight ratio was used. The reaction conditions used for most of runs were 410°C, a stirrer setting of 1000 rpm, and an initial hydrogen or nitrogen pressure of 2000 psig. A heat-up rate of about 12 to 20°C per minute was used, thus requiring a total heat-up time of about 30-35 minutes. After two hours of reaction, the autoclave contents were quenched to below 100°C within 15 minutes. Then all reaction products were collected in a container and cooled down to room temperature. Immediately, the products were subjected to analysis following the solvent extraction scheme. Each separated product was collected for sulfur analysis.

Usually 3 grams of coal and 6 grams of solvent (tetralin) were charged to the small tubing-bomb reactor (2.4 grams of coal and 4.8 grams of tetralin under hydrogen atmosphere). The reaction experimental procedures were similar to Neavel's (7). The vertical stirring rate was in the range of 100-500 times a minute. Immediately after reaction for 30 minutes in a fluidized sandbath and cooling down, all reaction products were collected by cleaning with benzene first and then with pyridine, then analyzed following the solvent extraction scheme. Each product was collected for sulfur analysis. The oil fraction was analyzed by gas chromatograph to see tetralin consumption during reaction.

About 9 grams of reaction products from the autoclave reactor or all products from the small tubing-bomb reactor were separated following a conventional solvent extraction scheme with pentane or hexane, benzene and pyridine, as shown in Figure 1. The actual weight of oil fraction was slightly higher than the difference between the original sample amount and the sum of asphaltene and benzene insolubles, indicating some solvent (benzene, hexane or pentane) remaining after rotaevaporation up to about 80-85°C under vacuum. To resolve this, the true value for oil or preasphaltene fraction was chosen as follows:

oil = sample - asphaltene - benzene insolubles
preasphaltene = benzene insolubles - pyridine insolubles

Good reproducibility was obtained with ±1% deviation, based on percentage of each separated product (±3% deviation, based on dmmf coal).

Results and Discussion

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 hydrogen transfer from hydrogen chemically interacted with the catalyst (coal minerals or other added catalyst), hydrogen on the hydroaromatic portion of a hydrogen donor solvent or perhaps hydrogen on the hydroaromatic portion of coal (5, 6, 7, 10, 11). The major role of catalyst in liquefaction appeared to be the replenishment of the hydrogen donor solvent in order to maintain the proper level of hydroaromatics (1, 12). The hydrogen atmosphere, the hydrogen donor ability of the solvent and the hydrogenation activity of the catalyst seem to be most important variables among others in liquefaction process.

A series of experiments using the autoclave reactor was performed to evaluate the sensitivity of the rates of hydrogenation and hydrodesulfurization and to a lesser degree, liquefaction of a coal/oil slurry to variations in atmospheric composition (H_2 or N_2), type of solvent (light recycle oil, LRO, or creosote oil), and presence of different catalysts (Table I). The selectivity of different catalysts in terms of overall effect on product distribution (gas, oil, asphaltene, preasphaltene, and pyridine insolubles) was also examined. Creosote oil and LRO were simply assumed to exist as oil after reaction. Creosote oil contains, however, about 3.5% by weight of asphaltene, affecting significantly the oil and asphaltene portions in runs B and D. In runs A, B, C, and D, as to be expected, both liquefaction (based on pyridine soluble degree) and hydrogenation (based on benzene soluble degree) occurred to a larger extent in a hydrogen atmosphere than in an inert nitrogen atmosphere -- the pyridine solubles yield being 35% higher and the benzene solubles yield, 25% higher -- irrespective of the type of solvent used, LRO or creosote oil.

Hydrogen donor species like tetralin and hydrophenanthrene are present in significant amounts in LRO; whereas only trace amounts of these species are present in creosote oil. As a result, LRO is considered to be a much better SRC solvent than creosote oil, which is used as an SRC startup and makeup solvent. Extent of liquefaction and hydrogenation are strongly dependent on solvent characteristics, or type. For example, the pyridine soluble yield was increased by 27% and the benzene soluble yield was increased by 21% -- irrespective of the atmosphere, H_2 or N_2 -- when LRO was used instead of creosote oil.

The results of runs A and E clearly demonstrate the pronounced effect of the presence of presulfided Co-Mo-Al -- a well known hydrogenation catalyst -- on product distribution: the oil fraction is increased by about 76% over that resulting in the absence of the catalysts; the preasphaltene fraction is decreased by about 71%; and the pyridine insoluble fraction is decreased from 12.5% to practically zero percent, with the asphaltene fraction remaining essentially the same. The presence of Fe (run F) and SRC residue (run G) had, on the other hand, a much less pronounced effect on product distribution. Most interestingly, in the presence of Fe the pyridine insoluble fraction decreased to practically zero; and the oil fraction increased by about 27%, with the asphaltene and preasphaltene fractions remaining essentially the same. Within the limits of experimental error, in the presence of SRC residue product distribution remained practically the same. Based on these results, Fe appears to be more effective than SRC residue in accelerating oil and pyridine soluble yields, with both being much less effective than presulfided Co-Mo-Al.

In Table II hydrogen consumption during reaction was compared, based on H_f/H_o value (the ratio of final hydrogen partial pressure to that in the initial charge at reaction temperature). The justification for using this value to gauge hydrogen consumption was presented in an earlier work (13) in which the kinetics of hydrogenation were described in detail. The presence of SRC residue and coal ash had significant effects on hydrogen consumption, being next to that of presulfided Co-Mo-Al and significantly higher than that of Fe. In fact, the presence of Fe had little, or no effect on hydrogen consumption (H_f/H_o) as compared to that occurring during noncatalytic reaction. Apparently, based on the gas analyses and in light of the above results with regard to product distribution (Table I), the higher hydrogen consumption that resulted in the presence of SRC residue are due partly to higher yields of gaseous products (H_2S, CH_4, CO_2, C_2-C_5, etc.). The results from previously reported (1) catalyst screening studies (Table IV) also support the hydrogen consumption data in Table II. In addition, the results of earlier HPLC analyses of creosote oil after hydrogenation in the presence of different catalysts (Table V)(14) indicated that the degree of hydrogenation was greater in the presence of SRC residue and coal ash than in the presence of Fe (pyrite). The peak height ratio of tetralin to napthalene in the gas chromatographic analyses of the liquid products (Table II) indicated a similar trend to that observed in the HPLC analyses (Table IV) and the H_f/H_o values (Table II), that is, that hydrogenation reactions are accelerated significantly more by SRC residue and coal ash than by Fe. In conclusion then, despite the more significant effect of Fe than that of SRC residue on overall product distribution, as was discussed earlier, the presence of Fe during reaction has little effect on hydrogen consumption; whereas that of SRC residue causes a significant increase in hydrogen consumption. Also, apparently based on the results given in Table III, solvent-to-coal ratio has little effect on hydrogen consumption.

Table VI shows the results from a series of runs in which 2:1 coal/oil slurries were reacted in the presence of different concentrations of Fe catalyst. Samples used to perform gas analyses and for determining the sulfur content of the liquid fraction (that fraction which passed through Whatman #51 filter paper) were collected immediately upon completion of the specified reaction period (2 hrs). In agreement with the findings of the other studies discussed earlier, the presence of Fe catalyst did not have an appreciable effect on gas make (CH_4, CO_2, and C_2-C_5) or H_f/H_o values. Also, as was observed earlier, Fe served to completely scrub out any H_2S produced.

Table VII shows the results of a set of experiments in which a small tubing-bomb reactor was used. When a vertical agitation rate in the range of 100-500 cycles per minute was used, with an air atmosphere the presence of Fe catalyst did not affect the product distribution. More importantly, even with a hydrogen atmosphere and in the presence of Co-Mo-Al catalyst, the product distribution was not drastically different from that obtained with an air atmosphere and in the absence of the catalyst. This insensitivity apparently is due to the poor mass transfer obtained at this low agitation rate; for with an agitation rate of above 1000 cycles per minute, the product distribution changed significantly, with substantially more hydrogenation occurring. Further reaction studies using the tubing-bomb reactor are currently in progress.

Hydrodesulfurization

As shown in Table VIII the rate of hydrodesulfurization (HDS) of a 3:1 coal/oil slurry was the same in a N_2 atmosphere as that in a H_2 atmosphere when no catalyst was present during reaction. An earlier more detailed study of non-catalytic HDS (13) showed that the rate of HDS is indeed insensitive to not only hydrogen partial pressure but also the concentration of hydrogen donor species in the solvent. However, as shown in both Table I and VIII, in the presence of Co-Mo-Al catalyst the rate of HDS was significantly higher in the presence of a H_2 atmosphere than that in a N_2 atmosphere. In fact, for a 3:1 coal/oil slurry the sulfur content of the liquid reaction products was lower even under a N_2 atmosphere when Co-Mo-Al catalyst was present during reaction. For a 2:1 coal/oil slurry, in the other hand, no detectable lowering in the sulfur content of the liquid products due to catalytic activity under a N_2 atmosphere was observed (Table I and VIII). This insensitivity of HDS reactions to catalytic activity at the lower solvent-to-coal ratio could be due to the rapid depletion of hydrogen donor species that occurs under a N_2 atmosphere. For instance, as shown in Table IX, the degree of conversion of coal to liquids (cresol solubles) under a nitrogen atmosphere was the same after two hours of reaction as that after 15 minutes, presumably because of the rapid depletion of donor species; for, in the presence of a H_2 atmosphere, a significant increase in conversion resulted when the reaction time was increased from 15 minutes to two hours. If the catalyst can serve to accelerate HDS reactions by facilitating the transfer of hydrogen from donor species to active sulfur bearing species, then the concentration of donor species does take on importance, and the observed decrease in catalytic activity.with a decrease in the solvent-to-coal ratio should be expected. Further experiments are in progress to ascertain the extent to which HDS catalysts can serve to accelerate reactions in this capacity. The major role of HDS catalysts appears nevertheless to be the acceleration of the transfer of gaseous hydrogen to reactive sulfur bearing species. Thus, a H_2 atmosphere must be present for a catalyst to be most effective in accelerating HDS reactions.

Apparently from Table II, Fe proved to be about as effective as a desulfurization catalyst as did presulfided Co-Mo-Al. Among the liquid products, Co-Mo-Al was selective in accelerating desulfurization reactions in that it affected the asphaltene fraction the most in both percentage of sulfur (0.92 → 0.50%) and absolute weight of sulfur (0.12 → 0.07 gr). The selectivity of Fe catalyst among the liquid products was not as apparent as that of Co-Mo-Al catalyst.

In an earlier study (13) H_2S was shown to inhibit the activity of HDS catalysts. This inhibition by H_2S could be due to either the blocking of active hydrogenation centers or back reaction by H_2S product. Fe reacts with product H_2S to form non-stoichiometric FeS_{1+x}, and as a result, is a much more effective HDS catalyst than either pyrite or reduced pyrite (Table IV), each of which rapidly form non-stoichiometric FeS_{1+x} during HDS (13). Further evidence of the inhibition of catalytic activity by H_2S is provided by comparing the results given in Table II and IV: during the HDS of a coal/oil slurry in the presence of coal ash too much H_2S was apparently produced for the ash to scrub out (Table II), and because of H_2S inhibition the coal ash was totally ineffective as an HDS catalyst; whereas during the HDS of creosote oil all of the H_2S product was scrubbed out by the coal ash (Table IV), and the coal ash was a very effective HDS catalyst. For similar reasons, as shown in Table II, SRC residue is essentially ineffective as a HDS catalyst. Because of the scrubbing action of H_2S product by Fe then, it is a very effective HDS catalyst. In fact, as shown in Table VI, Fe Catalyst appears to be selective in accelerating HDS reactions more than hydrogenation reactions, in that as its concentration was increased from one to 13.3 percent, sulfur removal increased significantly with little change in hydrogen consumption (H_f/HO).

Process Application

During startup of the Wilsonville SRC pilot plant it has been observed that mineral matter accumulates in the dissolver until steady state conditions are achieved. This mineral matter has been found to exert some catalytic activity, particularly with regard to liquefaction and hydrogenation reactions. This finding is in complete agreement with the results discussed above. Actual SRC residue obtained from the Wilsonville plant as well as several minerals indigenous to coal and even coal ash, for example, were shown to act as effective hydrogenation catalysts. However, two major disadvantages to the use of SRC residue were observed: 1) it is ineffective as a HDS catalyst; 2) it is not selective in the catalytic activity and contributes to excess hydrogen consumption due to excess gas formation, etc. The results obtained for SRC residue should be indicative of the catalytic behavior of the mineral matter that exists in the SRC dissolver. To illustrate: an appreciable H_2S atmosphere exists in the SRC dissolver during normal steady state operation. Like pyrite, reduced pyrite, and coal ash as well as SRC residue then -- all of which were observed to be ineffective HDS catalysts in a H_2S atmosphere -- indigenous mineral matter does not scrub out H_2S product, and as a result, should not exert a significant catalytic activity for HDS reactions. In addition, the hydrogen consumption required to obtain the typical conversion yields obtained at Wilsonville have been estimated using non-catalytic kinetics to be about one half of that actually required (15). The catalytic activity existed by indigenous coal minerals was suggested to be the major cause of this higher hydrogen consumption.

In contrast to the minerals indigenous to coal, Fe has been shown here to be most attractive as a catalyst for the SRC process: 1) it is an effective HDS catalyst; 2) it is somewhat selective with regard to accelerating hydrogenation reactions, with minimal contribution to increased hydrogen consumption.

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Figure 1: Block Diagram for Separation Procedures

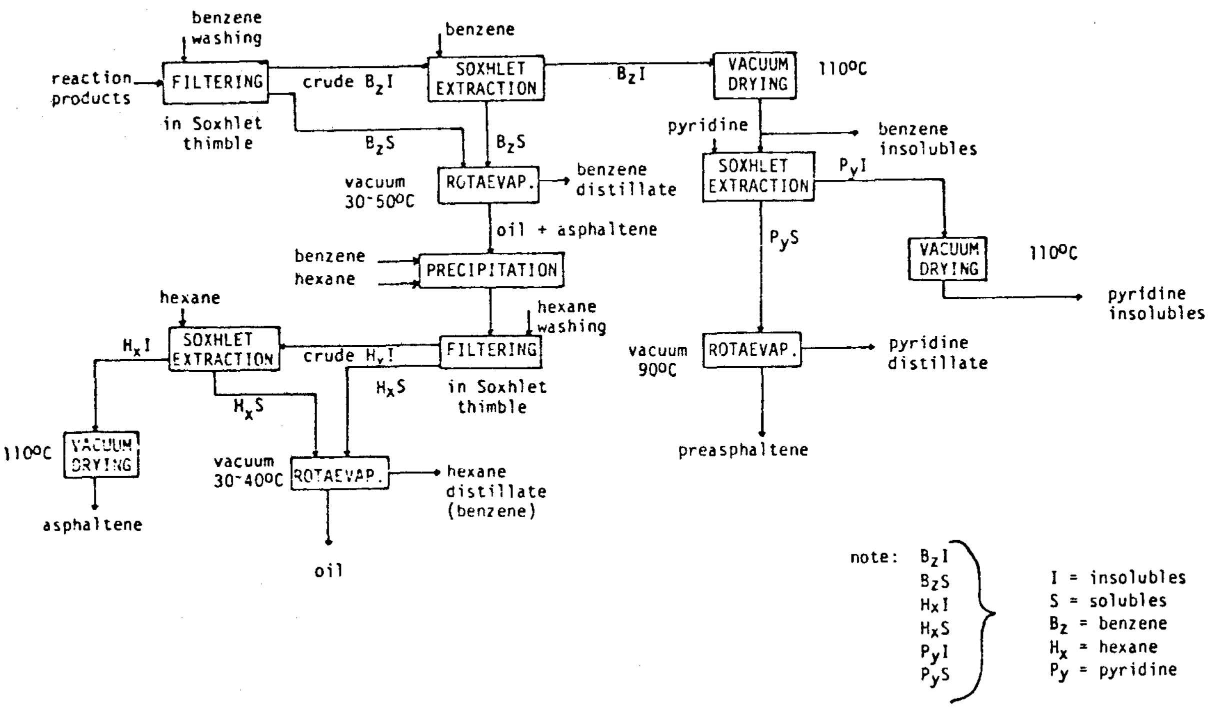

Table 1. Product and Sulfur Distribution by Different Solvent and Catalyst in Autoclave Reactor

solvent/coal = 2, T = 410°C, 120 minutes, 1000 rpm

runs	A	B	C	D	E	F	G
solvent	LRO	creosote	LRO	creosote	LRO	LRO	LRO
catalyst (14.3%)	-	-	Co-Mo-Al*	Co-Mo-Al*	Co-Mo-Al*	Fe	SRC residue
gas (psig)	H_2 (2000)	H_2 (2000)	N_2 (1000)	N_2 (1000)	H_2 (2000)	H_2 (2000)	H_2 (2000)
product, %**							
oil	32.6	7.1	16.5	4.0	57.4	41.4	33.0
asphaltene	38.4	42.5	28.7	19.3	37.8	38.5	45.2
preasphaltene	16.6	11.1	8.5	2.3	4.8	19.3	12.8
insolubles	12.5	39.3	46.3	74.4	0.0	0.9	9.1
sulfur, %							
oil	0.31	0.49	0.34	0.51	0.25	0.25	0.31
asphaltene	0.92	0.98	0.89	0.78	0.50	0.75	0.90
preasphaltene	0.55	0.63	0.65	0.99	0.78	0.30	0.63
insolubles	4.07	2.46	2.82	2.42	4.01	4.00	3.82
total sulfur, grams							
reactants	1.28	1.59	1.84	2.14	1.84	1.28	1.78
products (except gases)	0.80	1.03	1.56	1.71	1.32	1.36	1.60
oil	0.28	0.40	0.29	0.42	0.25	0.24	0.29
benzene solubles	0.40	0.55	0.38	0.47	0.32	0.34	0.41
pyridine solubles	0.43	0.57	0.40	0.48	0.33	0.36	0.44

*: presulfided Co-Mo-Al
**: based on dmmf coal and solvent-free

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

solvent (LRO)/coal = 2, T = 410^{o}C, 120 minutes, 1000 rpm

Catalyst	Initial Pressure ($1x10^{-3}$ psig)	Final Pressure ($1x10^{-3}$ psig)	Partial Pressures (psig)					Sulfur Content Of Liquid Products**	H_f/H_o***	Tetralin/Napthalene Ratio****
			H_2 (10^{-3})	H_2S	CO_2	CH_4	C_2-C_5			
Co-Mo-Al*	2.00	1.32	0.783	70	48	172	108	0.24	0.42	
" "	2.02	1.32	0.523	151	97	234	175	0.19	0.28	0.49
SRC Residue	2.01	1.52	0.842	41	115	244	132	0.38	0.45	
" "	2.00	1.36	0.739	35	115	206	125	0.37	0.40	
" "	2.02	1.51	0.834	48	132	219	137	0.39	0.44	0.33
Coal Ash	2.02	1.38	0.812	23	131	168	106	0.37	0.43	
" "	2.00	1.48	0.919	25	80	190	127	0.37	0.49	
" "	2.01	1.32	0.830	11	57	178	104	0.37	0.44	0.29
Fe	2.00	1.48	1.08	0.0	42	136	87	0.24	0.58	
"	1.99	1.44	1.01	0.0	45	156	92	0.27	0.55	
"	2.01	1.46	1.02	0.0	45	157	99	0.24	0.55	0.25
None	2.28	1.71	1.21	35	49	167	114	0.374	0.57	
"	1.92	1.59	1.11	37	56	155	95	0.417	0.62	0.16
"	2.09	1.70	1.25	36	44	135	90	0.350	0.64	
"	2.04	1.65	1.19	48	53	141	83	0.411	0.63	
"	2.01	1.54	--	--	--	--	--	0.402	--	

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* Presulfied 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 liquid products

Table III. Effect of Catalyst and Solvent (LRO)-to-Coal Ratio on Hydrogen Consumption

T = 410^{o}C, 120 minutes, 1000 rpm

Co-Mo-Al* Catalyst	Solvent-to-Coal Ratio	Initial Pressure (10^{-3} psig)	Final Pressure (10^{-3} psig)	Partial Pressures (psig)					H_f/H_o**
				H_2 (10^{-3})	H_2S	CO_2	CH_4	C_2-C_5	
None	3:1	2.02	1.72	1.16	31.3	37.4	280	73	0.62
None	3:1	2.00	1.70	1.34	7.4	41.8	108	68	0.72
15.0%	3:1	2.00	1.229	0.56	127	58	198	144	0.30
15.0%	3:1	2.02	1.360	0.82	54	55	169	118	0.44
None	2:1	2.00	1.48	0.95	50	45	137	93	0.62
15.0%	2:1	2.00	1.320	0.783	70	48	172	108	0.42
15.0%	2:1	2.02	1.320	0.523	151	97	234	175	0.28

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*,** same as in Table II

Table IV. Catalyst Screening Runs: Liquid % Sulfur, Final Total Pressure, Final Gas Composition, and Fractional Decrease in Hydrogen Pressure

15 grams catalyst, 100 grams creosote oil, T = 425°C,
Pi = 3000 psig H_2, 120 minutes, 2000 rpm

Mineral	% Sulfur*	Final Total Pressure (10^{-3} psig)	H_2 (10^{-3})	H_2S	CO_2	CH_4	C_2-C_5	H_F/H_0**
None	0.52	2.40	2.13	10.	2.5	64.	18.	0.74
None	0.46	2.42	2.23	7.1	2.0	62.	24.	0.78
Muscovite (-80)	0.39	2.18	1.94	8.5	1.0	51.	20.	0.68
Iron (-325)	0.27	1.98	1.75	< 1.	12.	16.	20.	0.61
Reduced Pyrite	0.36	1.96	1.85	17.	0.4	61.	18.	0.65
Coal Ash	0.23	1.92	1.72	< 1.	1.4	57.	15.3	0.60
Siderite	0.34	1.81	1.61	< 1.	67.	93.	29.	0.56
SRC Solids (-325)	0.32	1.73	1.48	13.	24.	85.	30.	0.52
Co-Mo-Al (-80, +150)	0.02	1.12	0.92	< 1.	1.9	128.	74.	0.32
Co-Mo-Al (-325)	0.02	1.02	0.73	1.7	1.3	138.	79.	0.26

* 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

Table V. 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-methylnapthalene	5.23	4.56	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	4.15	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.

Table VI. Effect of Iron Concentration on Hydrogen Consumption and Rate of Hydrodesulfurization of a Coal/Oil Slurry

solvent (LRO)/coal = 2, T = 410°C, 120 minutes, 1000 rpm

Wt. % Fe	Initial Pressure (1×10^{-3} psig)	Final Pressure (1×10^{-3} psig)	Partial Pressure (psig)					Sulfur Content of Liquid Products*		H_f/H_o**	
			H_2 (10^{-3})	H_2S	CO_2	CH_4	C_2-C_5		Average		Average
0.	2.28	1.71	1.21	35	49	167	114	0.374		0.57	
0.	1.92	1.59	1.11	37	56	155	95	0.417		0.62	0.62
0.	2.09	1.70	1.25	36	44	135	90	0.350	0,39	0.64	
0.	2.04	1.65	1.19	48	53	141	83	0.411		0.63	
0.	2.01	1.54	--	--	--	--	--	0.402		--	
1.0	2.21	1.70	1.19	5.9	54	200	114	0.374	0.37	0.57	0.57
2.0	1.52	1.23	0.773	0.0	42	172	102	0.318	0.35	0.56	0.56
2.0	1.66	1.34	0.851	0.0	64	189	112	0.373		0.56	
4.0	1.98	1.41	0.923	0.0	50	189	107	0.360	0.35	0.50	0.57
4.0	1.48	1.22	0.863	0.0	24	120	73	0.329		0.64	
7.7	2.10	1.62	1.15	0.0	49	172	107	0.294	0.28	0.59	0.59
7.7	2.04	1.55	1.11	0.0	46	152	98	0.273		0.58	
13.3	2.01	1.46	1.02	0.0	45	157	99	0.237		0.55	
13.3	1.99	1.44	1.01	0.0	45	156	92	0.271	0.25	0.55	0.56
13.3	2.00	1.48	1.08	0.0	42	136	87	0.24		0.58	

*,** same as in Table II

Table VII. Product and Sulfur Distribution in Small Tubing-Bomb Reactor

solvent(tetralin)/coal = 2, T = 410°C, 30 minutes

runs	A**	B	C	D
catalyst (7.7%)	-	Fe	Co-Mo-Al	Co-Mo-Al
gas (Pi)	air (1atm)	air (1atm)	H_2 (1360 psig)	H_2 (1200 psig)
cycles per minute	100-500	100	100	~1000
product, %*				
oil + gases	21.0	23.0	22.4	31.4
asphaltene	18.2	17.4	23.8	33.3
preaspnaltene	45.8	43.4	31.4	24.8
insolubles	15.1	16.2	22.4	10.5
sulfur, %				
oil	0.14	0.13	0.06	-
asphaltene	1.76	1.41	1.39	-
presphaltene	0.53	0.31	0.91	-
insolubles	4.29	3.66	3.38	-
total sulfur, grams				
reactants	0.080	0.081	0.065	-
products (except gases)	0.055	0.075	0.062	-
oil	0.009	0.009	0.003	-
benzene solubles	0.017	0.015	0.010	-
pyridine solubles	0.023	0.019	0.016	-
naphthalene/tetralin (GC peak ratio)	0.57	0.59	0.29	-

*: based on dmmf coal and solvent-free

**: average value of 4 runs at 100, 250, 350 and 500 cycles per minute.

Table VIII. Effect of Catalyst, Hydrogen Atmosphere, and Solvent-to-Coal Ratio on Rate of Hydrodesulfurization of a Coal/Oil Slurry

T = 410°C, 120 minutes, 1000 rpm

Weight Percent of Catalyst (Co-Mo-Al*)	Atmosphere	Solvent-to-Coal Ratio	Percent Sulfur Content of Liquid Fraction of Reaction Product **	Tetralin/ Naphthalene Ratio***
None	2000 psig H_2	3:1	0.42	0.190
None	2000 psig H_2	3:1	0.42	
None	2000 psig N_2	3:1	0.42	0.066
15.0	1000 psig N_2	3:1	0.30	0.066
15.0	1000 psig N_2	3:1	0.29	
15.0	2000 psig H_2	3:1	0.17	-
15.0	2000 psig H_2	3:1	0.17	
None	2000 psig H_2	2:1	0.39(avg of 4 runs)	0.16
15.0	2000 psig H_2	2:1	0.24	0.49
15.0	2000 psig H_2	2:1	0.19	
15.0	1000 psig N_2	2:1	0.36	-
15.0	1000 psig N_2	2:1	0.38	

*,**,*** same as in Table II

Table IX. Effect of Reaction Time and Atmosphere on Conversion of Coal to Liquid

Atmosphere	Reaction Time	Cresol Solubles(%)	Cresol Soluble Yield (%)*
H_2	2 hrs.	96.20	95.81
N_2	2 hrs.	89.78	66.81
H_2	15 min.	92.3	78.23
N_2	15 min.	89.73	66.58

Reaction Conditions:

Temperature = 410°C
Solvent-to-Coal Ratio = 2:1
Non-Catalytic

*Cresol Soluble Yield = $\frac{C - A}{C(1-M)} \times 100$ where C = charge of moisture free coal; A = the recovered insoluble residue; M = the fraction of mineral matter in dry coal.

A Dispersion Model for the Solvent Refined Coal Process

M. H. Lee, J. A. Guin, and A. R. Tarrer

Coal Conversion Laboratory
Department of Chemical Engineering
Auburn Univeristy
Auburn, Alabama 36830

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^{o}F through a gas-fired preheater connected to a dissolver section for further reaction. The coal is depolymerized by thermal cracking and reacts with hydrogen to produce lower molecular weight materials. At the same time some of the sulfur contained in the coal reacts with hydrogen to produce gaseous H_2S which is then removed by standard technology.

In this paper an axial dispersion model for two-phase flow is applied to study the kinetics of hydrogenation, desulfurization, and coal conversion in the SRC process. In applying the model, the Peclet number for the preheater section is assumed to be infinite, while the Peclet number for the dissolver will usually be around unity. Physically this means that the dissolver will experience a significant amount of axial dispersion. In applying the dispersion model to the SRC process, one needs to know reaction kinetics rate expressions for the pertinent reactions. Considerable research has been conducted concerning the kinetics of coal solvation and sulfur removal. Wen and Han (1975) have determined rate constants using coal liquefaction and desulfurization data gathered primarily from studies by Pittsburgh and Midway Coal Mining Co., the University of Utah, and the Colorado School of Mines. These researchers were able to fit data from the above sources with an empirical expression for the rate of coal dissolution; however, no kinetic expression was obtained for desulfurization and the effect of hydrogen partial pressure on coal dissolution and sulfur removal was not firmly established. It is likely that the different types of reactors and experimental procedures employed in the three laboratories made the data correlation more difficult. Very recently rate expressions describing the hydrogen transfer during the coal dissolution and hydrodesulfurization were determined by Pitts (1976). By performing batch autoclave experiments with Kentucky No. 9/14 coal, hydrogen gas, and creosote oil as solvent, he was able to develop kinetic models for rates of hydrogen consumption, coal dissolution and hydrodesulfurization. His results can be summarized as follows:

A. For hydrogenation: (Guin, et al., 1976)

$$r_{H_2} = -k_{H_2L} e^{-\Delta H/RT} c_{H_2L} \qquad (1)$$

where $k_{H_2L} = 1.06 \times 10^5$/minute and $\Delta H = 21$ Kcal/mole

B. For hydrodesulfurization: (Guin, et al., 1977)

Two parallel independent first order reactions indicative of two different classes of more specific compounds were proposed to represent hydrodesulfurization kinetics, they are:

$$r_{s_1} = -k_{s_1L}\, c_{s_1L} \tag{2}$$

$$r_{s_2} = -k_{s_2L}\, c_{s_2L} \tag{3}$$

where $k_{s_1L} = 5.939 \times 10^{11}\ e^{-40.78\ \mathrm{Kcal/RT}}$

$k_{s_2L} = 1.664 \times 10^{3}\ e^{-18.99\ \mathrm{Kcal/RT}}$

and the initial concentration of two sulfur species are

$c_{s_1}{}^{o} = 1.53 \times 10^{-3}$ grams organic sulfur/cm^3

$c_{s_2}{}^{o} = 6.51 \times 10^{-3}$ grams organic sulfur/cm^3

C. For coal dissolution:

Coal liquefaction was described by a model incorporating dissolved molecular hydrogen. The model assumed there are two differently reactive fractions of coal present in the reaction mixture. The rate equations were formulated to give two independent reactions, they are:

$$r_{c_1} = -k_{c_1L}c_{c_1L}c_{H_2L}^{2} \tag{4}$$

$$r_{c_2} = -k_{c_2L}c_{c_2L}c_{H_2L}^{2} \tag{5}$$

with initial ration of the reactive coal species given by $\dfrac{c_1{}^{o}}{c_2{}^{o}} = 0.771$ and

$$k_{c_1L} = 3.269 \times 10^{6}\ e^{-4.01\ \mathrm{Kcal/RT}} \tag{6}$$

$$k_{c_2L} = 6.988 \times 10^{10}\ e^{-21.4\ \mathrm{Kcal/RT}} \tag{7}$$

with these available rate expressions, one can now formulate the design equations for the SRC reactor. These equations will be presented below.

For the preheater section:

$$\frac{dC_{H_2g}}{dX} + \frac{k_c^I aL}{\hat{v}_g^I H}\left(C_{H_2g} - C_{H_2L}\right) = 0 \tag{8}$$

$$\frac{dC_{H_2L}}{dX} - \frac{k_c^I aL}{\hat{v}_L{}^I}\left(C_{H_2g} - C_{H_2L}\right) + \frac{k^I_{H_2L}L(1-f_g^I)}{\hat{v}_L^I}\, C_{H_2L} = 0 \tag{9}$$

$$\frac{dC_{c_1L}}{dX} + \frac{k^I_{c_1L}\ L(1-f_g^I)}{\hat{v}_L{}^I}\left(\frac{c_r}{H}\right)^2 C_{c_1L}\ C_{H_2L}{}^2 = 0 \tag{10}$$

$$\frac{dC_{c_2L}}{dX} + \frac{k^I_{c_2L}\ L(1-f_g^I)}{\hat{v}_L{}^I}\left(\frac{c_r}{H}\right)^2 C_{c_2L}C_{H_2L}{}^2 = 0 \tag{11}$$

$$\frac{dC_{s_1L}}{dX} + \frac{L\ (1-f_g^I)}{\hat{v}\ {}_L^I}\ k^I_{s_1L}\ C_{s_1L} = 0 \tag{12}$$

$$\frac{dC_{s_2L}}{dX} + \frac{L(1-f_g{}^{I})}{\hat{v}_L{}^{I}}\, k_{s_2L}^{I}\ C_{s_2L} = 0 \qquad (13)$$

with the conditions at X = 0:

$$C_{H_2g} = C_{H_2g}^{o} \qquad C_{c_1L} = C_{c_1L}^{o} \qquad C_{s_1L} = C_{s_1L}^{o}$$
$$C_{H_2L} = C_{H_2L}^{o} \qquad C_{c_2L} = C_{c_2L}^{o} \qquad C_{s_2L} = C_{s_2L}^{o} \qquad (14\ a\text{-}f)$$

For the Dissolver section:

$$\frac{1-X_1}{Pe,g}\ \frac{d^2C_{H_2g}}{dX^2} = \frac{d\ C_{H_2g}}{dX} + \frac{k_c^{II} aL}{\hat{v}_g{}^{II} H}\ (C_{H_2g} - C_{H_2L}) \qquad (15)$$

$$\frac{1-X_1}{Pe,L}\ \frac{d^2C_{H_2L}}{dX^2} = \frac{dC_{H_2L}}{dX} - \frac{k_c^{II} aL}{\hat{v}_L{}^{II}}\ (C_{H_2g} - C_{H_2L}) + \frac{k_{H_2L}L(1-f_g^{II})}{\hat{v}_L{}^{II}}\ C_{H_2L} \qquad (16)$$

$$\frac{1-X_1}{Pe,L}\ \frac{d^2C_{c_1L}}{dX^2} = \frac{dC_{c_1L}}{dX} + \frac{k_{c_1L}^{II}\ L(1-f_g{}^{II})}{\hat{v}_L{}^{II}}\ \left(\frac{c_r}{H}\right)^2 x\ C_{c_1L}\ C_{H_2L}^{2} \qquad (17)$$

$$\frac{1-X_1}{Pe,L}\ \frac{d^2C_{c_2L}}{dX^2} = \frac{dC_{c_2L}}{dX} + \frac{k_{c_2L}^{II}\ L(1-f_g{}^{II})}{\hat{v}_L{}^{II}}\ \left(\frac{c_r}{H}\right)^2 x\ C_{c_2L}\ C_{H_2L}^{2} \qquad (18)$$

$$\frac{1-X_1}{Pe,L}\ \frac{d^2C_{s_1L}}{dX^2} = \frac{dC_{s_1L}}{dX} + \frac{L(1-f_g{}^{II})}{\hat{v}_L{}^{II}}\ k_{s_1L}^{II}\ C_{s_1L} \qquad (19)$$

$$\frac{1-X_1}{Pe,L}\ \frac{d^2C_{s_2L}}{dX^2} = \frac{dC_{s_2L}}{dX} + \frac{L(1-f_g{}^{II})}{\hat{v}_L{}^{II}}\ k_{s_2L}^{II}\ C_{s_2L} \qquad (20)$$

with the conditions at $X = X_1$:

$$C_{H_2g}(X_1^-) = C_{H_2g}(X_1^+) - \frac{1-X_1}{Pe,g} \frac{dC_{H_2g}(X_1^+)}{dX} \tag{21}$$

$$C_{H_2L}(X_1^-) = C_{H_2L}(X_1^+) - \frac{1-X_1}{Pe,L} \frac{dC_{H_2L}(X_1^+)}{dX} \tag{22}$$

$$C_{c_1L}(X_1^-) = C_{c_1L}(X_1^+) - \frac{1-X_1}{Pe,L} \frac{dC_{c_1L}(X_1^+)}{dX} \tag{23}$$

$$C_{c_2L}(X_1^-) = C_{c_2L}(X_1^+) - \frac{1-X_1}{Pe,L} \frac{dC_{c_2L}(X_1^+)}{dX} \tag{24}$$

$$C_{s_1L}(X_1^-) = C_{s_1L}(X_1^+) - \frac{1-X_1}{Pe,L} \frac{dC_{s_1L}(X_1^+)}{dX} \tag{25}$$

$$C_{s_2L}(X_1^-) = C_{s_2L}(X_1^+) - \frac{1-X_1}{Pe,L} \frac{dC_{s_2L}(X_1^+)}{dX} \tag{26}$$

and the conditions at $X = 1$,

$$\frac{dC_{H_2g}}{dX} = 0 \qquad \frac{dC_{H_2L}}{dX} = 0 \tag{27 a,b}$$

$$\frac{dC_{c_1L}}{dX} = 0 \qquad \frac{dC_{c_2L}}{dX} = 0 \tag{28 a,b}$$

$$\frac{dC_{s_1L}}{dX} = 0 \qquad \frac{dC_{s_2L}}{dX} = 0 \tag{29 a,b}$$

where X_1^- designates the position just inside the exit of the preheater and X_1^+ is the position just inside the inlet of dissolver.

Numerical Solution Technique

The set of first order ordinary differential design equations (8)-(13) for the preheater and transfer line section of SRC reactor can be integrated numerically from $X = 0$ to $X = X_1$ using a Runge-Kutta 4th order method. Once these equations are solved, we then proceed to solve the set of second order differential design equations (15)-(20) for the dissolver section of the SRC reactor. Equations (15)-(20) can also be integrated from $X = X_1$ to $X = 1$ using a 4th order Runge-Kutta procedure. In performing the integration, these second order differential equations have to be transformed into a system of first order differential equations. In order to integrate the system of first order differential equations from $X = X_1$ to $X = 1$, it is necessary to specify as many additional boundary conditions at $X = X_1$ as there are conditions to be satisfied at $X = 1$, we need six additional conditions at $X = X_1$, namely $C_{H_2g}(X_1^+)$, $C_{H_2L}(X_1^+)$, $C_{c_1L}(X_1^+)$, $C_{c_2L}(X_1^+)$, $C_{s_1L}(X_1^+)$, and $C_{s_2L}(X_1^+)$.

These values have to be guessed initially and successively adjusted to satisfy boundary conditions at $X = 1$. The Newton-Raphson method is used to make this adjustment.

In some cases when some of the parameters appearing in the governing differential equations (8-13) and (15-20) become very large, these differential equations may suffer from a difficulty known as stiffness when numerical solution of the equations is attempted. In such cases, the classical fourth order Runge-Kutta integration technique may fail to integrate the system of stiff equations due to numerical instability. However, it has been found that Gear's method (1971 a,b) is very powerful for solving stiff differential equations, and therefore, its use is recommended when the fourth order Runge-Kutta integration technique fails.

Results and Conclusions

In this section, data from the Wilsonville SRC pilot plant will be compared with results predicted using the model proposed in this paper. The operating conditions and reactor configuration at Wilsonville will be employed in the calculation of the extent of coal dissolution, hydrodesulfurization and hydrogen consumption based on the present proposed model.

The following operating conditions and reactor configuration were used in the simulation:

Coal Type	Kentucky 9/14 mixture
Hydrogen Pressure	1700 psig
Dissolver Temperature	820° F
Slurry Concentration	25%
Coal Feed Rate	500lb./hr.
Gas Feed Rate	11.7 scf/lb. of coal
Hydrogen Concentration	85%
Dissolver Diameter	12 in.
Preheater Diameter	1½ in.
Transfer line Diameter	1½ in.
Preheater Volume*	1.6 ft.^3
Transfer line Volume	1.5 ft.^3
Dissolver Volume	18.0 ft.^3
Mean Reaction Temperature of Preheater and Transfer line	700° F

* The actual coal conversion reaction is initiated in the preheater coil. The temperature in this coil increases from 100° F to 800° F. Since the rate of conversion below 600° F is expected to be low, the reaction volume for the preheater was arbitrarily defined as the volume of that portion of the coil in which the temperature exceeds 600° F.

Based on the above conditions the following data can be obtained from literature correlating equations, which were needed in order to solve the design equations:

	Preheater/Transfer Line		Dissolver
$\hat{v}_L$	21.3 cm/sec	$\hat{v}_L$	0.335 cm/sec
$\hat{v}_g$	102.7 cm/sec	v_g	1.80 cm/sec
Z_1	253 ft.	Z_2	23 ft.
$N_{Pe,L}$	1.18×10^3	$N_{Pe,L}$	0.97
$N_{Pe,g}$	4.83×10^2	$N_{Pe,g}$	4.66
f_g	0.44	f_g	0.06
$k_c a$	3.57×10^{-1}/sec	$k_c a$	5.53×10^{-2}/sec

Preheater/Transfer Line (cont.)		Dissolver (cont.)	
Henry's Constant at 700°F	$2.8 \dfrac{\text{g/cc of } H_2 \text{ in vapor}}{\text{g/cc of } H_2 \text{ in liquid}}$	Henry's Constant at 820°F	$2.5 \dfrac{\text{g/c.c of } H_2 \text{ in vapor}}{\text{g/c.c of } H_2 \text{ in liquid}}$

Several cases were studied in this paper, and the parameters chosen for these are listed in Table 1.

Case A: simulates the Wilsonville SRC pilot plant. The yield of coal dissolution predicted by the present proposed model is 92% which is in good agreement with that measured under similar conditions in the Wilsonville pilot plant. The actual yield in the pilot plant was also around 92%.

Cases B & C: investigate the effect of mass transfer on the SRC process. In these two cases the mass transfer coefficients were chosen as 1/10 and 1/50 of that of Case A. The coal dissolution is reduced from 92% for Case A to 90.7% for Case B and to 85.5% for Case C. The reason for this is obvious because for the lower mass transfer coefficient, $k_c a$, the dissolved hydrogen concentration in the solvent will also be lowered. Since the coal dissolution rate depends on the second power of the dissolved hydrogen concentration as can be seen from eqs. (4) and (5), the reduction in coal dissolution is expected. However, the reduction of the hydrogen mass transfer coefficient does not effect the extent of hydrodesulfurization, because the desulfurization rate does not depend on the dissolved hydrogen concentration (eqs. 2 and 3).

Cases D & E: investigate the effect of Peclet number in the dissolver section on the yield of coal dissolution, hydrodesulfurization and hydrogen consumption. For a given reactor and given operating conditions, there will be a corresponding Peclet number. The higher the value of the Peclet number, the closer a plug flow condition will be approached; the lower the value of the Peclet number, the closer the well-mixed condition will be approached. If the Peclet number is in the intermediate range, say, $0.1 < N_{Pe} < 20$, then neither of the above mentioned idealized situations obtains. In this intermediate region, the axial dispersion model may be used. In general, the yield for a reactor with higher Peclet number is higher than that with lower Peclet number. This can be seen from Cases D & E where both the gas phase and liquid phase Peclet number in the dissolver section were chosen as 0.1, and the mass transfer coefficients were chosen respectively as equal to Cases A and C. The coal liquefaction yield for Case D is 89.1%, which is about 2.9% lower than that for Case A; for Case E the coal dissolution is 82%, which shows a 3.5% decrease compared to Case C. The Peclet numbers for both Cases A & C are $N_{Pe,L} = 0.97$ and $N_{Pe,g} = 4.66$. From the above comparisons, we see that the effect of Peclet number on coal dissolution becomes more significant when the mass transfer coefficient is low.

The detailed concentration profiles are given in Figs. 1-4. Figs. 1 and 2 show the hydrogen concentration profile in the vapor phase and liquid phase, respectively, along the reactor. The coal concentration, $C_c = C_{c_1}L + C_{c_2}L$, profiles are shown in Fig. 3, and also shown in Fig. 4 is the organic sulfur concentration, $C_s = C_{s_1}L + C_{s_2}L$, profiles. The yields of coal liquefaction, hydrodesulfurization and hydrogen consumption rate for Cases A to E are also tabulated in Table 2.

In addition to the above five cases, cases for which the mass transfer coefficient was twice and ten times that of Case A were also simulated. The results showed that the hydrogen consumption and coal dissolution were not significantly different from Case A. This implies that the Wilsonville SRC pilot plant is already operating in a kinetically limited regime and that mass transfer is not the rate controlling step. These two cases were not plotted on Figs. 1-4 because they were essentially indistinguishable from Case A. This result is reasonable, since no external catalyst, other than the naturally occuring coal mineral matter, is present in the SRC reactor. It is known, however, that coal minerals can and do catalyze both hydrogenation and desulfurization reactions in the SRC process (Henley, et al, 1976; Prather, et al, 1976; Guin, et al, 1977). Under operating conditions near those of Case A studied here, the organic sulfur removal and the hydrogen consumption at the Wilsonville SRC pilot plant averaged around 50% and 2% based on weight of maf coal feed, respectively. As observed from Table 2, the corresponding values from the model are about 50% lower than those determined experimentally in the Wilsonville SRC pilot plant under apparently similar operating conditions. There are two reasonable explanations for this deviation. First, it should be noted that in the present model the hydrogen consumption only includes the actual amount of hydrogen chemically reacting in the preheater and dissolver, i.e., no other losses such as from flash systems, waste vents, imcomplete separations, leaks, etc., are included. Secondly and perhaps more importantly, it has been observed that because of the very low upward liquid velocity, an accumulation of coal mineral matter occurs in the Wilsonville SRC reactor. This would cause increased desulfurization and hydrogenation because of the catalytic nature of these minerals. Recent lower hydrogen consumption with an initially clean reactor at Wilsonville tends to verify this latter result. Also it has recently been shown (Guin, et al, 1977), that the addition of iron compounds, predominant in coal minerals, can increase the extent of organic sulfur removal by around 100%. Finally, it should be noted that the kinetics rate expressions used herein are strictly valid only for the Kentucky 9/14 coal with a creosote oil solvent. For other coals and solvents, different rate expressions would be required for the most accurate results.

CONCLUSIONS

1. The mixing and flow pattern of the multi-phase reactor is taken into account through the axial dispersion term, which has not been previously utilized for the SRC reactor modeling.
2. The mass transfer of hydrogen from the gas phase into the liquid phase is also 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 probably due to the accumulation of catalytic coal minerals in the Wilsonville reactor, giving higher rate constants.

Nomenclature:

D_g	gas phase axial dispersion coefficient
D_L	liquid phase axial dispersion coefficient
v_{slip}	two phase slip velocity
v_g	bubble phase velocity, m/sec
v_L	liquid phase velocity, m/sec
$\hat{v}_g$	bubble phase superficial velocity, m/sec
v_L	liquid phase superficial velocity
f_g	gas holdup
a	specific gas-liquid interfacial area
Pe, g	$= \frac{v_g (L-z_1)}{Dg}$, gas phase Peclet number in the dissolver section
Pe,L	$= \frac{v_L(L-z_1)}{D_L}$, liquid phase Peclet number in the dissolver section
z_1	length of preheater plus transfer line section
z_2	length of dissolver
X_1	dimensionless axial length of preheater plus transfer line z_1/L
X	dimensionless axial coordinate, z/L
K_c	liquid phase mass transfer coefficient
$K_c a$	volumetric liquid phase mass transfer coefficient
z	coordinate in the axial direction
H_o	Henry's law constant of hydrogen in creosote oil
c_{ij}	feed concentration of component i in phase j
L	total length of reactor, $L = Z_1 + Z_2$
C_{ij}	$= c_{ij}/(H_j^k c_r)$ dimensionless concentration for ith component in the j phase.
c_{ij}	concentration of component i in the j phase
c_r	reference concentration

Superscript:

o	denotes initial condition
I	in the preheater section
II	in the dissolver section
k	= 0 for gas phase; = 1 for liquid phase

Subscript:

g	gas phase
L	liquid phase

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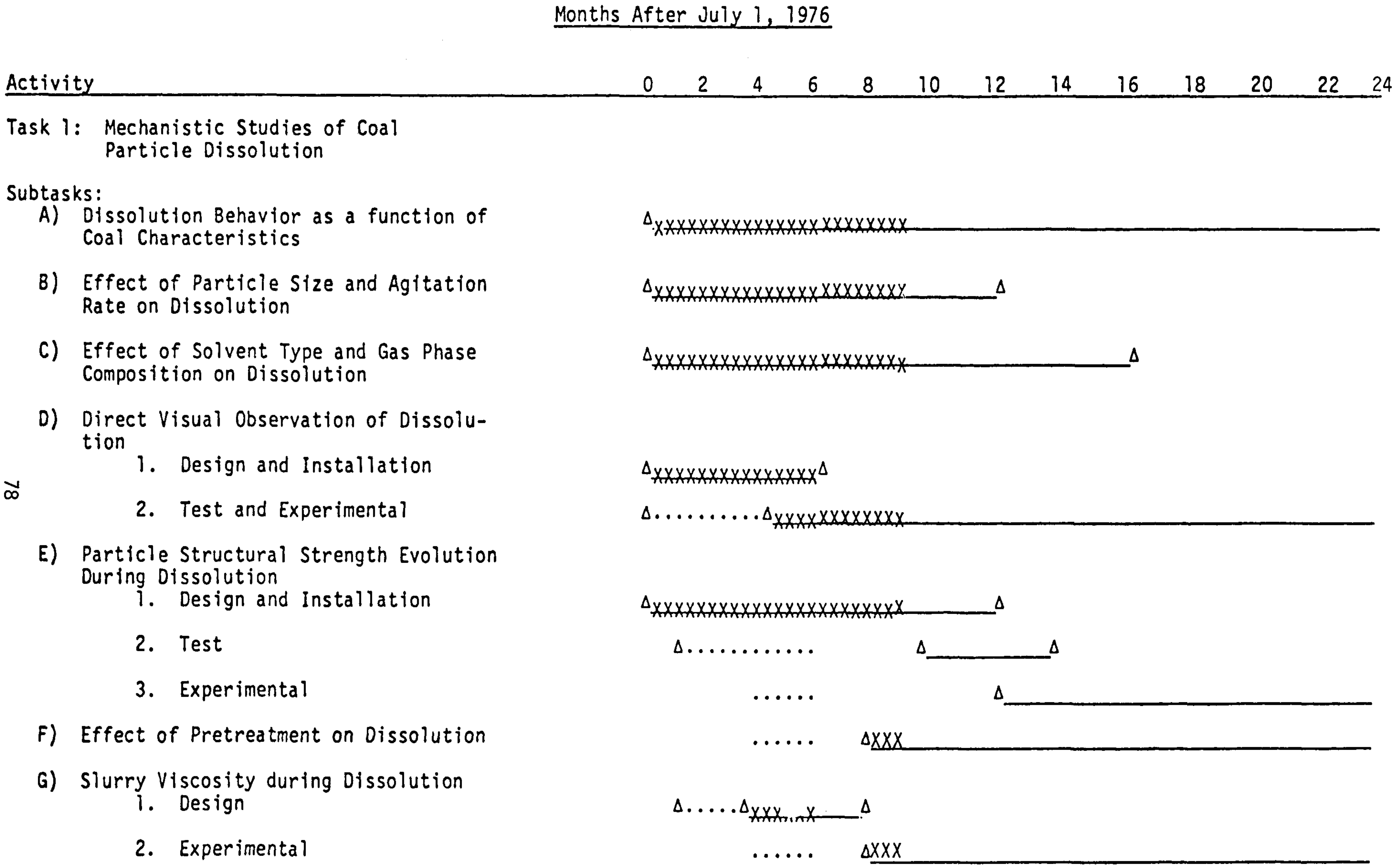

Figure 1. Work Schedule

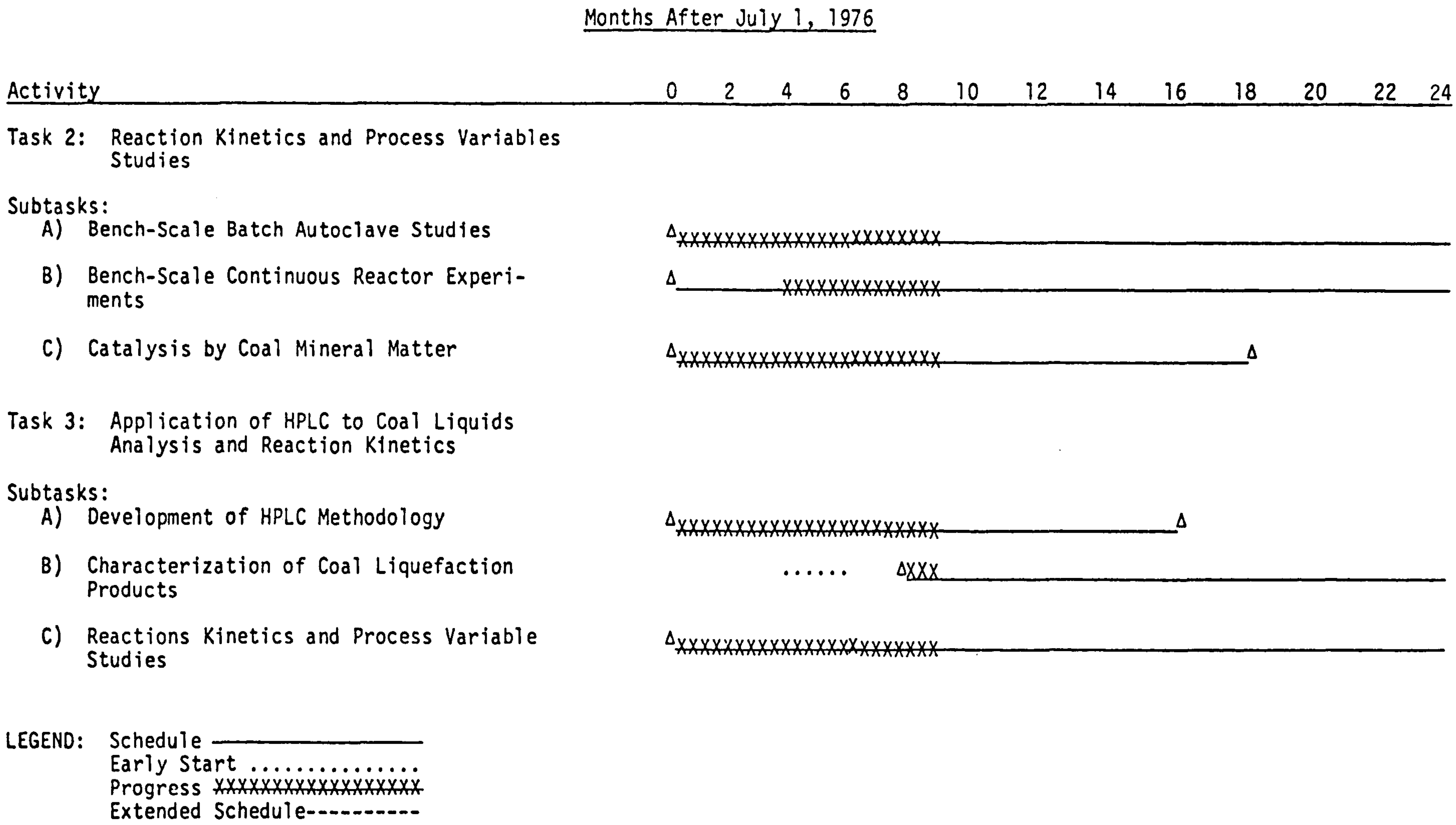

Figure 1 (continued)

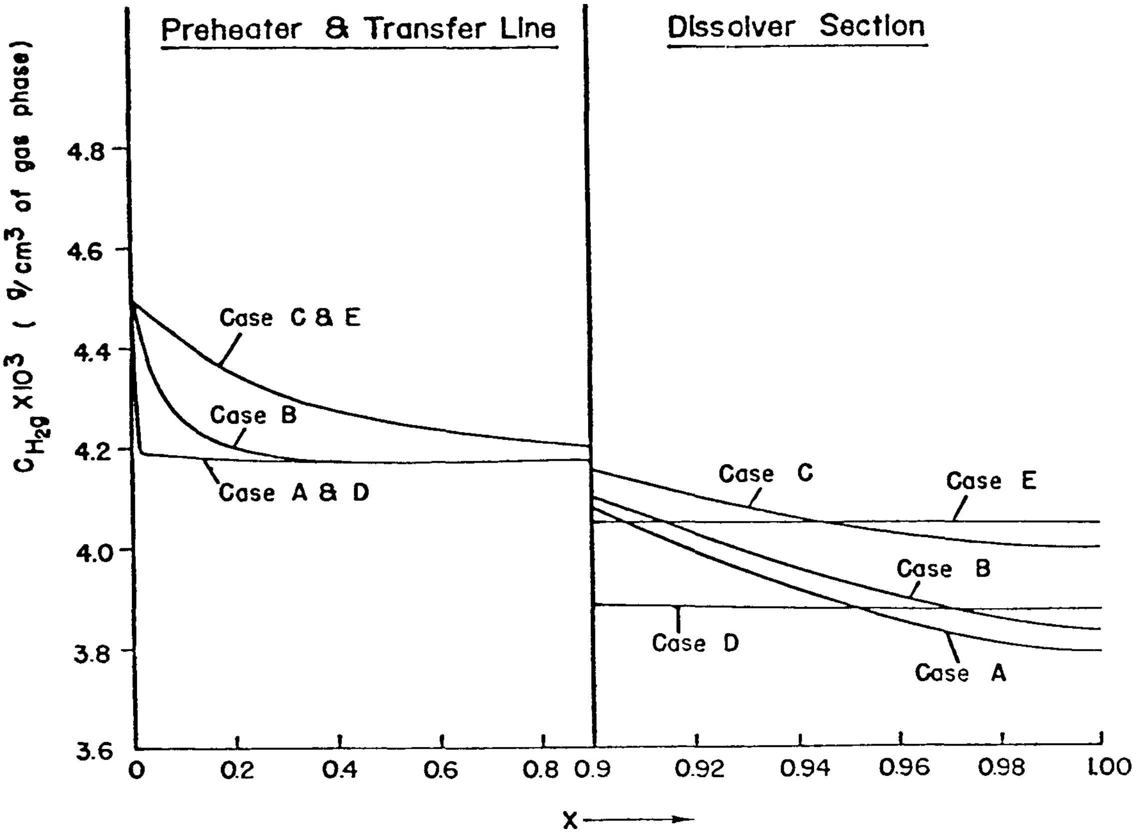

Figure 1. Vapor Phase Hydrogen Concentration vs. X

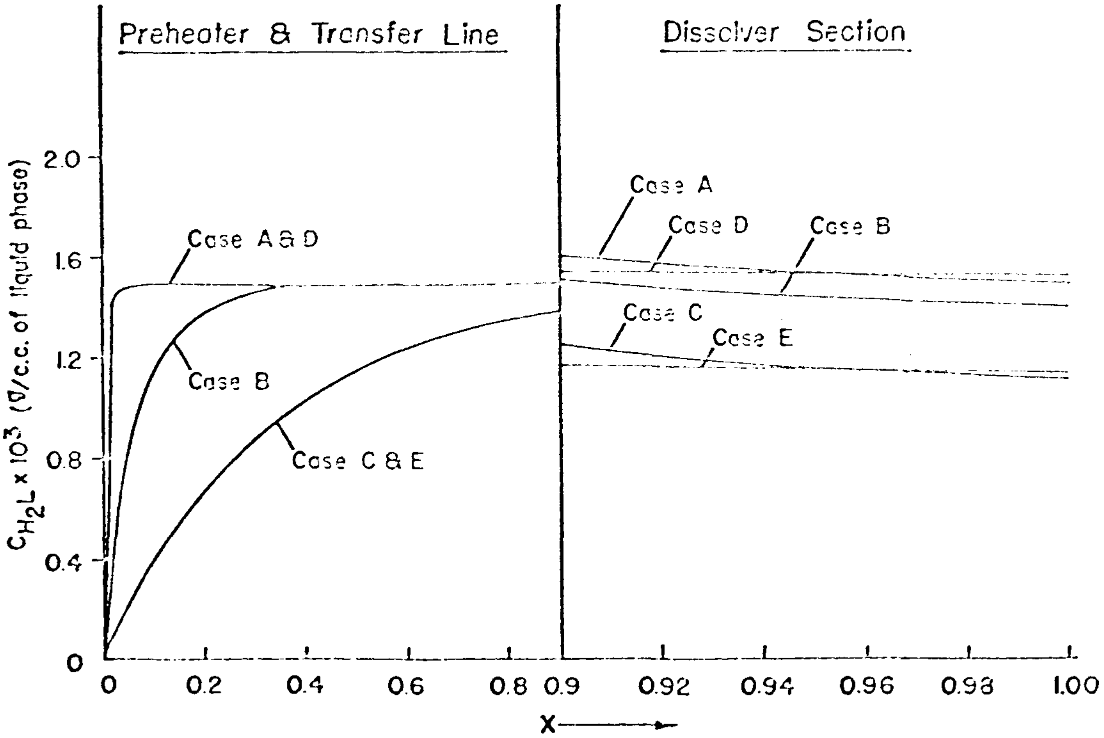

Figure 2. Liquid Phase Hydrogen Concentration vs. X

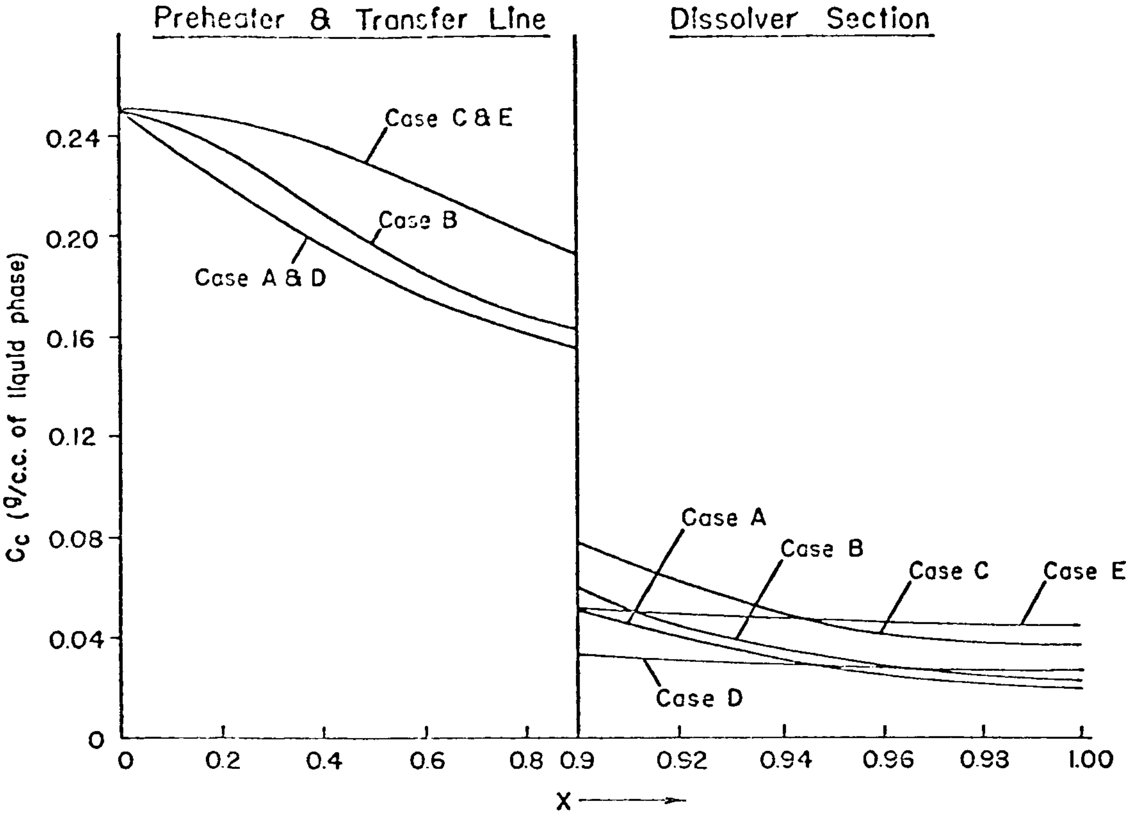

Figure 3. Coal Concentration vs. X

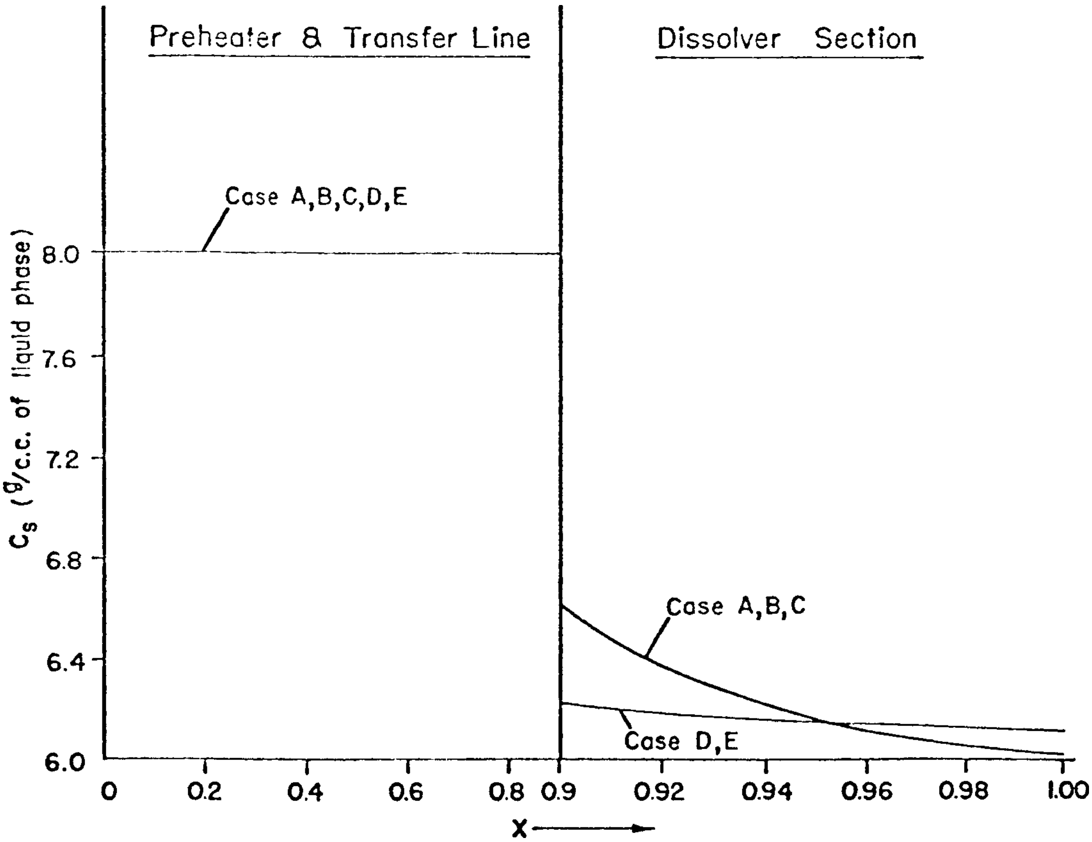

Figure 4. Sulfur Concentration vs. X

X-ray Fluoresence Analysis of Trace Metals in Solvent Refined Coal

J. W. Prather, A. R. Tarrer and J. A. Guin

Chemical Engineering Department
Auburn University
Auburn, Alabama 36830

Introduction

This work was undertaken to ascertain the ability of Energy Dispersive X-ray Fluoresence (EDXRF) analysis to determine trace element content of Solvent Refined Coal (SRC). As a result of recent improvements in the design of solid state detectors for X-ray Fluoresence it is now possible to do very rapid simultaneous quantitative analysis of a large number of elements. In this work some 17 elements are quantitatively analyzed in both raw feed coal and product SRC from the Wilsonville SRC Pilot Plant, Wilsonville, Alabama.

The content of trace metals in SRC product and in feed coal is important for several reasons: Certain metals, particularly 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, then trace metals such as Ca, Na, and V present potential corrosion or fouling problems. When the feed coal has a high oxygen and a low sulfur content, a substantial portion of western, sub-bituminous coal, for example, has a low sulfur (~0.7%) and a high oxygen (~17%) content, trace metals such as Ca react with CO_2 formed in the SRC dissolver and tend to collect in the dissolver, eventually resulting in plugging problems. Trace metals such as As in SRC product present potential environmental problems. Also, metals such as Fe and Al are present in sufficient quantity in the feed coal that the SRC mineral residue represents an attractive source of these metals when current sources have been depleted.

Analysis of trace elements in coal has been the subject of many earlier papers (1,2,3). In fact, analytical methods, specifically, atomic absorption, (4,5) have been presented for determining the content of trace metals in clean coal products such as SRC product. However, because of the large number of analyses required to maintain reasonable quality control of SRC product, etc., alternative methods that are hopefully more rapid and less expensive than those currently available are needed. Application of EDXRF to perform assays of feed coals and SRC products is attractive because it allows simultaneous analysis of trace elements found in feed coals and SRC products. This work demonstrates that EDXRF is an effective method for determining the content of trace metals in coal and coal-derived products.

Experimental

Equipment

All EDXRF analyses were done on a Kevex 0810RW X-ray Fluoresence System (Kevex Corporation, Burlingame, Ca. 94010) consisting of a 0810A X-ray Subsystem, 5100C analyzer, 5100 X-ray Spectrometer Rigaka Gigerflex 3kW X-ray generator, (60 kV and 180 ma) Digital Electronics Corporation PDP 11/03 Computer with RX01 dual floppy disk bulk storage. The system uses a high power X-ray tube (Ag target) to produce X-ray from a series of selectable secondary targets (ti, Ge, Mo, and Sn). The spectrometer uses a solid state detector of 30 mm^2 active area that has resolution of <165eV @ 1KHz.

Atomic Absorption experiments for iron were done on a Perkin-Elmer Model 305A Atomic Absorption spectrophotometer (Perkin-Elmer Corporation, Norwalk, Connecticut 06856) using an acetylene/air flame and a wavelength setting of 249 nm. Sulfur determinations were made using a Leco model 521-500 sulfur analyzer specially fitted for low level sulfur detection (Laboratory Equipment Corporation, St. Joseph, Michigan 49085).

Procedure

Approximately 10 g. samples of all coals and SRC's were first ground so that the entire sample passed through a 325 mesh screen. The samples were then dried in a vacuum oven at 105°C for at least 3 hours. From these samples 1.25 inch pellets were made using a boric acid backing and were analyzed by EDXRF under a vacuum of 5×10^{-4} torr. Also, fractions of the same samples were used to perform Leco sulfur, C, H and N, and Atomic Absorption analyses.

The raw EDXRF data were analyzed using the Kevex matrix correction program, and adaptation of the shell EXACT (6) program. The EXACT program employs a fundamental parametric method which accounts for matrix interactions due to absorption and enhancement for all the elements in the sample. The EXACT model is basically similar to models presented by Sherman (7), Shiraiwa (8) and Criss and Birks (9) with simplifications.

Results

Table 1 gives a comparison between EDXRF and two methods, Atomic Absorption (AA) and Leco, commonly used in this laboratory for analysis of iron and sulfur, respectively. At the bottom of Table 1 are analyses for three standards (Certified Atomic Absorption Standard, 1000 ppm iron, Fisher Scientific, FairLawn, New Jersey 07410; Calibration Standard no. 764-547 (2.02 ± 0.03% S) and Calibration Standard no. 764-545 (0.31 ± 0.02% S) LECO Corporation, 3000 Lakeview, St. Joseph, Michigan 49085). These standards were purchased for use in calibration of atomic absorption and LECO analysis. In all cases EDXRF gave the best accuracy for the standards analysis.

Table 2 gives the EDXRF elemental analyses for 12 coals and SRC's. As expected smaller amounts of the 17 elements analyzed for were detected in the SRC products than in the respective feed coals.

Little would actually be gained by an element by element comparison of the various coals and SRC's. On the other hand, Figure 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. At this time experiments are in progress to show that the same relationship is also true for SRC product.

Summary and Conclusion

It has been shown that EDXRF is capable of analyzing coals and SRC's for elemental content. These analyses provide simultaneous results for several important elements, namely sulfur, iron and calcium, as well as percent ash. These analyses presently take well over 2 hours per sample to complete, but by using EDXRF this time can be reduced to less than one hour per sample. Furthermore, EDXRF has an added feature in that it may be automated, leading to even shorter analysis times per sample. Thus, EDXRF can be concluded to be an effective tool that can provide very accurate and rapid analyses of coals and SRC product for their elemental content.

Acknowledgement

The authors are grateful to the Fossil Fuel Division of the Energy Research and Development Administration for support of this work under Contract No. E(49-18)-2454. They also wish to thank the personnel of Southern Services, Inc. who kindly supplied coal and SRC samples for this work. The authors also wish to acknowledge the technical assistance of G. A. Thomas and W. R. Glass of the Auburn University Coal Conversion Laboratory.

TABLE 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	
Pittsburg #8				
Fe	0.561	0.615		
S	2.22		2.87	
Monterrey				
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

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TABLE 2

EDXRF Analysis of SRC and Coal

Element	A	B	C	D	E	F
			wt.%			
Al						
Si		1.612		1.813		2.097
P	0.0755	0.183	0.0657	0.186	0.0840	0.251
S	0.723	2.24	1.04	2.22	0.755	2.76
Cl	0.0097	0.0177	0.0053	0.105		
K	0.001	0.0977		0.100		0.112
Ca	0.0087	0.0817	0.0144	0.910	0.0024	0.148
Ti	0.0092	0.0383	0.0088	0.0537	0.0178	0.0549
V	0.0037	0.0089	0.0049	0.0099	0.0036	0.0149
Cr		0.0036	0.0026	0.0025	0.0023	0.0058
Mn	0.0018	0.0022	0.0008	0.0043	0.0026	0.0048
Fe	0.0427	0.697	0.0191	0.561	0.0199	0.629
Ni	0.0002	0.0010	0.0008	0.0038	0.0010	0.0020
Cu	0.0003	0.0012	0.0006	0.0028	0.0014	0.0017
Zn	0.0005	0.0013	0.0007	0.0038	0.0006	0.0015
As	0.0001	0.0008	0.0002	0.0005	0.0001	0.0006
Br	0.0002	0.0003	0.0004	0.0009	0.0003	0.0005
Sr		0.0014		0.0132		0.0014

A	Western Kentucky SRC
B	Western Kentucky 9/14 Coal
C	Pittsburg #8 SRC
D	Pittsburg #8 Coal
E	Illinois #6 SRC
F	Illinois #6 Coal

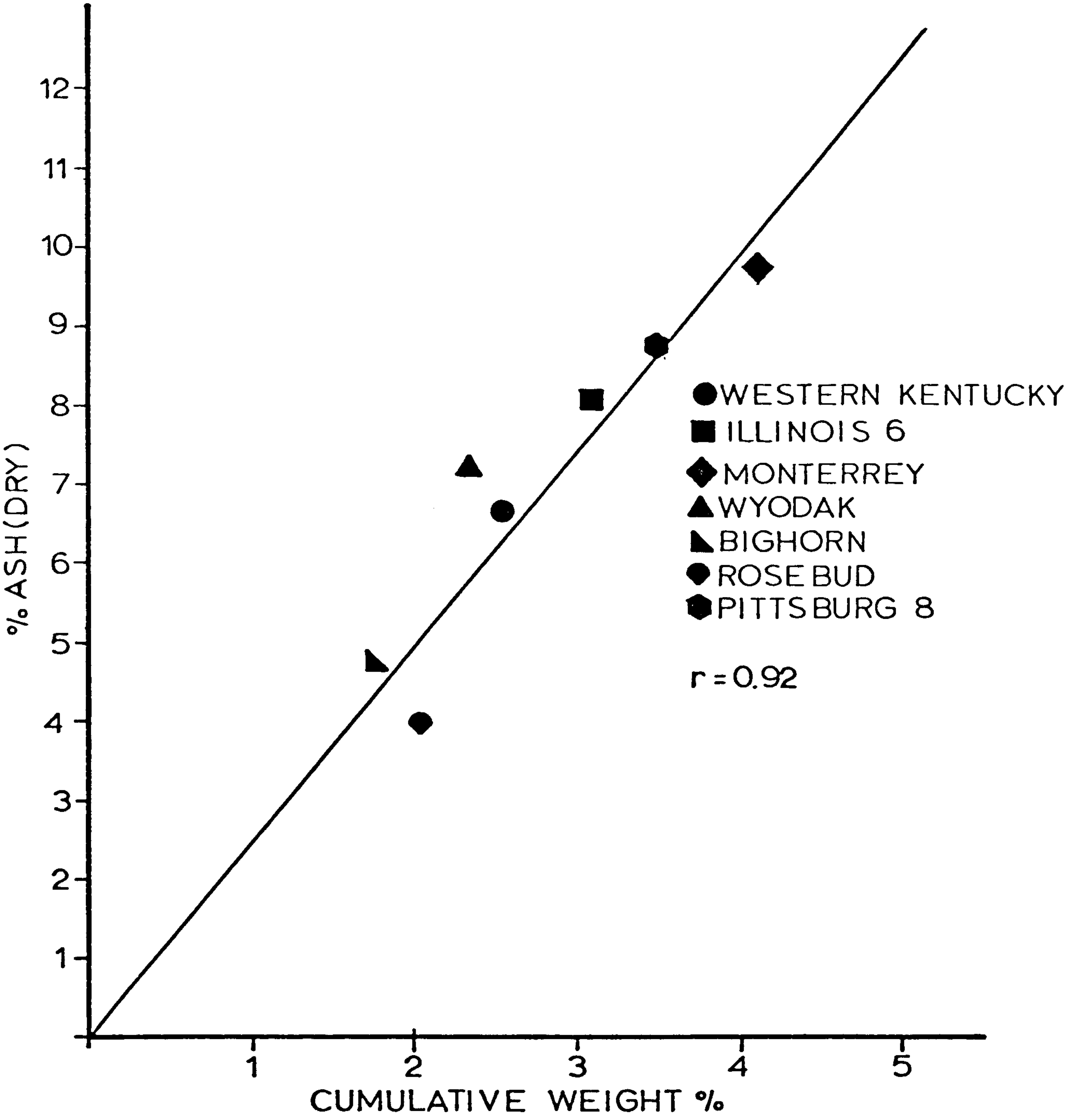
TABLE 2 CONTINUED

EDXRF Analysis of SRC and Coal

			wt.%			
Element	G	H	I	J	K	L
Si		1.073	0.1021	2.578	0.821	0.903
P	0.0306	0.143	0.0953	0.2193	0.122	0.101
S	0.152	0.6371	1.172	3.070	0.976	0.582
Cl	0.0036	0.0536		0.241	0.106	
K		0.0310	0.0040	0.1245	0.0266	0.0204
Ca	0.0162	0.858	0.0022	0.2750	0.557	0.473
Ti	0.0078	0.0585	0.0133	0.0617	0.0352	0.0511
V	0.0023	0.0353	0.0034	0.0104	0.0124	
Cr	0.0017	0.0033		0.0090	0.0110	0.0041
Mn	0.0012	0.0031		0.0087	0.0063	0.0025
Fe	0.0228	0.2615	0.0450	0.1651	0.466	0.2667
Ni	0.0013	0.0006		0.0015	0.0019	0.0014
Cu	0.0017	0.0056	0.0010	0.0201	0.0017	0.0058
Zn	0.0005	0.0020	0.0004	0.0016	0.0004	0.0013
As	0.0001	0.0004	0.0001	0.0006	0.0003	0.0005
Br		0.0002	0.0004	0.0005	0.0008	0.0001
Sr	0.0001	0.0137	0.0007	0.0013	0.0088	0.0074

G Wyodak (Amax) SRC
H Wyodak (Amax) Coal
I Illinois (Monterrey) SRC
J Illinois (Monterrey) Coal
K Rosebud Coal
L Big Horn Coal

FIGURE 1


% ASH(DRY)
12
11
10
9
8
7
6
5
4
3
2
1
1
2
3
4
5
CUMULATIVE WEIGHT %
● WESTERN KENTUCKY
■ ILLINOIS 6
◆ MONTERREY
▲ WYODAK
◣ BIGHORN
⬟ ROSE BUD
⬢ PITTSBURG 8
r = 0.92

Particle Size Analysis in the SRC Process by Coulter Counter

C.W. Curtis, A.R. Tarrer and J.A. Guin

Chemical Engineering Department
Auburn University
Auburn, Alabama 36830

Introduction

This work was undertaken to develop an effective rapid technique for determining particle size of undissolved solids in the Solvent Refined Coal (SRC) Process. Particle size distributions for SRC filter feed from the Wilsonville SRC Pilot Plant and autoclave reaction mixtures from the Auburn Coal Conversion Laboratory were measured using a Coulter Counter Model TA.

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] Presently, the Coulter technique is being applied to the 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[5] has shown the need for a reproducible method of determining particle size in SRC process streams.

Experimental

Equipment

Particle size determinations were performed on a Coulter Counter Model TA (Coulter Electronics, Hialeah, Florida) equipped with a Model TA External Size Calibrator II and an adjacent sample stand. The orifices normally used for the analyses were 100, 140, 200 and 280 µm.

Electron microscopy was performed using an AMR Model 1000 scanning Electron Microscope operating at 20KV with a tungsten source and an aluminum coated detector. The samples were coated with 60:40 gold-palladium using a Denton DV 502 vacuum evaporator. Optical microscopy was performed using a Wild Model M21 microscope equipped with a Polaroid MP-3 Land Camera.

Chemicals

Reagent grade ammonium thiocyanate (NH_4SCN) and dimethylformamide (DMF) obtained from Mallinckrodt prepared in a 5% solution was the electrolyte used for Coulter analysis. Metricel alpha -8 filters with 0.20µm pore size were used for filtering the electrolyte solution. Carbowax 400 obtained from Union Carbide was the dispersant used for optical microscopy.

Procedure

Calibration of each orifice was performed using polystyrene calibration standards of known diameter (supplied by Coulter Electronics) dispersed in isoton.

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

For scanning electron microscopy samples were prepared by sonicating and further diluting the Coulter samples. The particles were filtered on a 0.2µm filter and air dried. For optical microscopy, autoclave reaction mixtures were first sonicated and then dispersed in Carbowax 400. Hanging drop as well as slide preparations were used.

Verification

Verification of the Coulter technique by optical microscopy can be seen in Figure 1. Rigid polystyrene calibration spheres (9.99μm in diameter supplied by Coulter Electronics) were measured by optical microscopy under 500x magnification to have a diameter of 10.0μm. Subsequent analysis of the polystyrene's particle size by Coulter Counter agreed fully with the microscopy.

Results and Discussion

The Coulter technique measures the particle volume size distribution. The smallest particles measured had a diameter of 1.59μm with an overall diameter range of 1.59 to 128μm. All measurements were taken within the optimum range of the orifice. Particle size distributions were obtained for autoclave reaction mixtures and Wilsonville filter feed of Amax, Western Kentucky, Pittsburgh Seam, and Monterey coals. The particle size distribution measurements for each coal sample can be accurately reproduced within ± 10%. A mean particle size is obtained graphically by plotting the normalized cumulative particle volume percent versus particle diameter and then obtaining the mean particle size at the 50% volume level.

The initial mean particle size for unreacted coal was between 28.8 - 40.0μm. Table I shows the mean particle size in terms of particle diameter for four autoclaved coals reacted at 410°C for three different time intervals. Under autoclave conditions, the mean particle size varies significantly among the different coals. Within the time range studied the mean particle size for Monterey and Pittsburgh Seam coals remained essentially constant; however, the mean particle size of Western Kentucky coal increased with time while that of Amax coal decreased. The mean of Amax coal leveled off at 9.6μm after 4 hours. The temporal behavior of the particle size of each coal can be directly correlated to its dissolution rate and behavior. Both Monterey and Pittsburgh Seam coals dissolve very rapidly, leaving essentially only mineral matter after 15 minutes of reaction. Amax coal, however, is a slow dissolver which accounts for the decrease in particle size over the time period studied. Western Kentucky coal dissolves very rapidly but is sticky and adhesive; increasing reaction time allows the particles time to adhere to one another forming larger particles.[6]

The Wilsonville filter feed particle size distributions for each coal closely resembled the autoclave reaction distribution (an example is shown in Table II) except for Western Kentucky coal which showed a significant shift to smaller particles. Generally, the Wilsonville filter feed distributions showed greater variation within each sample than did the autoclave reactions resulting in a larger standard deviation for each volume range. A comparison of the mean particle size of Wilsonville filter feed to Auburn autoclave reaction mixtures is shown in Figure III. For each coal the mean particle sizes compare very closely with the exception of Western Kentucky coal. This difference can again be attributed to the adhesive nature of the Western Kentucky particles. In the filter feed the particles will tend to adhere to one another forming larger particles which stay in the dissolver while the smaller particles are elutriated out of the dissolver.

Optical and electron microscopy verified the presence, size, and character of the particles being counted by the Coulter Counter. Optical microscopy allowed observation of the particles in a solution matrix. Scanning electron microscopy permitted isolation of the particles from the oil matrix and allowed the particles to be individually observed. The unregular nature and individual character of the particles are shown in the micrographs in Figure 2-7.

Process Applications

Filterability of a solid/liquid slurry depends on the size distribution of the particulates entrained in the slurry as well as other factors such as viscosity, adhesive forces among the particles (i.e., whether the particles are sticky or discrete and unattractive) etc. 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 are compared with their associated cake resistivities.

Filtration rates for Amax, Western Kentucky and Monterey coal/oil slurries have been extensively studied under test conditions and without the incorporation of bodyfeed at the Wilsonville SRC Pilot Plant. Pittsburgh Seam coal/oil slurries have only been tested with bodyfeed. Table IV shows the cake resistivities calculated for the slurries run 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 taken into account, Western Kentucky ranks second in filterability as well as mean particle size. Cake resistivity is a function of the porosity of the cake which is directly related to particle volume. Particle volume is measured directly by the Coulter technique. In conclusion, the Coulter Counter can give a good indication of the filterability of a particular SRC process stream and, thus, should prove to be a useful tool in optimizing operational conditions for solids separation.

The present Coulter technique has two main limitations. First, since particles less than 1.6μm are difficult to detect, the total particle size range of the SRC effluents cannot be studied. The effect of the very small particles on filterability is not precisely known; however, it is very likely that particles below 2μm play a significant role in screen blinding. The second limitation is that carbonaceous agglomeration of SRC itself is difficult to detect because approximately 96% of SRC dissolves in the electrolyte. Detection of the formation of solid agglomerates would be highly desirable; for the accumulation of solids in the SRC dissolver has presented significant problems in processing certain types of coals, particularly those containing high concentrations of calcium. One reason for this accumulation, however, is commonly thought to be the formation and growth of calcium carbonate ($CaCO_3$) crystals. Inorganic agglomeration due to $CaCO_3$ crystal formation should be easily detectable by the Coulter technique presented herein since $CaCO_3$ is essentially insoluble in DMF.

On-line Coulter analysis of the SRC process stream would allow immediate detection of changes in the size distribution of the solvent stream particles. Through on-line analysis more precise correlations between mean particle size and filterability would be possible. Also, by monitoring the size distribution of particulates in the upstream and downstream to the filter, a direct reading on filtering efficiency could be obtained. Coulter analysis is also an effective method for determining the efficiency of other solid-liquid separation techniques, such as centrifuging and hydrocloning, currently being tested in the SRC process.

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TABLE I

Mean Particle Size of Autoclave Reacted Coals
at 15, 30 and 60 Minutes

Autoclave Conditions
Temperature: 410°C
Pressure: Hydrogen 2000 psi
Solvent/Coal: 3/1
Stirrer: 1000 rpm

Time (min)	Mean Particle Size (μm)*			
	Amax	Western Kentucky	Monterey	Pittsburgh Seam
15	14.0	7.0	5.2	6.0
30	9.1	8.2	5.5	5.5
60	8.0	10.6*	4.8	6.0

---

* Through subsequent calculations, the population mean can be calculated. For example, Western Kentucky coal, reacted for 60 minutes, has a population of 2.0μm.

TABLE II

Particle Size Distributions of Amax Coal Autoclave Reaction Mixture and Wilsonville Filter Feed

Particle Diameter (μm)	% Volume Distributions Amax Autoclave 60 minute	Amax Wilsonville filter feed
1.59	10.9 ± 0.6	10.4 ± 1.8
2.00	8.7 ± 1.2	6.3 ± 1.4
2.52	6.6 ± 0.64	5.7 ± 0.6
3.17	5.5 ± 0.35	6.7 ± 0.7
4.00	5.6 ± 0.36	7.6 ± 0.8
5.04	6.4 ± 0.42	9.3 ± 0.7
6.35	6.9 ± 0.49	8.6 ± 1.0
8.00	8.2 ± 0.57	8.8 ± 1.1
10.08	9.0 ± 0.68	9.2 ± 1.3
12.7	9.7 ± 1.6	9.2 ± 1.7
16.0	9.2 ± 1.5	5.7 ± 0.8
20.2	7.0 ± 1.8	4.6 ± 2.0
25.4	4.6 ± 2.6	4.6 ± 2.8
32.0	1.3 ± 1.0	2.3 ± 2.7
40.3	0.6 ± 0.05	0.6 ± 0.1

TABLE III

Comparison of the Mean Particle Size of Wilsonville Filter Feed and Auburn Autoclave Reaction Mixtures

Coal Type	Date	Wilsonville Filter Feed Mean Particle Size μm	Auburn Autoclave Mean Particle Size μm
Monterey	10-20-76	4.5	
Monterey	11-15-76	3.7	
Monterey	11-10-76	3.8	
Monterey	Average	4.0	4.8
Amax	- - - -	7.2	
Amax	12-19-76	6.4	
Amax	1-28-77	7.5	
Amax	Average	7.0	8.0
Western Kentucky	4-17-76	6.8	
Western Kentucky	5-29-76	4.6	
Western Kentucky	Average	5.7	10.6
Pittsburgh Seam	7-22-75	6.2	6.0

TABLE IV

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 7)
Western Kentucky	1.13×10^{12}	60	5.7	(Ref 8)
Monterey	1.22×10^{12}	60	4.0	(Ref 8)

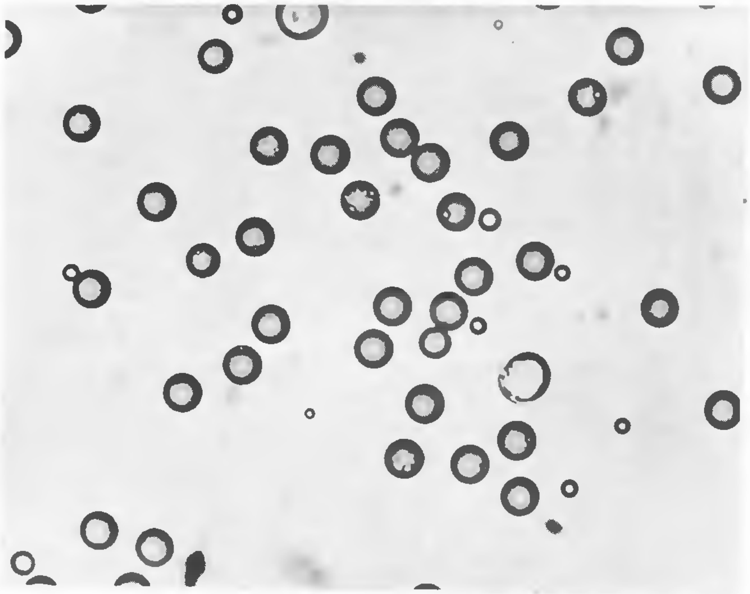


Figure 1

Verification of polystyrene particle size

1 cm = 20μm

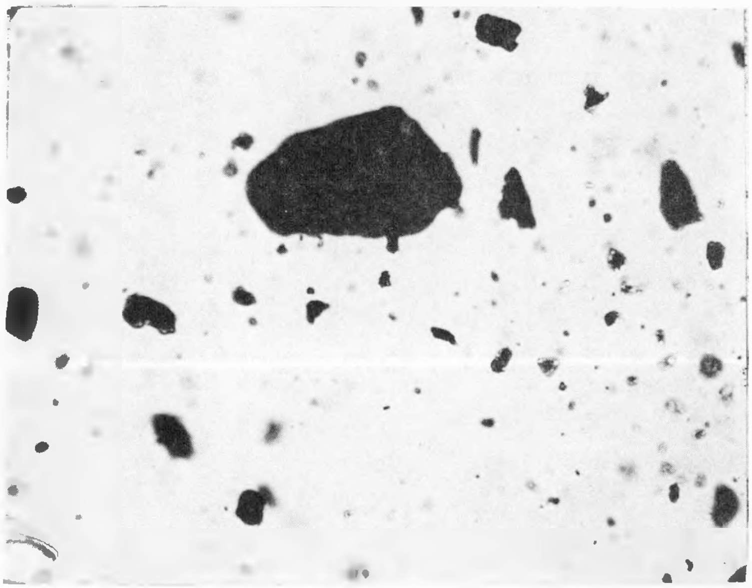


Figure 2

Photomicrograph of Amax coal particles (suspended in Carbowax) after 60 minute autoclave reaction (500x)

1 cm = 20μm

Figure 3

Photomicrograph of
Pittsburgh Seam coal particles
(suspended in carbowax) after
60 minute autoclave reaction
(500x)

1 cm = 20μm

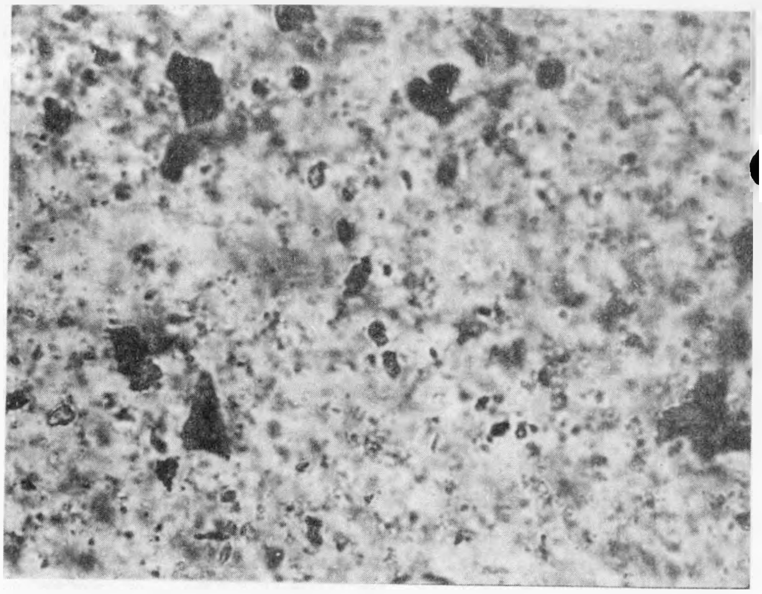


Figure 4

Photomicrograph of
Western Kentucky coal particles
(suspended in carbowax)
after 60 minute autoclave
reaction (500x)

1 cm = 20μm

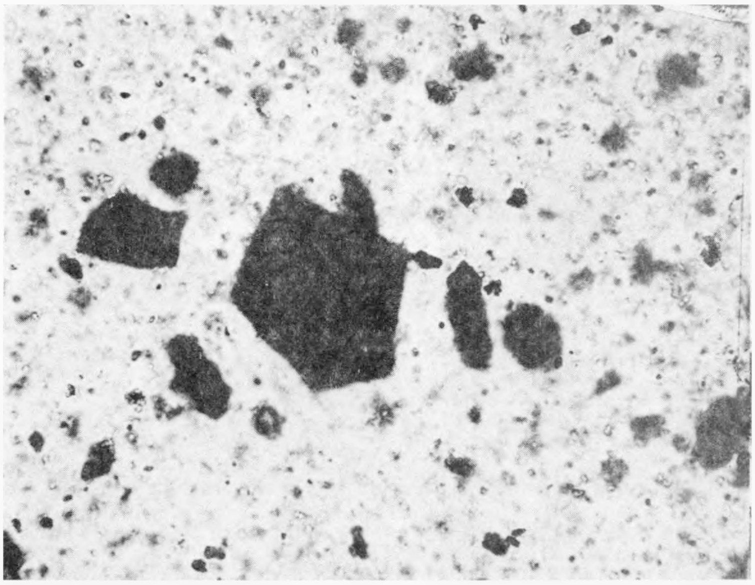


Figure 5

Electronicrograph of
Western Kentucky coal particles
(on a Metricel filter)
after 60 minute autoclave
reaction (2000x)

1 cm = 5μm

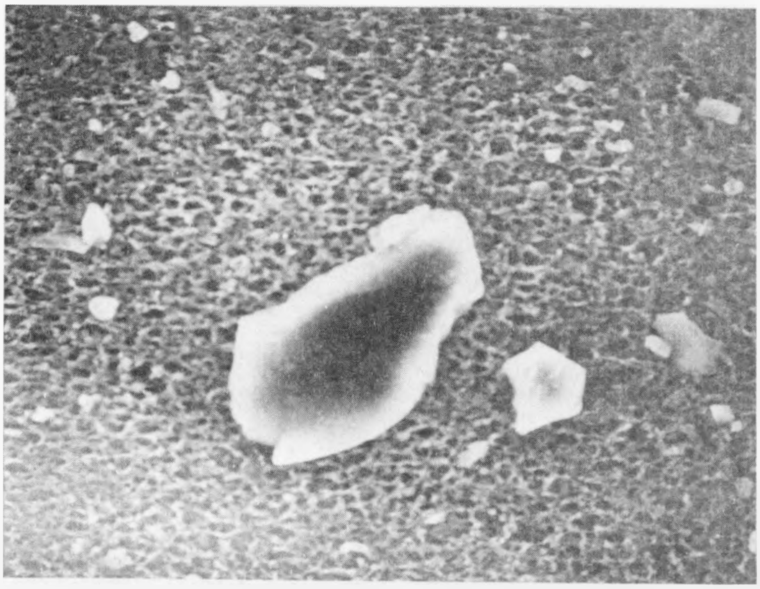


Figure 6

Electronmicrograph of Pittsburgh Seam coal particles (on a Metricel filter) after 60 minute autoclave reaction (10,000x)

1 cm - 1μm

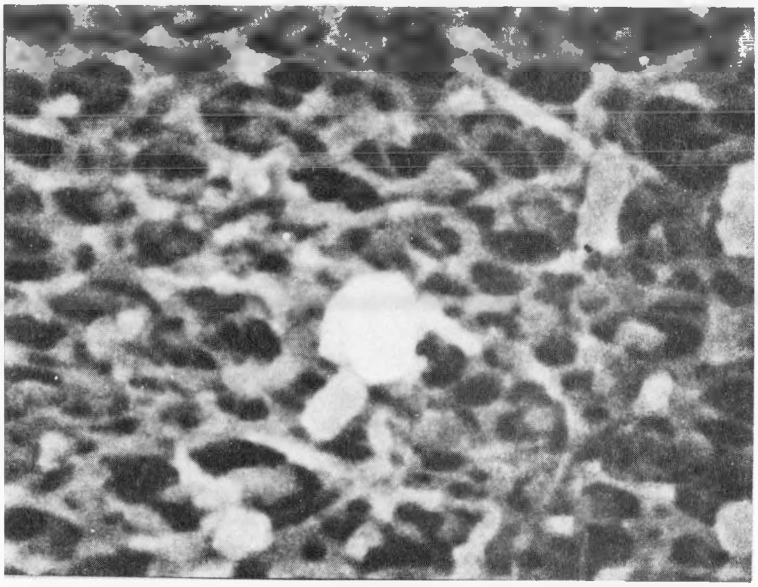
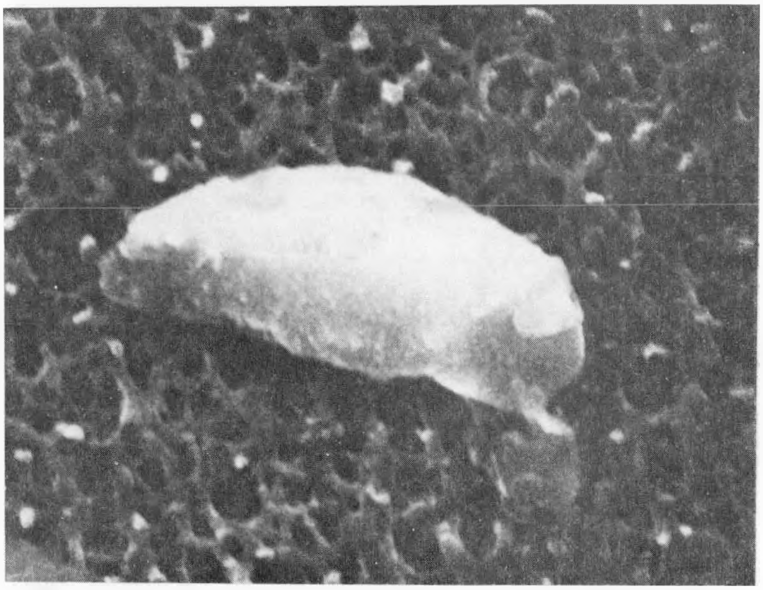


Figure 7

Electromicrograph of Monterey coal particle (on a Metricel filter) after 60 minute autoclave reaction (10,000x)

1 cm = 1μm



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