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EXPLORATORY RESEARCH ON SOLVENT REFINED COAL LIQUEFACTION

Quarterly Technical Progress Report for January 1—March 31, 1980

January 1982

Work Performed Under Contract No. AC22-79ET14800

The Pittsburg & Midway Coal Mining Company
Shawnee Mission, Kansas

U. S. DEPARTMENT OF ENERGY

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EXPLORATORY RESEARCH
ON
SOLVENT REFINED COAL LIQUEFACTION

QUARTERLY TECHNICAL PROGRESS REPORT
FOR THE PERIOD
JANUARY 1, 1980 THROUGH MARCH 31, 1980

THE PITTSBURG & MIDWAY COAL MINING CO.
P. O. BOX 2970
SHAWNEE MISSION, KANSAS 66201

January 1982

PREPARED FOR THE
U. S. DEPARTMENT OF ENERGY
DIVISION OF COAL CONVERSION AND UTILIZATION
UNDER CONTRACT DE-AC22-79ET14800

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ABSTRACT

This report summarizes the progress of the Exploratory Research on Solvent Refined Coal Liquefaction project by The Pittsburg & Midway Coal Mining Co.'s Merriam Laboratory for the period January 1, 1980 through March 31, 1980. A series of experiments was conducted with three western coals to study the relationship between coal properties and liquefaction behavior. All three coals were low in iron (0.2-0.4%, dry coal basis) and processing in both the SRC I and SRC II modes does not appear to be feasible at normal conditions without added catalyst. Adding 1-2% pyrite to the feed slurry increased oil yields considerably while reducing SRC and IOM yields and improved operability. Product quality was also generally improved by the catalyst. Operability and oil yields were generally found to be better at 450°C than at 465°C.

I. SUMMARY

A number of experiments, in both the SRC I and SRC II modes, were conducted with Amax Belle Ayr, Kaiparowits and Wadge seam coals to study the relationship between the physical and chemical properties of a selected group of coals and their liquefaction behavior.

All three coals were low in iron (0.2-0.4%, dry coal basis) and processing in both the SRC I and SRC II modes does not appear to be feasible at normal conditions without added catalyst.

A. Comparison of Coals

In the SRC II mode at 450°C with added pyrite, the Amax Belle Ayr coal was by far the most reactive of the three coals studied this quarter and also had the largest response to pyrite addition. The Kaiparowits coal with 1% added pyrite was slightly more reactive than the Wadge seam coal with 2% added pyrite.

B. Amax Belle Ayr Coal

The liquefaction behavior of the Amax Belle Ayr coal was improved considerably by pyrite addition (1% on slurry) in the SRC II mode of operation. Total oil yield at 450°C was increased from 25 to 50% by weight of MF coal while SRC yield was reduced from 31 to 19% and insoluble organic matter (IOM) from 14 to 1%. The hydrogen level in the heavy distillate was also increased significantly by pyrite addition. The sulfur level in the heavy distillate remained below 0.1% throughout the SRC II runs due to the low organic sulfur level in the coal.

Although operability and yields were improved considerably by pyrite addition in the SRC I mode, sustained operation does not appear to be feasible at 30 minutes residence time and 1500 psig. Solvent loss was still 5%, at best, and all of the SRC I runs were ended prematurely by operability problems.

Operation and yields in both modes were generally better at 450°C than at 465°C. There was little effect of temperature in this range on product quality.

Although the unit was plagued with plugging problems throughout the SRC I runs and SRC II run without pyrite addition, there did not appear to be a systematic enrichment of calcium carbonate in the mineral matter found in the dissolver.

Detailed studies have been conducted on the chemistry of Belle Ayr coal in the SRC II process and on the characterization of specific products and these are included as appendices to this report.

C. Kaiparowits Coal

Good operability and yields were obtained in the SRC I mode with 1% pyrite in the feed at SRC II conditions (1 hour residence time, 2250 psig and 4% hydrogen on slurry). In the SRC II mode, however, the slurry was thick and difficult to pump even though oil yields were improved considerably by pyrite addition. Total oil yield was increased by 14% (based on MF coal) to 43% and there was a corresponding decrease in SRC (26 vs 33%) and IOM (3.6 vs 8.2%) yields with catalyst addition.

An increase in temperature from 450°C to 465°C in the SRC II mode increased gas yield by 4% based on MF coal but decreased total oil yield by the same amount.

Pyrite addition generally increased product hydrogen level and decreased the fusion point of the SRC or distillation residue. The sulfur level in the heavy distillates was very low (less than 0.1%), as with Belle Ayr coal, due to the low organic sulfur level in the feed coal.

D. Wadge Seam Coal

Excellent operability and yields were obtained in the SRC I mode at 450°C, 2250 psig and 1 hour residence time with 2% pyrite in the feed slurry. Yields quickly deteriorated when pyrite was removed from the feed, however. Performance was only marginal when the temperature was raised to 465°C, even with 2% pyrite added. Temperature had little effect on product quality in the SRC I mode, except for slightly higher hydrogen levels at 450°C.

In the SRC II mode, total oil yield was increased by 7% (based on MF coal) to 40% when the pyrite addition level was raised from 1 to 2%, based on slurry. Increasing the temperature from 450 to 465°C generally had a detrimental effect on yields which was more pronounced at the higher additive level. The hydrogen contents of the SRC II heavy distillate and distillation residue were lower at 465°C than at 450°C. At 450°C, product hydrogen level was greater when the level of pyrite was increased. At 465°C, however, hydrogen level was lowered when the pyrite level was increased.

II. INTRODUCTION

This report covers work at The Pittsburg & Midway Coal Mining Co.'s Merriam Laboratory on the Solvent Refined Coal (SRC) process during the period January 1, 1980 through March 31, 1980.

A. Reports of Previous Work

Previous work at this laboratory has been described in interim, final, monthly, quarterly and annual reports to the Office of Coal Research, the Energy Research and Development Administration and the Department of Energy. A summary of these documents appears in the second quarter 1979 report* along with a description of the

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* Exploratory Research on Solvent Refined Coal Liquefaction, Quarterly Technical Progress Report for the Period April 1, 1979 through June 30, 1979; January 1980, FE/14800-10.

current contract objectives and a history of the Merriam Laboratory in solvent refining of coal.

B. Currently Reported Work

All work reported this quarter was part of Task III, "Coal Properties and Liquefaction Behavior," of the current contract.

The objective of this study is to evaluate a carefully selected group of coals in both SRC I and SRC II operation to extend understanding of the relationship between the physical and chemical properties of the coals and their liquefaction behavior.

It was hoped that all of the coals could be processed using a standard set of conditions. As this was not feasible, a secondary objective has become determination of the conditions appropriate for liquefaction of each coal. In particular, addition of pyrite to coals with low levels of iron is being investigated.

Six coals representing a variety of organic and mineral matter compositions have been selected for SRC I and SRC II trial experiments. In addition, one or more trials will be made with coal blends simulating those anticipated for the SRC II Demonstration Plant.

Experiments with coals from the Amax Belle Ayr Mine, Kaiparowits Plateau, and Wadge seam are discussed below. The next quarterly report will detail results with coals from the Amax Ayrshire Mine (Indiana), Consol Georgetown #24 Mine (Ohio), Consol Ireland Mine (West Virginia) and a blend of coals from the Ireland and Consol Blacksville #2 Mines (West Virginia).

III. EXPERIMENTAL

A. Run Conditions

Each coal investigated in the current task was to be processed in four phases at standard conditions:

Phase	Mode	Temperature, °C	Pressure, psig	Residence Time, hr
1	SRC I	450	1500	0.5
2	SRC I	465	1500	0.5
3	SRC II	450	2250	1.0
4	SRC II	465	2250	1.0

It was hoped that, by selecting these rather generous conditions, all of the coals in the task could be run in the same way.

1. Amax Belle Ayr Coal

Run DOE 349 was attempted at phase 1 conditions. Difficulties in operation led to a switch to phase 3 conditions for run DOE 350RA, with finely divided ($\approx 1 \mu m$) pyrite in the slurry formulation. A catalyst addition level of 2.35%, based on slurry, was used initially. Due to excessive hydrogenation and a high solids level in the feed slurry, this level was reduced to 1%.

Run DOE 350RB was made at phase 4 conditions with the same pyrite addition level. In run DOE 350RC, the temperature was dropped back to 450°C and the pyrite was removed from the feed.

Runs DOE 351A and 351B were made with 1% pyrite in the feed slurry at phase 1 and phase 2 conditions, respectively. Run DOE 352 was a repeat of run DOE 349 at phase 1 conditions without pyrite.

2. Kaiparowits Coal

The same sequence of run conditions that proved to be convenient for the SRC II processing of Belle Ayr coal was repeated for run DOE 353R:

Part A: 450°C with 1% pyrite in the feed slurry

Part B: 465°C with pyrite

Part C: 450°C without pyrite

The other conditions were standard for this task.

The Kaiparowits coal did not behave as well as Belle Ayr coal in the SRC II mode, and the Belle Ayr coal did poorly in the SRC I mode at the standard conditions for this task. Run DOE 354 was started at more generous conditions, therefore, in an attempt to achieve satisfactory operation in the SRC I mode.

Since SRC II type conditions were indicated, pressure, residence time and hydrogen rate were matched with the SRC II run, DOE 353R. The first part of the run was made with 1% pyrite in the slurry and the second part without catalyst; both at 450°C.

3. Wadge Seam Coal

The experimental plan for processing this coal was set up initially based on experience with the first two coals investigated in this task. An SRC II experiment at 450°C with 1% added pyrite in the slurry (DOE 355RA) was conducted first, therefore, followed by a temperature increase to 465°C (DOE 355RB). The recycled solvent level in the slurry formulation was increased from 8% to 12% during the second part of the run in an attempt to improve operability.

As operability and yields were marginal with a pyrite addition level of 1%, the catalyst concentration was increased to 2% for run DOE 356R instead of eliminating additive from the feed as was done with Kaiparowits coal. Part A of the experiment was conducted at 450°C and part B at 465°C.

The same generous conditions which provided for successful operation with the Kaiparowits coal in the SRC I mode were employed in run DOE 357. Part A was at 450°C and part B at 465°C, both with 2% added pyrite in the feed slurry. Part C was at 450°C without pyrite.

B. Coals

1. Amax Belle Ayr Coal

The Amax coal was from the Belle Ayr Mine located in Wyoming (Wyodak-Anderson seam) and ranks as subbituminous B.

Two different lots of coal, both supplied by the Wilsonville SRC Pilot Plant, were used in this series of runs. The first, SN21648, was used in runs DOE 349 and 350RA, and the second, SN23324, in runs DOE 350RB, 350RC, 351 and 352. Analyses of both lots appear in Table 2. The iron and sulfur levels were essentially the same.

2. Kaiparowits Coal

This coal was from the Kaiparowits Plateau in Utah (Red seams) and ranks as high volatile C bituminous. An analysis is shown in Table 2. The higher rank of the Kaiparowits coal in comparison to the Belle Ayr coal is evidenced by its lower oxygen and equilibrium moisture contents. The two coals are of similar ash (8.2-8.4%), iron (0.3-0.4%) and sulfur (0.5-0.6%) contents.

3. Wadge Seam Coal

The coal used in these experiments was from the Energy Fuels Corporation Energy Mine No. 1 located in Colorado (Wadge seam) and also ranks as high volatile C bituminous. The essentially equivalent rank of the Kaiparowits and Wadge seam coals is shown by their very similar moist mineral-matter-free calorific values (12,300 vs 12,000 BTU/lb). The Wadge seam coal is also low in iron (0.2%) and sulfur (0.6%). A lower reactivity for the Wadge seam coal might be predicted in view of its higher ratio of fixed carbon to volatile matter (1.32 for Wadge seam vs 1.09 for Kaiparowits).

C. Additive

1. Amax Belle Ayr Coal Experiments

The pyrite used with this coal designated as Pyrite II in earlier work) was obtained from the coal cleaning operation of the U. S. Steel Robena Mine, Green County, Pennsylvania. It was ground to an average particle size of 1.7 μm (Coulter Counter method) by The Jet Pulverizer Company, Palmyra, New Jersey. The purity of the material, as received, was 64.6%

FeS_2. An elemental analysis and particle size distribution data for the additive are shown in Table 3 and Figure 1, respectively. The additive level, when used, was 1% crude pyrite (0.65% as FeS_2) based on slurry.

2. Kaiparowits and Wadge Seam Coal Experiments

The pyrite used in these runs, obtained from Matheson, Coleman and Bell, was mined in Georgia as a discrete mineral. It was ball milled and passed through a 140 mesh screen before use (average particle size approximately 65 μm). An analysis of the material, given in Table 3, indicates about 94% FeS_2.

The additive level, when used, was 1% crude pyrite (0.94% as FeS_2) with the Kaiparowits coal and 1 or 2% (0.94 or 1.88% as FeS_2) with the Wadge seam coal, based on slurry.

IV. OPERATION

A. Amax Belle Ayr Coal

1. Run DOE 349 (SRC I, without Pyrite)

The unit was plagued with plugging problems from the onset of this run. A plug formed in the preheater about 10 hours after start up, shutting down the unit. The slurry letdown valve plugged when the unit was restarted and about two days after finally getting on stream the dissolver plugged, ending the run.

Analysis of plug material from several locations in the dissolver indicated about the same proportion of calcium in the ash as in the feed coal. There was no evidence, therefore, for enrichment of calcium carbonate in the mineral matter found in the dissolver during this particular run. Accumulation of calcium carbonate in the dissolver has been reported for the Wilsonville SRC I Pilot Plant and has also been observed in earlier runs with Belle Ayr coal at Merriam.

The high water content of the coal plus the relatively high water yield led to problems in the product separation system. Water and light oil were carried into the refrigerated separator, plugging the gas letdown valve. The intermediate temperature, high pressure (ITHP) separator was operated at 180°C, instead of the normal 200°C, to alleviate the problem.

2. Runs DOE 350RA and 350RB (SRC II, with Pyrite)

Operability was improved considerably during run DOE 350RA with added pyrite at SRC II conditions. It was still necessary to operate the ITHP separator at a lower than normal temperature and to drain the refrigerated separator frequently.

3. Run DOE 350RC (SRC II, without Pyrite)

Operability became steadily worse after pyrite was removed from the feed in the last part of run DOE 350. Increasing feed slurry viscosity forced a change in formulation from 8% to 12% recycled oil. Even after this change, plugging continued and six days after pyrite removal a blocked transfer line to the preheater forced a shutdown.

A sample of solid material taken from the preheater had a calcium level in the ash similar to that in the feed coal.

4. Run DOE 351 (SRC I, with Pyrite)

The slurry letdown valve was hampered by soft plugs throughout the run and became completely blocked nine hours after the temperature was raised to 465°C for part B.

A sample of material from the bottom of the dissolver had 26% calcium in the ash whereas the feed coal had only about 12%. There is, therefore, some evidence for an accumulation of calcium carbonate in this particular run.

5. Run DOE 352 (SRC I, without Pyrite)

The average dissolver temperature for this run was 5°C below target due to a faulty heater in conjunction with a malfunctioning thermocouple on the transfer line between the preheater and dissolver. This resulted in a temperature of only 430°C in the first zone of the dissolver.

On the second day of the run, the rupture discs on both pumpheads burst. When the unit was subsequently switched to pumping oil, the rupture disc on the preheater burst, forcing a shutdown.

B. Kaiparowits Coal

1. Runs DOE 353RA and 353RB (SRC II, with Pyrite)

Even though oil yields were fairly high in runs DOE 353RA and 353RB, there were difficulties in pumping the slurry and a number of rupture discs burst on the front end.

2. Run DOE 353RC (SRC II, without Pyrite)

Three days after pyrite was removed from the feed, the slurry became so thick that a steady pump rate could not be maintained and the unit was shut down.

3. Run DOE 354A (SRC I, with Pyrite)

This run was uneventful.

4. Run DOE 354B (SRC I, without Pyrite)

Operation quickly deteriorated after pyrite was removed from the feed, with plugs occurring at the hydrogen inlet and in the transfer line between the high and intermediate temperature separators.

C. Wadge Seam Coal

The slurry was generally thick and difficult to pump during run DOE 355R, in the SRC II mode with 1% added pyrite, and the experiment ended when the slurry feed rate could no longer be maintained. In the SRC II run with 2% pyrite in the feed, DOE 356R, the slurry was manageable during the 450°C part of the run but became viscous when the temperature was increased to 465°C in part B.

The SRC I run, DOE 357, ran without difficulty during parts A and B with 2% added pyrite in the feed. The run was ended by a plug in the slurry feed section of the unit shortly after pyrite was removed in part C.

D. Material Balances

Although overall mass balance closures were satisfactory for these experiments, relatively large discrepancies were encountered in the ash balances. It appears that this is due to loss of volatile material from the slurry mix and feed pots and from the product collection vessels. This problem seems to be exaggerated when high moisture coals are processed or when water is added to the feed.

The vent lines on the ambient temperature separator bottoms, atmospheric distillation overhead and atmospheric distillation bottom product collection vessels now have dry ice traps to collect volatile materials. In addition, a metal (pressurized) trap is under construction for use on the unfiltered coal solution (UFCS) collection vessel. An experiment will also be conducted during the next shutdown to estimate weight loss during circulation and mixing of the feed slurry at typical operating temperatures.*

V. RESULTS

The discussion of results is broken down into five major categories:

A. Yields and Hydrogen Consumption
B. Product Quality
C. Viscosity Measurements
D. Solvent Extraction of Distillation Residues
E. Yields and Compositions for Detailed Product Arrays

In categories A through D, each discussion begins with a comparison of the three western coals studied this quarter. The comparisons, for both the SRC I and SRC II modes, are based on runs at 450°C with added pyrite. These were the most stable experiments and produced the best

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* The yields from these runs are corrected for volatile losses in later reports by use of a forced ash balance.

operation and yields. A discussion of each coal follows, detailing the effect of temperature and pyrite addition in both the SRC I and SRC II modes of operation.

In category E, the yield and composition of detailed product arrays (water phase, 10% by weight fractions of distillable material and fractions from sequential extraction of distillation residue with hexane, toluene and pyridine) are described.

A. Yields and Hydrogen Consumptions*

The yields and hydrogen consumptions for all runs reported this quarter are shown in Table 1.

1. Comparison of Coals

a. SRC I Mode

Although the Amax Belle Ayr coal responded well to pyrite addition in the SRC II mode, processing of this coal at the SRC I conditions originally selected for this task (30 minutes residence time and 1500 psig) does not appear feasible, whether pyrite is added or not.

These conditions were changed for the Kaiparowits and Wadge seam coal experiments, and the yields for those two coals are compared below:

Conditions*		
Coal	Kaiparowits Plateau	Wadge Seam
Pyrite Addition Level, Wt % feed slurry	1	2
Yields, Wt % MF Coal		
C_1-C_4	7.5	8.7
Recycle Solvent	6.5	12.6
Total Oil	19.5	26.9
SRC	47.2	41.8
IOM	8.0	5.8
H_2 Consumption	3.1	4.1

* All at 450°C, 2250 psig and 1 hour residence time.

The Wadge seam coal with a pyrite addition level of 2% (based on slurry) was significantly more reactive in the SRC I mode than the Kaiparowits coal with 1% added pyrite. In both cases, a substantial excess of recycle solvent was obtained. A viable SRC I process may therefore be possible under less generous conditions such as reduced pyrite level, reduced pressure or reduced residence time.

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* The yields from these runs are corrected for volatile losses in later reports by use of a forced ash balance.

b. SRC II Mode

The yields and hydrogen consumptions in the SRC II mode with added pyrite for the three coals are compared below:

Conditions*				
Coal	Amax Belle Ayr	Kaiparowits Plateau	Wadge Seam	
Pyrite Addition Level, Wt % feed slurry	1	1	1	2
Yields, Wt % MF Coal				
C_1-C_4	10.4	11.4	12.0	12.1
Total Oil	50.1	43.3	33.4	40.4
SRC	19.3	25.8	28.5	27.3
IOM	1.2	3.6	7.9	4.5
H_2 Consumption	5.6	5.2	4.0	5.0

* All at 450°C, 2250 psig, 1 hour residence time.

The Amax Belle Ayr coal was by far the most reactive under these conditions and also had the largest response to pyrite addition. Total oil yield from the Belle Ayr coal was increased from 25% to 50% by adding 1% pyrite to the feed while the yield from Kaiparowits coal was increased about 14% (from 29 to 43%). Wadge seam coal was not run in the SRC II mode without pyrite. Some of the difference between the Belle Ayr and Kaiparowits coal yields may be due to use of finely divided pyrite with the former coal and coarse catalyst with the latter. The Kaiparowits coal with 1% added pyrite was more reactive in the SRC II mode than the Wadge seam coal with 2% catalyst. In all cases, there was a corresponding decrease in SRC and IOM yields when oil yields increased.

A comparison of the coals without pyrite addition can not be made because the corresponding runs were not completely lined out.

2. Amax Belle Ayr Coal

Although the lot of Belle Ayr coal was changed during run DOE 350R, no effect on operability or yields was observed at the time of the change and a comparison of results between runs DOE 349 and 352, at essentially the same conditions, indicates the influence of any variation in coal composition was far outweighed by pyrite addition or temperature changes.

a. SRC I Mode

The SRC I runs were conducted with some difficulty and data were collected over relatively short periods of time.

The results from run DOE 349, in particular, should be considered qualitative. In the SRC I work with Belle Ayr coal, complete equilibrium was generally not achieved and the data were influenced by the continual decline in solvent quality up until the time the runs were terminated.

i. Effect of Pyrite Addition

The effect of pyrite addition on yields can be seen by comparing runs DOE 349 and 352 without pyrite to run DOE 351A with 1% pyrite in the feed. While the hydrocarbon gas yield was unchanged, the recycle solvent yield went from a 26% loss (MF coal basis) to a 5% loss and total oil yield went from a 9-13% loss to an 11% gain, with pyrite addition. There was a corresponding decrease in IOM yield from 40-41% to 17%. Hydrogen consumption was about twice as high in the pyrite catalyzed run.

ii. Effect of Temperature

The effect of increasing the temperature from 450 to 465°C while adding pyrite can be seen by comparing runs DOE 351A and 351B. Hydrocarbon gas yield was increased from 4.7 to 7.0% based on MF coal at the higher temperature while total oil yield increased from 11.4 to 14.7%. There was a corresponding decrease in SRC yield from 47 to 38%. Recycle solvent loss was increased, however, from 5.0 to 11.9% by raising the temperature.

b. SRC II Mode

i. Effect of Pyrite Addition

The effect of pyrite addition on yields can be observed by comparing the results of run DOE 350RA, with pyrite, to run DOE 350RC which had a steady decline in pyrite level. The effect of iron concentration in the slurry on yields is shown qualitatively in Figure 2*. The addition of 1% pyrite to the feed in run DOE 350RA resulted in an iron level of about 2.5% in the equilibrated feed slurry. When pyrite addition was stopped in run DOE 350RC, the iron level in the slurry dropped to about 0.35% before the run was terminated by a plug in the preheater. As iron concentration decreased over this range, total oil yield dropped from about 43 to 25%, SRC yield increased from 16 to 26% and IOM yield increased from 1 to 15%. There was little effect on hydrocarbon gas yield.

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* These results were obtained from analysis of individual products as described in Appendix B and do not match the average yields given in the body of the report.

ii. Effect of Temperature

The effect of temperature while adding pyrite can be seen by comparing runs DOE 350RA and 350RB at 450 and 465°C, respectively. Hydrocarbon gas yield was about 4% (absolute) higher at the higher temperature while total oil yield was about 6% lower. There was also a shift to lighter oil products at the higher temperature. SRC and IOM yields were slightly higher at the higher temperature.

3. Kaiparowits Coal

a. SRC I Mode

The effect of pyrite addition on yields in the SRC I mode at 450°C can be seen by comparing runs DOE 354A and 354B. There was a 7.3% loss (based on MF coal) of recycle solvent in the uncatalyzed run, DOE 354B, whereas there was a 6.5% gain when pyrite was added in run DOE 354A. There was also an increase in total oil (19.5 vs 9.4%) and SRC (47.2 vs 41.4%) yields and a decrease in IOM (8.0 vs 22.0%) yield with pyrite addition. Total hydrocarbon gas yield was similar in the runs with and without additive. Hydrogen consumption was slightly higher with catalyst in the system.

The effect of temperature was not determined in the SRC I mode.

b. SRC II Mode

i. Effect of Pyrite Addition

The effect of pyrite addition at 450°C in the SRC II mode can be determined from a comparison of runs DOE 353RA and 353RC. Total oil yield was 14% (based on MF coal) higher with pyrite addition in run DOE 353RA. There was a corresponding decrease in SRC (26 vs 33%) and IOM (3.6 vs 8.2%) with catalyst addition, although hydrocarbon gas yield was unaffected. Hydrogen consumption was about 1% higher (based on MF coal) when pyrite was added to the feed.

ii. Effect of Temperature

The effect of temperature can be seen by comparing run DOE 353RA at 450°C with run DOE 353RB at 465°C. Hydrocarbon gas yield was about 4% (based on MF coal) higher at 465°C, as expected, but total oil yield was 4% lower. IOM yield was slightly greater and SRC yield slightly less at the higher temperature, while hydrogen consumption increased by 1%.

4. Wadge Seam Coal

a. SRC I Mode

i. Effect of Pyrite Addition

The effect of pyrite addition on yields in the SRC I mode at 450°C can be seen by comparing runs DOE 357A and 357C. There was a dramatic reduction in total oil yield (13.4 vs 26.9%, based on MF coal) and recycle solvent yield (8.0% loss vs 12.6% gain) when pyrite was removed from the feed in run DOE 357C. There was a corresponding increase in SRC (52.4 vs 41.8%) and IOM (8.6 vs 5.8%) yields. Hydrogen consumption was about 1% higher in the catalyzed run and there was little effect on hydrocarbon gas yield.

ii. Effect of Temperature

The effect of temperature with 2% pyrite in the feed can be seen by comparing run DOE 357A at 450°C with run DOE 357B at 465°C. Total oil yield was about 6% lower (based on MF coal) at the higher temperature while hydrocarbon gas yield was about 5% greater. The recycle solvent balance was changed from a 13% gain to a near break-even level by increasing the temperature. SRC and IOM yields and hydrogen consumption were essentially unchanged by temperature.

b. SRC II Mode

Runs DOE 355RA, 355RB, 356RA and 356RB constituted a 2^2 factorial in temperature and pyrite level:

Temperature, °C	Pyrite Level 1%	 2%
450	355RA	356RA
465	355RB	356RB

The results of the factorial are summarized in Table 4.

i. Effect of Pyrite Addition

The effect of pyrite addition level on yields can be seen by comparing run DOE 355RA to 356RA at 450°C and run DOE 355RB to 356RB at 465°C.

At 450°C, the total oil yield was increased from 33 to 40% (based on MF coal) by increasing the pyrite addition rate from 1% to 2%, based on slurry. There was a corresponding decrease in SRC yield of about

1% and IOM yield of 3.4%. Hydrogen consumption was 1.0% greater at the higher catalyst level and hydrocarbon gas yield was unchanged.

At the higher temperature, total oil yield was decreased from 28 to 24% by increasing the level of pyrite in contrast to the results at 450°C. There was a corresponding increase in SRC yield from 26 to 33%. IOM yield was 2.8% lower at the higher addition level, however. Hydrogen consumption increased slightly at the higher additive level while hydrocarbon gas yield was slightly lower.

ii. Effect of Temperature

The gas yield was increased by 3-4% (based on MF coal) by increasing the temperature from 450 to 465°C while total oil yield decreased by 5-17%. IOM yield was about 6% higher at the higher temperature at both pyrite addition levels but SRC decreased by 2.8% at the 1% pyrite addition level and increased by 6.1% at the 2% pyrite level when temperature was raised. Hydrogen consumption increased slightly with temperature at the lower catalyst addition level but decreased slightly with temperature at the higher level. These variations in hydrogen consumption were near the experimental error, however.

B. Product Quality

The heavy distillate (or recycle solvent) and distillation residue (or SRC) analyses for all runs reported this quarter are shown in Table 1.

1. Comparison of Coals

a. SRC I Mode

Processing of Kaiparowits (DOE 354A) and Wadge seam (DOE 357A) coals at 450°C with added pyrite resulted in similar product qualities.

The recycle solvent analyses are essentially the same except for a higher sulfur level (0.34 vs 0.24%) with the Wadge seam coal. This is expected due to the higher organic sulfur level in this coal (0.51 vs 0.42%).

The SRC from the Wadge seam coal also had a higher sulfur level (0.22 vs 0.13%), due to the higher organic sulfur level in the feed, and a higher nitrogen content.

b. SRC II Mode

Heavy distillate and distillation residues from processing Amax Belle Ayr and Kaiparowits coals at 450°C with 1%

added pyrite had essentially the same analyses except for higher sulfur and ash levels in the distillation residue from Belle Ayr coal (due to the higher conversion of SRC to oil with the Belle Ayr coal).

The products from Wadge seam coal processed in the SRC II mode at 450°C with 1 or 2% added pyrite were considerably different than those from the other two coals with 1% added pyrite, however.

The heavy distillates from processing the Wadge seam coal at both additive levels had significantly lower hydrogen contents and the sulfur and nitrogen concentrations were higher.

The distillation residues derived from the Wadge seam coal had significantly higher nitrogen levels and fusion points at both additive levels than those from the other coals. The hydrogen level in the distillation residue from the Wadge seam coal run with 2% added pyrite was about the same as that from the Kaiparowits coal run when 1% pyrite was added.

2. Amax Belle Ayr Coal

a. SRC I Mode

i. Effect of Pyrite Addition

The recycle solvent analyses for runs DOE 349 and 352 without pyrite and run DOE 351A with pyrite are virtually the same.

In addition, there is little difference in the SRC analyses between runs DOE 351A and 352 except for the fusion point which was lowered about 50°C in the catalyzed run. It is not possible to include the distillation residue from run DOE 349 in the comparison because the distillation was performed on UFCS instead of filtrate.

ii. Effect of Temperature

Raising the temperature from 450°C to 465°C also had little effect on recycle solvent and SRC composition except for decreasing the hydrogen content, as seen from a comparison of runs DOE 351A and 351B.

b. SRC II Mode

i. Effect of Pyrite Addition

The effect of pyrite addition on product quality can be seen by comparing the analyses for run DOE 350RA with pyrite to those from DOE 350RC with a steady decline of pyrite. The hydrogen level in the heavy distillate dropped as soon as pyrite was removed from the feed and continued to drop to the level shown for run 350RC-5 (at this point the system became inoperable because of plugging). The sulfur level in the heavy distillate remained at an extremely low level during all of the runs. This is apparently due to the low organic sulfur level in the coal (0.48-0.52%). There was little change in nitrogen level.

The hydrogen level in the distillation residue decreased from 6.1 to 4.5% on an ash free basis while nitrogen level remained the same (1.7%) as pyrite left the system. There was also a significant increase in fusion point as iron level decreased.

ii. Effect of Temperature

A comparison of runs DOE 350RA and 350RB at 450 and 465°, respectively, indicates a lower level of hydrogen in both the heavy distillate and distillation residue at the higher temperature. Other analyses are relatively unchanged by temperature.

2. Kaiparowits Coal

a. SRC I Mode

There was little difference in recycle solvent or SRC analyses brought about by pyrite addition (run DOE 354A vs 354B) except for higher hydrogen levels. The fusion point of the SRC was also lowered about 40°C by the catalyst.

b. SRC II Mode

i. Effect of Pyrite

A comparison of the heavy distillate analyses for runs DOE 353RA with pyrite and 353RC without additive, indicates that they are similar in composition except for a higher level of hydrogen with catalyst. The sulfur level in the heavy distillates was very low (less than 0.1%), as was the case in the Belle Ayr coal runs, due to the low organic sulfur level in the feed coal.

The distillation residue from the run with pyrite had a slightly higher hydrogen level and a significantly higher sulfur level than that from the uncatalyzed run. The fusion point of the residue from the run without pyrite was above the range normally measured at Merriam and was at least 150°C higher than that from the run with added pyrite.

ii. Effect of Temperature

The heavy distillate analyses were relatively unaffected by temperature (compare runs DOE 353RA at 450°C and 353RB at 465°C) except for a higher level of hydrogen at 450°C.

The distillation residue from the run at 450°C had a higher hydrogen level, less sulfur and a lower fusion point than that from the run at 465°C.

3. Wadge Seam Coal

a. SRC I Mode

The effect of temperature can be seen by comparing run DOE 357A at 450°C with run DOE 357B at 465°C. The recycle solvent and SRC analyses are essentially the same except for somewhat more hydrogen in both products from the lower temperature run.

The effect of pyrite addition in the SRC I mode can not be determined because samples from the uncatalyzed part of the run are not available.

b. SRC II Mode

i. Effect of Pyrite Level

The heavy distillate from the run at 450°C with 1% pyrite in the feed, DOE 355RA, had slightly less hydrogen than that from the run at the same temperature with 2% pyrite, DOE 356RA. When the temperature was raised to 465°C, however, the product from the 1% catalyst run, DOE 355RB, had more hydrogen than that from the 2% catalyst run, DOE 356RB. Increasing the pyrite level resulted in increased heavy distillate nitrogen at both temperatures due to increased conversion to distillable products. Other heavy distillate analyses were unchanged by catalysts.

There was an increase in distillation residue ash free hydrogen level* at 450°C when the pyrite level was increased, although there was a decrease at 465°C. The sulfur level increased considerably at the higher catalyst concentration, as expected, due to material derived from pyrite in the residue. There was little change in ash free nitrogen level due to the catalyst addition rate. The fusion point was also greater at the higher additive level, particularly at 465°C.

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* See Table 3 for distillation residue analyses calculated ash free.

ii. Effect of Temperature

As mentioned above, the hydrogen level in the heavy distillate was reduced by increasing the temperature, particularly at the higher additive level. Other heavy distillate analyses were relatively unaffected by temperature.

Hydrogen level in the distillation residue was also reduced by increasing the temperature while the fusion point was increased. Nitrogen and sulfur levels were not affected by temperature.

C. Viscosity Measurements

1. Comparison of Coals

a. SRC I Mode

The unfiltered coal solution (UFCS) viscosities for runs DOE 354A and 357A are compared in Figure 3. The UFCS from the Wadge seam coal experiment with 2% added pyrite had a lower viscosity than that from the Kaiparowits coal experiment with 1% added pyrite. This is in conjunction with the higher total oil yield obtained under these conditions with the Wadge seam coal.

b. SRC II Mode

The unfiltered coal solution (UFCS) viscosities for runs DOE 350RA, 353RA and 356RA are compared in Figure 4. The UFCS viscosities from the three runs were in the order:

Wadge seam > Kaiparowits > Amax Belle Ayr
(2% pyrite) (1% pyrite) (1% pyrite)

← Increasing viscosity
(decreasing total oil yields)

The runs having lower UFCS viscosities in the SRC II mode were also those having higher oil yields.

The feed slurry viscosities are compared in Figure 5. Whereas the Kaiparowits coal with 1% added pyrite was found to be more reactive than the Wadge seam coal with 2% added pyrite, the latter had a feed slurry with a lower viscosity.

2. Amax Belle Ayr Coal

Unfiltered coal solution (UFCS) viscosity data are shown in Table 5 and feed slurry viscosity data in Table 6.

a. SRC I Mode

A comparison of UFCS viscosities for the SRC I Belle Ayr coal runs is given in Figure 6. Runs DOE 349 and 352 were made under the same conditions except for a 5°C lower average dissolver temperature in the latter. In addition, different lots of coal were used.

Run DOE 352 produced a slightly higher viscosity UFCS than run DOE 349 at all shear rates. These results are in conjunction with the slightly lower conversion in run DOE 352.

The viscosities of the UFCS from runs DOE 349 and 352 were significantly higher than those from run DOE 351 due to the catalytic effect of the pyrite added in the latter.

b. SRC II Mode

The viscosities of the UFCS from the various parts of run DOE 350R are compared in Figure 7. The samples from the two catalyzed parts of the run, DOE 350RA and 350RB, were similar although there was a slightly higher viscosity measured for the UFCS from the higher temperature run, DOE 350RB. Removal of pyrite from the system in run DOE 350RC resulted in an order of magnitude increase in UFCS viscosity.

The viscosities of the feed slurries from the various parts of run DOE 350R are compared in Figure 8. Whereas typical feed slurries with bituminous coals exhibit a minimum in viscosity in the temperature range 230-270°F, this characteristic was not observed with Belle Ayr coal.

The slurry from run DOE 350RA gave essentially a straight line relationship between viscosity and temperature. When the slurry from run DOE 350RB was tested in the normal manner, there was a maximum in viscosity in the range of 230-250°F. When another sample from the same run was tested, a curve of the same shape was obtained, although the viscosities were slightly higher.

A third trial was conducted by heating a sample to 270°F for 45 minutes and then cooling to 210°F to begin the viscosity measurements. This time the viscosity decreased with increasing temperature although there was still no minimum.

The first two samples from run DOE 350RB were heated to about 217°F prior to the viscosity measurements so they would pour from the sample jar. It is presumed that this would remove free water. It is possible that water remains complexed with phenolic materials, however. When the third sample was heated to 270°F it was observed to swell and boil. This activity was essentially complete before making the viscosity measurements, so the complexes may have been dissociated by the treatment, resulting in a different viscosity profile.

3. Kaiparowits Coal

Unfiltered coal solution (UFCS) viscosity data are listed in Table 7 and feed slurry viscosity data in Table 8.

a. SRC I Mode

The UFCS viscosities for the SRC I experiments with and without added pyrite, runs DOE 354A and 354B, respectively, are compared in Figure 9. The UFCS from the catalyzed experiment had a much lower viscosity than that from the run without pyrite which agrees with the fusion point and solubility data. As usual, there was less temperature dependence at lower viscosities.

b. SRC II Mode

~~The UFCS viscosities for the three parts of run DOE 353R~~ are shown in Figure 10.

The UFCS from run DOE 353RC at 450°C without pyrite had a significantly higher viscosity than that from the run at 450°C with pyrite, DOE 353RA, due to the catalytic effect of the additive.

The experiment at 450°C with pyrite, run DOE 353RA, produced a UFCS with a higher viscosity than run DOE 353RB at 465°C with pyrite. The solids (ash and IOM) level in the UFCS from the two runs was essentially the same (23%), so the lower viscosity apparently reflects the shift to lighter liquid products at the higher temperature.

The feed slurry viscosities for the three parts of run DOE 353R are compared in Figure 11.

The feed slurry viscosity for the uncatalyzed run, DOE 353RC, was an order of magnitude greater than for the run with pyrite and could only be measured at the higher temperatures and lowest shear rate (to keep the reading on scale) normally used.

The effect of temperature was fairly small, run DOE 353RA at 450°C producing a feed slurry viscosity slightly higher than run DOE 353RB at 465°C.

4. Wadge Seam Coal

Unfiltered coal solution (UFCS) viscosity data are listed in Table 9 and feed slurry viscosity data in Table 10.

a. SRC I Mode

The UFCS viscosities for the three parts of run DOE 357 are compared in Figure 12. The UFCS viscosities for parts A and B of the run, at 450 and 465°C, respectively, were essentially the same even though the yields for these experiments were quite different. This is associated with the similarity in solids levels and SRC content of the two unfiltered coal solutions and the nearly identical SRC fusion points.

The higher viscosity of the UFCS from the uncatalyzed experiment, run DOE 357C, apparently stems from a higher molecular weight liquid, since the solids levels are nearly the same. It is noted, however, that the solids are comprised of a higher IOM and lower ash content in the uncatalyzed run.

b. SRC II Mode

The UFCS viscosities for runs DOE 355R and 356R are shown in Figure 13. A direct comparison of viscosities is difficult because several different shear rates were used. The UFCS viscosity for run DOE 356RA at a shear rate of 3.32 sec^{-1} should fall close to the two values shown, however, and the value for UFCS at this shear rate from DOE 356RB should fall between the two values given.

Increasing the level of pyrite decreased the viscosity of UFCS from the 450°C runs (DOE 356RA vs DOE 355RA) while an increase was observed in the runs at 465°C (DOE 356RB vs DOE 355RB). This correlates with the SRC concentration in the UFCS which increases or decreases in the same direction as the viscosity.

The feed slurry viscosities for the SRC II runs are compared in Figure 14.

For the runs at 450°C, there was little difference in feed slurry viscosities brought about by a change in pyrite level except for flatter viscosity vs temperature profiles at the lower additive level.

A comparison of run DOE 355RA at 450°C and 355RB at 465°C, both with 1% pyrite in the feed, indicates that the viscosity was about twice as great at a shear rate of 0.830 sec^{-1} for slurry from the higher temperature run.

When the run temperature was increased to 465°C at an additive level of 2%, a feed slurry with the highest viscosity ever measured at this laboratory resulted. Even though the smallest diameter spindle was used (to minimize the scale readings), the temperature had to be raised to 320°F before a measurement could be made. As the slurry samples from run DOE 355R were heated, volatiles were observed boiling off (as was the case with Amax Belle Ayr coal) although no swelling was noted. A recheck was made on the sample from run DOE 355RB by heating to 270°F for one hour prior to cooling to 210°F and beginning the measurements. The overall viscosity of the sample increased slightly and the shape of the curve was altered.

D. Solvent Extraction of Distillation Residues

1. Comparison of Coals

a. SRC I Mode

A comparison cannot be made in the SRC I mode because solubility data are not available for the different coals at the same run conditions.

b. SRC II Mode

The solubility ratios of the distillation residues from runs DOE 350RA, 353RA, 355RA and 356RA are compared below:

Conditions*

Coal	Amax Belle Ayr	Kaiparowits Plateau	Wadge Seam	
Pyrite Addition Level, wt % feed slurry	1	1	1	2
Ratio of Average Solubilities				
Hexane/Pyridine	0.632	0.503	0.223	0.334
Toluene/Pyridine	0.897	0.854	0.690	0.805

* For all: 450°C, 1 hour residence time, 2250 psig.

The solubilities were in the same order as the general reactivities of the coals under these conditions:

Amax Belle Ayr (1% pyrite) > Kaiparowits (1% pyrite) > Wadge Seam (2% pyrite) > Wadge Seam (1% pyrite)

← Increased solubility

2. Amax Belle Ayr Coal

a. SRC I Mode

The solubilities of the SRC products in hexane, toluene and pyridine are shown in Table 11. When the temperature was increased from run DOE 351A to 351B, the solubility of the residue decreased slightly, suggesting an increase in repolymerization reactions at 465°C.

Residue from run DOE 352, without pyrite addition, shows substantially reduced solubility compared to that from run DOE 351A which was at essentially the same conditions but with pyrite addition.

b. SRC II Mode

The solubilities of the distillation residues in the various solvents are shown in Table 12. The solubilities in all solvents were significantly greater at 450°C than at 465°C, with pyrite in the feed. The temperature was lowered to 450°C in run DOE 350RC and pyrite addition to the feed was stopped. The solubility in pyridine first increased in response to the temperature change and then decreased as pyrite was worked out of the system. There was a steady decline in the hexane/pyridine and toluene/pyridine ratios as the pyrite left the system during run DOE 350RC.

3. Kaiparowits Coal

The solubilities of the distillation residues in hexane, toluene and pyridene are shown in Table 13.

a. SRC I Mode

The solubilities of the SRC products from the uncatalyzed experiment, run DOE 354B, in hexane and toluene were slightly less than those from the run with pyrite, DOE 354A, which is in agreement with the higher fusion points.

b. SRC II Mode

The solubilities of the residues in all of the solvents were significantly greater for the experiment at 450°C, run DOE 353RA, compared to those from the run at 465°C, DOE 353RB. This result was also obtained with Amax Belle Ayr coal and suggests an increase in repolymerization reactions at the higher temperature.

In run DOE 353RC, the temperature was dropped from 465°C to 450°C and pyrite was removed from the feed. The solubilities were found to first increase in response to lowering the temperature, then decrease as pyrite left the system. This characteristic was also observed in the experiments with Belle Ayr coal.

4. Wadge Seam Coal

The solubilities of the distillation residues in hexane, toluene and pyridine are listed in Table 14.

a. SRC I Mode

The effect of temperature or additive level on solubilities cannot be determined since samples were only available from part B of the run.

b. SRC II Mode

There was an increase in the solubility ratios when the level of pyrite was increased from 1.0% in run DOE 355RA to 2.0% in run DOE 356RA at 450°C. (The ratios should be compared instead of the absolute solubilities to avoid confounding of results due to different levels of conversion.) This is in contrast to the increased fusion point observed with the 2% pyrite addition level which may be associated with the higher ash level in the distillation residue. There was no significant difference in solubility brought about by an increase in additive level at 465°C (run DOE 356RB vs 355RB).

The increase in temperature in going from part A to B of each run generally resulted in a decrease in solubility, which is in agreement with the increased fusion points.

E. Yields and Compositions for Detailed Product Arrays

1. Amax Belle Ayr Coal

The product array from run DOE 350RC has been separated into a large number of fractions by distillation and extraction. These fractions comprise four main groups:

a. Substances normally volatile at room temperature and atmospheric pressure.

b. Substances normally liquid at room temperature which can be distilled.

c. Substances which are soluble in hot pyridine but will not distill.

d. Insoluble organic matter and ash.

The first group may be further characterized by gas chromatography to provide well identified gaseous reaction products. The distillable liquid product is too complex for such treatment and was therefore broken down into ten narrow boiling ranges. Functional group titrations have been performed on these cuts to aid in qualitative analysis of the oils. The fractions isolated in the last three groups and their properties are shown in Table 15. The yields and elemental analyses for the entire product array are shown in Table 16.

This is not lined out data as the samples were taken about half way through run DOE 350RC while pyrite was leaving the system. The main objective, however, was to develop a procedure for looking at the chemistry of the coal conversion process in more than the usual amount of detail. It is felt that the yields in Table 16 correspond to operation with approximately 1/2% added pyrite catalyst in the feed slurry. These studies provide a check on elemental balances and information on the location of various elements and functional groups within the yield structure.

2. Kaiparowits Coal

A similar blend of oils was prepared from the lined out portion of the Kaiparowits coal run at 450°C with added pyrite in the SRC II mode (run DOE 353RA). These were proportioned based on preliminary yields for products 41 through 65. The blend was distilled into ten equal weight fractions and a corresponding distillation residue sample was sequentially extracted using hexane, toluene and pyridine. The pyridine insoluble fraction was split into two portions and one portion was thoroughly extracted with a mixture of hydrochloric and hydrofluoric acids. The resulting fractions were analyzed for carbon, hydrogen, sulfur, nitrogen and oxygen (by difference). Where oil fractions could be titrated, the material reacting with perchloric acid in glacial acetic acid was considered as having a basic nitrogen functional group and that reacting with tetrabutyl ammonium hydroxide (sample dissolved in dimethyl sulfoxide) as having an acidic oxygen functional group. It is possible that some nitrogen compounds are acidic enough to react with the latter reagent, however.

A summary of elemental and functional group determinations is presented in Table 17. The functional group determinations usually accounted for much of the nitrogen determined by Kjeldahl or oxygen by difference, respectively. For the eighth and ninth product fractions, however, the titration indicated more oxygen than was found by difference, which suggests that some of the "acidic" material may actually contain nitrogen structures instead.

When infrared spectra of any of the fractions in this set are compared to those of similar fractions from Amax Belle Ayr coal, they are found to match well. This includes spectra of the hexane soluble fraction.

The yields and elemental analyses for the entire product array and elemental balance are shown in Table 18.

3. Wadge Seam Coal

A proportional blend of SRC II products was prepared using a preliminary yield structure from the 450°C segment of the run catalyzed with 2% pyrite (DOE 356RA). The blend was also distilled to obtain ten equal weight fractions and the vacuum distillation residue was extracted sequentially with hexane, toluene and pyridine. The residue insoluble in pyridine was split into two portions and one portion was exhaustively extracted with a mixture of hydrochloric acid and hydrofluric acid to remove the mineral matter. The elemental and functional group analyses for this set of samples is presented in Table 19.

The first proportional blend was based on a trial calculation using product 38 as the basis for establishing the yields. When the elemental analysis results were combined with approximate yield data from the same part of the run, a reasonable accounting of material element by element was obtained. These results are given in Table 20.

A second sample of oil from Wadge seam coal was extracted with dilute sulfuric acid followed by extraction with dilute sodium hydroxide solution. The resulting "neutral oil" was then distilled into ten equal weight fractions. The elemental analyses for these samples are incomplete since total nitrogen is not available. The other results are given in Table 21.

In general, it appears that the aqueous extraction procedure has been more effective in removing oxygenated material than in removing nitrogenated material from the oil. It is not clear if this is the consequence of low solubility of the nitrogen containing materials as ionic products, or because the nitrogen compounds are only weakly basic. The functional group titration is done using perchloric acid in glacial acetic acid and is capable of reacting very weak bases in comparison to an aqueous reagent system. It is also evident that the lighter weight products tend to be extracted by the aqueous reagent system more completely than the higher molecular weight products.

VI. ANCILLARY STUDIES

A. Comparison of Product Fractions from the Amax Belle Ayr, Kaiparowits and Wadge Seam Coals

Even though the Amax Belle Ayr, Kaiparowits and Wadge seam coals are from different states or provinces, were run with different slurry formulations and had different levels of pyrite addition, the product fractions* produced have similar composition and boiling ranges. This can be seen by comparing the detailed elemental analyses, fraction by fraction, for the Amax Belle Ayr coal (Table 14), Kaiparowits coal (Table 16) and Wadge seam coal (Table 18). An even more detailed study can be made by comparing the infrared spectra of these fractions. This collection of spectra is too voluminous to include in the quarterly report**, but comments regarding such a comparison follow.

1. The spectrum for fraction 0 (water phase) in products derived from any of the three western coals contains a

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* These fractions refer to the narrow boiling range cuts and sequential extractions as described in section V-E.

** It is anticipated that these spectra will be included in a topical report comparing the liquefaction behavior of these coals.

small carbonyl band. This is associated with a carboxylic acid which resembles propionic acid and which can be isolated by ether extraction of the acidified water phase. In all cases, the yield is small and the material is of interest principally because little has been observed in products from the bituminous coals previously studied.

2. The last distillation fraction contains a wax-like component which gives a characteristic band of higher intensity at a wave number of 2850 than is normal for a bituminous coal product. The western coals all contain a wax which can be extracted from the coal with a suitable solvent (such as methylene chloride for example) and which passes through the reactor without being much altered. Some indication of this material can be seen in fractions 7, 8 and 9.

3. Phenolic material is substantially absent from fraction 1 and increases to a peak in the third fraction, as a rule. This is the fraction boiling from near the boiling point of phenol (182°C) to about 220°C, therefore the fraction includes phenol itself and some methyl phenols also. The oxygen content of the fraction is a little higher than can be accounted for by the phenolics determined by titration, and IR spectra generally show only the presence of phenolic material to account for oxygen present. The intensity of the OH band is in good relative agreement with the oxygen content for all fractions until about the 7th or 8th. At this point, the oxygen content trends upward and this increase is due to hetero oxygen which will not be indicated clearly by IR.

4. The nitrogen concentration is lowest in the first fraction and increases smoothly throughout the series, with a dip at fraction 7 using functional group data but not using total nitrogen data (by Kjeldahl). Both nitrogen and oxygen increase in the distillation residue fractions. Nitrogen functions are obscured by phenolic bands at the same general location in the infrared spectra.

B. Inspection of Products by Infrared Spectroscopy and Simulated Distillation Gas Chromatography

Several product streams from the SRC II processing of Amax Belle Ayr coal were studied in detail by infrared spectroscopy and simulated distillation gas chromatography to elucidate the number and kinds of substances derived. In particular, the products collected in vessels 2 (ambient temperature separator bottoms) and 4 (atmospheric distillation overhead) were chemically separated to produce neutral oils, saturates, water soluble and insoluble phenols and bases. The subsequent physical separations by simulated distillation and infrared analysis have provided considerable insight into the nature of some of the light and intermediate molecular weight oils from coal liquefaction. The details of the study are given in Appendix A.

C. Chemistry of Amax Belle Ayr Coal Liquefaction

The decreasing iron level in the dissolver during run DOE 350RC has been related to the yield structure and various properties of the distillation residue. The details of this work are given in Appendix B.

VII. MAINTENANCE AND MODIFICATIONS

A. Maintenance

A waxy material built up on the filter for the distillation column during run DOE 350RA at 450°C with Belle Ayr coal but was absent during run DOE 350RB at 465°C. A sample of this material was washed with acetone and an IR analysis indicates that it is similar to a methylene chloride extract of the feed coal (a montan wax).

On the fourth day of run DOE 356R, the hydrogen feed differential pressure controller failed. The backup Aminco compressor was brought into service while the controller was repaired. The problem was apparently due to a loose circuit board connector. On the sixth day of the run, a mounting screw in the Fluke data logger became loose and a washer fell onto the display printed circuit board causing the display to malfunction. No permanent damage resulted.

B. Modifications

The new DOE 3 dissolver was used for the first time in run DOE 357. It has a volume of 1064 cm^3 with an I.D. of 2.79 cm (1.1 in.) in the main part of the vessel, as shown in Figure 15. The dissolver is constructed of 321 stainless steel with a Grayloc hub that separates the 1 1/2 in. Schedule XX pipe into two equal sections, each about 76.0 cm (30.0 in.) in length. The entire cross section of the dissolver is exposed when opened, to aid in cleaning. The ends of the vessel are fabricated from 2.54 cm (1 in.) O.D., 1.75 cm (0.56 in.) I.D. pipe and a 20 cm nipple was added for an overall length of 210 cm (82.8 in.). The dissolver is very close to the standard DOE 1 dissolver in volume and length to diameter ratio.

The relays on the Love temperature controllers continue to malfunction. Modifications which are being tested to alleviate the problem include use of external, heavy duty relays and substitution of the mechanical relays with solid state devices.

TABLE 1

Summary of Process Conditions, Yields and Product Analyses

	DOE 349	DOE 350RA	DOE 350RB	DOE 350RC-5	DOE 351A	DOE 351B	DOE 352
Conditions							
Coal	← Amax (Belle Ayr Mine) →						
Operating Mode	SRC I	← SRC II →			← SRC I →		
Dissolver	← DOE 1 →						
Nominal Slurry Residence Time, hr.	0.52	1.05	1.05	1.05	0.52	0.52	0.51
Coal Feed Rate, lb/hr/ft^3	53.8	20.4	20.5	20.4	54.3	54.0	55.4
Average Dissolver Temperature, °C	450	450	465	450	450	465	445
°F	842	842	869	842	842	869	833
Dissolver Pressure, psig	1500	2250	2250	2250	1500	1500	1500
Hydrogen Feed							
Wt %, based on slurry	1.92	4.22	4.21	4.22	1.91	1.92	1.83
MSCF/ton of coal	18.7	53.3	53.2	53.3	18.6	18.7	17.8
Pyrite Addition Rate, Wt % based on coal[a]	--	2.15	2.15	--	1.66	1.66	--
Slurry Formulation, Wt %							
Coal	39.0	30.0	30.0	30.0	39.0	39.0	39.0
Recycled Coal Solution	--	65.0	61.0	58.0	--	--	--
Recycled Solvent	61.0	4.0	0.0	12.0	60.0	60.0	61.0
Pyrite	--	1.0	1.0	--	1.0	1.0	--
Slurry Blend Composition, Wt %							
Coal		30.0	30.0	30.0			
Middle Distillate (193-288°C, 380-550°F)		4.3	3.2	2.4			
Heavy Distillate (>288°C, >550°F)		26.7	28.3	29.6			
SRC		24.4	23.3	22.5			
Ash (from recycle coal solution)		12.0	10.8	5.5			
Insoluble Organic Matter (from recycle coal solution)		1.6	3.4	10.0			
Pyrite		1.0	1.0	--			
Total Solids		44.6	45.2	45.5			
Yields, Wt % Based on MF Coal[b]							
H_2O	7.5	9.5	10.0	8.2	7.6	8.8	10.4
CO	1.0	1.7	1.5	0.9	0.7	0.8	0.8
CO_2	7.4	5.6	5.6	6.3	6.2	6.7	6.3
H_2S[c]	0.5	1.0	0.6	0.5	0.5	0.5	0.3
NH_3	0.1	0.6	0.6	0.3	0.1	0.2	0.1
C_1	2.2	3.8	5.5	4.3	2.1	3.3	1.9
C_2	1.6	2.9	4.0	2.8	1.4	2.0	1.4
C_3	1.1	2.6	3.4	2.2	0.9	1.3	0.9
C_4	0.4	1.1	1.2	0.8	0.3	0.4	0.3
Total C_1-C_4	5.3	10.4	14.1	10.1	4.7	7.0	4.5
Naphtha, C_5-193°C (380°F)	6.9	11.8	15.8	8.7	7.3	14.3	6.4
Wash Solvent, 193-249°C (380-480°F)[d]	9.8	17.5	18.0	13.7	9.1	12.3	6.8
Recycle Solvent, >249°C (>480°F)(loss)[e]	(25.7)	20.8	9.9	3.1	(5.0)	(11.9)	(26.4)
Total Oil (loss)	(9.0)	50.1	43.7	25.5	11.4	14.7	(13.2)
SRC	40.3	19.3	21.1	31.0	47.3	38.2	44.1
Insoluble Organic Matter	41.1	1.2	3.0	13.8	16.8	18.5	40.3
Ash	6.9	7.0	7.2	7.5	7.3	7.3	7.1
Total	101.1	106.4	107.4	104.1	102.6	102.7	100.7
H_2 Consumed (gas balance)	1.1	5.6	6.6	4.1	2.0	2.1	0.7
Pyrite Conversion Byproducts	--	0.8	0.8	--	0.6	0.6	--
Product Analyses							
Recycle Solvent Analyses[e]							
% C	88.59	87.65	88.40	88.52	88.23	88.44	88.97
% H	7.37	8.47	8.01	7.71	7.56	7.29	7.35
% S	0.40	0.07	0.03	0.06	0.38	0.37	0.41
% N	0.73	1.07	1.14	0.98	0.78	0.78	0.72
% O (by difference)	2.91	2.74	2.42	2.73	3.05	3.12	2.55
Specific Gravity	1.0583	1.0328	1.0483	1.0550	1.0640	1.0663	1.0646
SRC Analyses[f]							
% C	82.65	56.69	56.37	74.27	87.72	88.88	88.77
% H	4.05	3.66	2.99	3.75	5.37	4.96	6.14
% S	0.48	3.33	3.21	0.47	0.28	0.25	0.29
% N	--	1.05	0.97	1.41	1.53	1.55	1.38
% O (by difference)	--	--	--	--	4.31	3.90	4.05
% Ash	7.26	39.52	40.41	16.55	0.79	0.46	0.37
Fusion Point, °C	165	107	121	188	167	184	218

a) As pure FeS_2. b) Based on distillation of filtrate for runs DOE 351 and 352; based on distillation of UFCS for others. c) Includes H_2S derived from the added pyrite. d) Middle Distillate (193-288°C, 380-550°F) for run DOE 350R. e) Heavy Distillate (>288°C, >550°F) for run DOE 350R. f) UFCS distillation residue for runs DOE 349 and 350.

TABLE 1 (Continued)

Conditions	DOE 353RA	DOE 353RB	DOE 353RC	DOE 354A	DOE 354B
Coal	Kaiparowits Plateau (Utah)				
Operating Mode	SRC II			SRC I	
Dissolver	DOE 1				
Nominal Slurry Residence Time, hr	1.01	1.01	1.04	1.01	1.03
Coal Feed Rate, $lb/hr/ft^3$	20.9	20.7	20.3	26.9	26.5
Average Dissolver Temperature, °C	450	464	450	451	450
°F	842	867	842	844	842
Dissolver Pressure, psig	2250				
Hydrogen Feed					
Wt %, based on slurry	4.05	4.07	4.17	4.06	4.12
MSCF/ton of coal	52.2	52.7	53.8	40.6	41.2
Pyrite Addition Rate, Wt % based on coal[a]	3.14	3.13	--	2.40	--
Slurry Formulation, Wt %					
Coal	30.0	30.0	30.0	39.0	39.0
Recycled Coal Solution	65.0	61.0	62.0	--	--
Recycled Solvent	4.0	8.0	8.0	60.0	61.0
Pyrite	1.0	1.0	--	1.0	--
Slurry Blend Composition, Wt %					
Coal	30.0	30.0	30.0		
Middle Distillate (193-288°C, 380-550°F)	2.8	3.9	2.1		
Heavy Distillate (>288°C, >550°F)	24.9	30.1	26.8		
SRC	26.7	21.2	27.6		
Ash (from recycle coal solution)	10.9	10.0	6.7		
Insoluble Organic Matter (from recycle coal solution)	3.7	3.8	6.8		
Pyrite	1.0	1.0	--		
Total Solids	45.6	44.8	43.5		
Yields, Wt % based on MF Coal[b]					
H_2O	7.0	8.0	7.5	6.5	6.9
CO	1.3	1.6	0.9	0.8	0.8
CO_2	4.2	4.2	4.9	5.7	4.5
H_2S[c]	1.0	1.4	0.4	0.6	0.4
NH_3	0.5	0.6	0.3	0.2	0.2
C_1	4.5	6.5	5.0	3.3	3.9
C_2	3.0	4.3	3.0	2.0	2.2
C_3	2.7	3.6	2.3	1.6	1.6
C_4	1.2	1.4	0.9	0.6	0.7
Total C_1-C_4	11.4	15.8	11.2	7.5	8.4
Naphtha, C_5-193°C (380°F)	10.8	13.2	9.4	6.5	7.5
Middle Distillate, 193-288°C (380-550°F)[d]	13.0	17.7	13.4	6.5	9.2
Heavy Distillate, >288°C (>550°F)(loss)[e]	19.5	8.5	6.7	6.5	(7.3)
Total Oil	43.3	39.4	29.5	19.5	9.4
SRC	25.8	23.3	33.1	47.2	41.4
Insoluble Organic Matter	3.6	4.2	8.2	8.0	22.0
Ash	8.2	8.8	8.0	7.9	8.5
Total	106.3	107.3	104.0	103.9	102.5
H_2 Consumed (Gas Balance)	5.2	6.2	4.0	3.1	2.5
Pyrite Conversion Byproducts	1.1	1.1	--	0.8	--
Product Analyses					
Heavy Distillate Analyses[e]					
% C	87.84	88.78	88.70	88.70	88.97
% H	8.56	7.92	7.77	7.61	7.50
% S	0.05	0.04	0.08	0.24	0.24
% N	1.15	1.18	1.09	0.78	0.76
% O (by difference)	2.40	2.08	2.36	2.67	2.53
Specific Gravity	1.0305	1.0486	1.0494	1.0517	1.0587
Distillation Residue Analyses[f]					
% C	60.87	56.95	66.74	88.40	89.59
% H	3.58	3.01	3.40	5.69	5.09
% S	2.44	2.77	0.76	0.13	0.11
% N	1.17	1.06	1.34	1.81	1.75
% O (by difference)	--	--	--	3.84	3.25
% Ash	33.56	39.18	25.39	0.13	0.21
Fusion Point, °C	104	124	(g)	139	178

a) As pure FeS_2. b) Based on distillation of UFCS for run DOE 353R and distillation of filtrate for run DOE 354. The yields from these runs are corrected for volatile losses in later reports by use of a forced ash balance. c) Includes H_2S derived from the added pyrite. d) Wash solvent (193-249°C, 380-480°F) for run DOE 354. e) Recycle Solvent (>249°C, >480°F) for run DOE 354. f) SRC for run DOE 354. g) The last two samples from this run had fusion points above 250°C.

TABLE 1 (Continued)

Conditions	DOE 355RA	DOE 355RB	DOE 356RA	DOE 356RB	DOE 357A	DOE 357B	DOE 357C
Coal	Wadge Seam (Energy Mine)						
Operating Mode	SRC II				SRC I		
Dissolver	DOE 1				DOE 3		
Nominal Slurry Residence Time, hr.	1.03	1.03	1.02	1.00	1.03	1.03	1.03
Coal Feed Rate, lb/hr/ft^3	20.1	20.0	20.2	20.6	25.5	25.7	25.7
Average Dissolver Temperature, °C	450	464	450	465	450	465	449
°F	842	867	842	869	842	869	840
Dissolver Pressure, psig	2250						
Hydrogen Feed							
Wt %, based on slurry	4.11	4.11	4.05	3.96	4.11	4.08	4.08
MSCF/ton of coal	52.6	52.9	52.2	51.0	41.2	40.9	40.9
Pyrite Addition Rate, Wt % based on coal[a]	3.14	3.13	6.23	6.25	4.79	4.81	--
Slurry Formulation, Wt %							
Coal	30.0	30.0	30.0	30.0	39.0	39.0	39.0
Recycled Coal Solution	61.0	57.0	60.0	57.0	--	--	--
Recycled Solvent	8.0	12.0	8.0	11.0	59.0	59.0	61.0
Pyrite	1.0	1.0	2.0	2.0	2.0	2.0	--
Slurry Blend Composition, Wt %							
Coal	30.0	30.0	30.0	30.0			
Middle Distillate (193-288°C, 380-550°F)	7.1	7.8	7.5	5.7			
Heavy Distillate (>288°C, >550°F)	22.5	24.0	25.1	23.0			
SRC	23.3	18.8	21.2	22.7			
Ash (from recycle coal solution)	9.6	8.5	10.7	9.3			
Insoluble Organic Matter (from recycle coal solution)	6.5	9.9	3.5	7.3			
Pyrite	1.0	1.0	2.0	2.0			
Total Solids	47.1	49.4	46.2	48.6			
Yields, Wt % based on MF Coal[b]							
H_2O	8.7	7.1	7.6	8.1	7.8	8.0	6.6
CO	0.6	0.6	0.8	0.6	0.7	0.9	0.6
CO_2	3.0	3.6	2.5	3.4	2.8	3.5	3.3
H_2S[c]	1.0	1.0	1.9	2.1	1.6	1.4	0.1
NH_3	0.5	0.6	0.7	0.7	0.3	0.5	0.4
C_1	5.1	7.3	5.0	6.8	3.8	6.2	3.7
C_2	3.2	4.1	3.2	3.9	2.3	3.7	2.3
C_3	2.6	3.0	2.8	3.0	1.8	2.7	1.6
C_4	1.1	1.2	1.1	1.1	0.7	1.0	0.6
Total C_1-C_4	12.0	15.6	12.1	14.8	8.7	13.6	8.2
Naphtha, C_5-193°C (380°F)	10.3	12.0	10.4	9.4	8.3	12.2	12.1
Middle Distillate, 193-288°C (380-550°F)[d]	9.7	13.1	16.2	14.8	6.0	9.6	9.3
Heavy Distillate, >288°C (>550°F)(loss)[e]	13.4	3.2	13.8	(0.6)	12.6	(1.0)	(8.0)
Total Oil	33.4	28.3	40.4	23.6	26.9	20.8	13.4
SRC	28.5	25.7	27.3	33.4	41.8	42.1	52.4
Insoluble Organic Matter	7.9	13.5	4.5	10.7	5.8	6.0	8.6
Ash	9.5	9.4	9.3	9.3	9.3	9.3	9.3
Total	105.1	105.4	107.1	106.7	105.7	106.1	102.9
H_2 Consumed (gas balance)	4.0	4.3	5.0	4.6	4.1	4.4	2.9
Pyrite Conversion Byproducts	1.1	1.1	2.1	2.1	1.6	1.7	--
Product Analyses							
Heavy Distillate Analyses[e]							
% C	88.51	88.70	88.10	88.79	88.68	88.86	--[g]
% H	7.84	7.53	8.03	7.26	7.66	7.47	--
% S	0.23	0.19	0.17	0.24	0.34	0.28	--
% N	1.29	1.34	1.67	1.59	0.92	1.00	--
% O (by difference)	2.13	2.24	2.13	2.12	2.40	2.39	--
Specific Gravity	1.0560	1.0635	1.0509	1.0751	1.0546	1.0550	--
Distillation Residue Analyses[f]							
% C	67.80	66.34	59.12	60.34	87.84	89.39	--[g]
% H	3.85	3.48	3.61	3.15	5.57	5.21	--
% S	1.94	1.85	3.81	3.92	0.22	0.17	--
% N	1.80	1.80	1.69	1.65	2.49	2.52	--
% O (by difference)	--	--	--	--	3.13	2.19	--
% Ash	24.03	25.98	32.55	31.89	0.75	0.52	--
Fusion Point, °C	145	158	168	216	154	150	--

a) As pure FeS_2. b) Based on distillation of UFCS for runs DOE 355R and 356R and distillation of filtrate for run DOE 357. The yields from these runs are corrected for volatile losses in later reports by use of a forced ash balance. c) Includes H_2S derived from the added pyrite. d) Wash solvent (193-249°C, 380-480°F) for run DOE 357. e) Recycle Solvent (>249°C, >480°F) for run DOE 357. f) SRC for run DOE 357. g) Single sample from this part of run was inadvertently discarded.

TABLE 2

Analyses of Feed Coals[a]

a. Compositional Analyses

Coal Identification				
Company	Amax		Mono Power	Energy Fuels
Mine	Belle Ayr		(Kaiparowits Plateau)	Energy Mine No. 1
Seam	Wyodak-Anderson		Red	Wadge
	Lot SN21648	Lot 23324		
Proximate Analysis				
% Ash	7.30	8.24	8.42	9.48
% Volatile	47.84	44.30	43.88	39.01
% Fixed Carbon	44.86	47.46	47.70	51.51
	100.00	100.00	100.00	100.00
% Moisture	8.14	7.91	6.51	6.88
Heating Value, Btu/lb	11,890	11,713	12,399	12,258
Sulfur Forms				
% Pyrite	0.13	0.058	0.045	0.038
% Sulfate	0.00	0.038	0.004	0.007
% Organic	0.48	0.524	0.421	0.505
% Total	0.61	0.620	0.470	0.550
Free Swelling Index	0	0	0	0
Ultimate Analyses, Wt %				
Carbon	67.35	68.74	71.43	70.34
Hydrogen	5.14	4.78	4.85	5.04
Nitrogen	1.31	1.21	1.43	1.95
Chlorine	0.01	0.11	0.10	0.12
Sulfur	0.61	0.62	0.47	0.55
Ash	7.30	8.24	8.42	9.48
Oxygen (difference)	18.28	16.30	13.30	12.52
	100.00	100.00	100.00	100.00
Mineral Analysis of Ash, Wt %, ignited basis				
Silica, SiO_2	29.77	31.42	40.59	56.32
Alumina, Al_2O_3	16.02	17.20	12.15	26.08
Titania, TiO_2	1.25	1.24	0.73	0.89
Ferric Oxide, Fe_2O_3	5.06	5.17	6.17	3.25
Lime, CaO	24.20	21.35	22.18	5.28
Magnesia, MgO	3.48	3.57	4.04	1.23
Potassium Oxide, K_2O	0.57	0.41	0.54	0.86
Sodium Oxide, Na_2O	1.69	0.81	0.87	0.29
Sulfur Trioxide, SO_3	17.10	16.56	12.25	4.41
Phos. Pentoxide, P_2O_5	0.61	1.39	0.16	1.11
Strontium Peroxide, SrO_2	--	0.41	0.01	0.01
Barium Oxide, BaO	--	0.45	0.28	0.25
Manganese Oxide, MnO	--	0.02	0.03	0.02
Undetermined	0.25	--	--	--
	100.00	100.00	100.00	100.00
% Iron in coal	0.26	0.30	0.36	0.22
Fusion Temperature of Ash, °F (Reducing)				
Initial Deformation	--	1760	1750	2440
Softening (H=W)[b]	--	1860	1850	2540
Softening (H=1/2W)	--	1980	1980	2680
Fluid	--	2110	2100	2700+
% Equilibrium Moisture		19.80[c]	9.21	10.83

a) All analyses performed by Commercial Testing & Engineering Company. All analyses except moisture are on a dry coal basis.

b) H = cone height; W = cone width.

c) Test on -150 mesh material; not ASTM 1412-74.

TABLE 2 (Continued)

b. Kaiparowits Coal Petrographic Analysis

MACERAL ANALYSIS
(Volume Percent)
(Mineral-Matter Free Basis)

MACERAL		MACERAL GROUP	
Vitrinite	70.0	Vitrinite	71.6
Pseudovitrinite	1.6		
Exinite	4.8	Exinite (Liptinite)	6.7
Resinite	1.9		
Semi-Fusinite	6.1		
Semi-Macrinite	1.1		
Fusinite	9.4	Inertinite	21.7
Macrinite	1.3		
Micrinite	3.8		
TOTAL	100%		100%

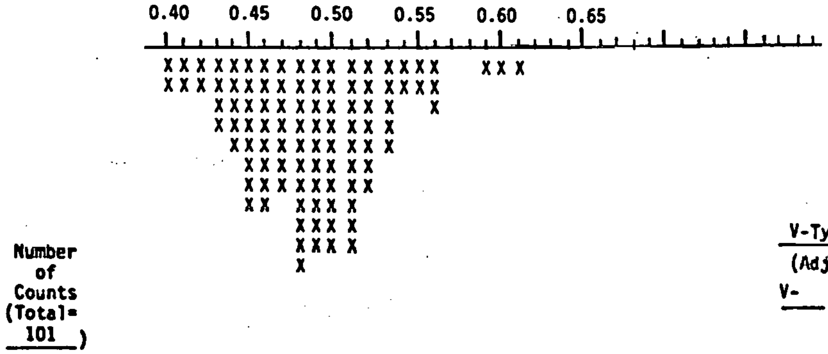
COMMENTS: Approximately 4% of the coal particles showed evidence of oxidation ranging in degree from mild to severe.

REFLECTANCE ANALYSIS

Mean-Maximum Vitrinite Ro- 0.49

Distribution of Vitrinite Reflectance Readings:

%Ro



V-Type Table for Vitrinites (=100%)

V- 4	V- 5	V- 6	V-
58.4	39.6	2	

V-Type Table for Vitrinites (= %)
(Adjusted to = Maceral % of Reactive Vitrinites)

V-	V-	V-	V-

TABLE 2 (Continued)

c. Energy Mine Coal Petrographic Analysis

MACERAL ANALYSIS
(Volume Percent)
(Mineral-Matter Free Basis)

MACERAL		MACERAL GROUP	
Vitrinite	79.6	Vitrinite	85.5
Pseudovitrinite	5.9		
Exinite	4.0	Exinite (Liptinite)	5.3
Resinite	1.3		
Semi-Fusinite	1.8		
Semi-Macrinite	0.4		
Fusinite	3.0	Inertinite	9.2
Macrinite	0.5		
Micrinite	3.5		
TOTAL	100%		100%

REFLECTANCE ANALYSIS

Mean-Maximum Vitrinite Ro- 0.61

Distribution of Vitrinite Reflectance Readings:

%Ro

```
0.50      0.55      0.60      0.65      0.70      0.75
|.........|.........|.........|.........|.........|...........
  X X X   X X X X X X X X X X X X X X X X X
    X     X X X X X X X X X X X X X X   X
    X     X X X X X X X X X X X X   X
    X     X X X X X X X X X X X X
          X X X X X X X X X X X X
          X X         X X X X X X
          X X         X X X X X X
          X X         X X X
                      X X
                        X
                        X
```

Number of Counts (Total= 100)

V-Type Table for Vitrinites (=100%)

V- 5	V- 6	V- 7	V-
37	60	3	

V-Type Table for Vitrinites (= %)

(Adjusted to = Maceral % of Reactive Vitrinites)

V-	V-	V-	V-

TABLE 3

Additives Analyses

	Pyrite Source	
	U. S. Steel Robena Mine	Matheson, Coleman and Bell
Weight %[a]		
Fe	30.20	43.61
S	34.38	53.01
C	5.81	0.09
H	0.69	0.04
Moisture[b]	1.40	0.20
Ash	75.70	68.13
Mole Ratio S/Fe	1.99	2.12
Purity, as FeS_2	64.58	93.59
Average Particle Size, μm	1.7[c]	65[d]

a) Dry basis.

b) As volatiles at 110°C under He atmosphere.

c) By Coulter Counter, particle size distribution shown in Figure 1.

d) Estimated.

TABLE 4

Summary of 2^2 Factorial in Temperature and Pyrite Addition Level

Constant Conditions

SRC II Mode
1.0 hr residence time
2250 psig pressure
Wadge Seam Coal

Variable Conditions

	Factors	Levels -	Levels +
A	Temperature, °C	450	465
B	Pyrite, % in slurry	1.0	2.0

		A	B	Yields, Wt. % MF Coal Basis						Product Properties						
										Heavy Distillate			Distillation Residue			
Run No.	Yates Order	Temperature	Pyrite Level	C_1-C_4	Heavy Distillate	Total Oil	SRC	IOM	H_2 Consumed	% H	% S	% N	% S	% Ash	% H*	% N*
355RA	1 1	-	-	12.0	13.4	33.4	28.5	7.9	4.0	7.84	0.23	1.29	1.94	24.03	5.07	2.47
355RB	2 a	+	-	15.6	3.2	28.3	25.7	13.5	4.3	7.53	0.19	1.34	1.85	25.98	4.70	2.43
356RA	3 b	-	+	12.1	13.8	40.4	27.3	4.5	5.0	8.03	0.17	1.57	3.81	32.55	5.35	2.51
356RB	4 ab	+	+	14.8	(0.6)	23.6	33.4	10.7	4.6	7.26	0.24	1.59	3.92	31.89	4.62	2.42
		Main Effects														
			A	3.15	-12.30	-10.95	1.65	5.90	-0.05	-0.54	0.02	0.04	0.01	0.65	-0.55	-0.07
			B	-0.35	-1.70	+1.15	3.25	-3.10	0.65	-0.04	-0.01	0.27	1.97	7.22	0.10	0.02
		Two Factor Interaction														
			AB	-0.45	-2.10	-5.85	4.45	0.30	-0.35	-0.23	0.06	-0.02	0.10	-1.31	-0.18	-0.03

* Ash Free Basis

TABLE 5

UNFILTERED COAL SOLUTION VISCOSITIES[a]
Runs DOE 349, 350R, 351 and 352, Belle Ayr Coal

Run No. DOE	Temperature °F	Shear Rate sec^{-1}	Viscosity cP
349 P-39	210	3.96	103
	210	7.93	82.0
	210	15.86	76.8
	210	39.64	70.9
	230	7.93	64.0
	230	15.86	55.3
	230	39.64	49.9
	230	79.28	45.4
	250	15.86	41.0
	250	39.64	35.1
	250	79.28	32.3
	270	15.86	32.0
	270	39.64	26.9
	270	79.28	24.1
350RA P-56	210	3.32	163
	210	8.30	146
	210	16.61	137
	230	8.30	99.9
	230	16.61	95.2
	270	8.30	61.9
	270	16.61	54.7
350RB P-86	210	3.32	230
	210	8.30	189
	210	16.61	167
	230	8.30	133
	230	16.61	116
	270	8.30	82.5
	270	16.61	70.6

TABLE 5 (Continued)

Run No. DOE	Temperature °F	Shear Rate sec^{-1}	Viscosity cP
350RC P-141	210	0.415	6.06 $X10^3$
	210	0.830	5.80 $X10^3$
	210	1.66	5.50 $X10^3$
	230	0.830	2.52 $X10^3$
	230	1.66	2.25 $X10^3$
	230	3.32	2.15 $X10^3$
	270	3.32	642
	270	8.30	560
	270	16.61	516
351 P-32	210	15.86	35.0
	210	39.64	30.9
	210	79.28	29.5
	230	15.86	27.0
	230	39.64	22.8
	230	79.28	21.2
	270	39.64	13.9
	270	79.28	12.5
352 P-22	210	3.96	123
	210	7.93	112
	210	15.86	102
	210	39.64	94.7
	230	7.93	72.5
	230	15.86	67.3
	230	39.64	61.1
	270	15.86	37.0
	270	39.64	32.7
	270	79.28	31.0

a) Brookfield Model LV viscometer.
Spindle No. 18 for runs DOE 349, 351.
Spindle No. 28 for run DOE 350R.
Procedure: 45 minute initial warmup and equilibration;
20-30 minute equilibration after temperature change;
10 minute equilibration after shear rate change.

TABLE 6

Feed Slurry Viscosities
Run DOE 350R, Belle Ayr Coal

Run No. DOE	Temperature °F	Shear Rate sec^{-1}	Viscosity 10^3 cP
350RA P-56	210	0.083	155
	230	0.083	136
	270	0.083	83.1
	270	0.166	58.3
350RD[h] P-86	210	0.083	71.8
	210	0.166	49.2
	230	0.083	134
	270	0,083	76.1
	270	0.166	52.7
350RB[b,c] P-86	210	0.083	94.5
	210	0.166	60.8
	230	0.083	155
	250	0.083	148
	270	0.083	92.5
	270	0.166	58.8
350RB[d] P-86	210	0.083	114
	230	0.083	85.0
	230	0.166	61.4
	270	0.083	76.1
	270	0.166	48.8
350RC[b,e] P-141	230	0.083	137
	270	0.083	76.9
	270	0.166	52.7
	270	0.415	25.2
	270	0.830	15.3

a) Brookfield Model LV viscometer
Spindle No. 28
Procedure: 45 min. initial warmup and equilibration;
20-30 min. equilibration after temperature change;
10 min. equilibration after shear rate change.

b) Feed slurry samples swelled as the temperature increased from 210°F to 230°F. The samples returned to original volumes as the temperature rose from 230°F to 250°F.

c) Product 86 was run again as a check on the original measurements.

d) Product 86 was run a third time using a modified procedure. The sample was first heated to 270°F for 45 minutes. This was sufficient time to dive off any volatiles and eliminate swelling. The sample was then cooled to 210°F and the normal procedures followed for making measurements. No swelling was observed using this method.

e) Measurements at 210°F exceeded the range of the spindle in use.

TABLE 7

Unfiltered Coal Solution Viscosities[a]
Runs DOE 353R and 354, Kaiparowits Coal

Run No. DOE	Temperature, °F	Shear Rate sec^{-1}	Viscosity cP
353RA P-65	210	4.08	295
	210	10.20	258
	210	20.40	237
	230	4.08	182
	230	10.20	152
	230	20.40	136
	270	10.20	79.0
	270	20.40	68.0
353RB P-87	210	3.96	114
	210	7.93	92.5
	210	15.86	79.8
	210	39.64	70.9
	230	7.93	67.5
	230	15.86	55.0
	230	39.64	47.6
	230	79.28	43.8
	270	15.86	36.8
	270	39.64	27.7
	270	79.28	24.2
353RC P-111	210	0.204	6.55 $X10^3$
	210	0.510	6.40 $X10^3$
	210	1.02	6.23 $X10^3$
	230	0.510	2.74 $X10^3$
	230	1.02	2.63 $X10^3$
	230	2.04	2.48 $X10^3$
	230	4.08	2.38 $X10^3$
	270	1.02	770
	270	2.04	700
	270	4.08	622
	270	10.20	558

TABLE 7 (Continued)

Run No. DOE	Temperature, °F	Shear Rate sec^{-1}	Viscosity cP
354A P-52	190	7.93	32.5
	190	15.86	28.5
	190	39.64	26.1
	190	79.28	25.1
	210	15.86	20.2
	210	39.64	17.6
	210	79.28	17.4
	230	15.86	17.5
	230	39.64	13.5
	230	79.28	12.4
	270	39.64	8.40
	270	79.28	7.40
354B P-75	190	15.86	9.75
	190	39.64	8.50
	190	79.28	7.60
	210	39.64	7.20
	210	79.28	6.45
	230	39.64	6.40
	230	79.28	5.70
	270	39.64	5.50
	270	79.28	5.35

a) Brookfield Model LV viscometer
Spindle No. 31 for runs DOE 353RA and 353RC.
Spindle No. 18 for runs DOE 353RB, 354A and 354B.
Procedure: 45 minute initial warmup and equilibration;
20-30 minute equilibration after temperature change;
10 minute equilibration after shear rate change.

TABLE 8

Feed Slurry Viscosities[a]
Run DOE 353R, Kaiparowits Coal

Run No. DOE	Temperature °F	Shear Rate sec^{-1}	Viscosity 10^3 cP
353RA P-65	210	0.083	33.5
	210	0.166	21.1
	210	0.415	12.0
	210	0.830	8.34
	210	1.66	5.25
	230	0.166	20.3
	230	0.415	10.2
	230	0.830	6.22
	230	1.66	4.02
	230	3.32	2.76
	270	0.830	4.57
	270	1.66	3.08
	270	3.32	2.01
	270	8.30	1.22
353RB P-87	210	0.083	23.9
	210	0.166	15.9
	210	0.415	9.52
	210	0.830	6.01
	210	1.66	3.70
	210	3.32	2.31
	230	0.415	7.07
	230	0.830	4.66
	230	1.66	3.03
	230	3.32	1.97
	230	8.30	1.17
	270	0.830	4.66
	270	1.66	2.83
	270	3.32	1.76
	270	8.30	1.02
	270	16.61	0.731

TABLE 8 (Continued)

Run No. DOE	Temperature ^{0}F	Shear Rate sec^{-1}	Viscosity 10^3 cP
	255	0.083	154
353RC[b] P-111	270	0.083	124
	290	0.083	99.1
	290	0.166	71.1

a) Brookfield Model LV viscometer
Spindle No. 28
Procedure: 45 minute initial warmup and equilibration;
20-30 minute equilibration after temperature change;
10 minute equilibration after shear rate change.

b) The sample swelled as it was heated from 225^{0}F to 230^{0}F. It returned to its original volume above 230^{0}F. For the spindle used, readings were not possible until the temperature reached 255^{0}F, and then only at the lowest possible shear rates.

TABLE 9

Unfiltered Coal Solution Viscosities[a]
Runs DOE 355R, 356R and 357, Wadge Seam Coal

Run No. DOE	Temperature °F	Shear Rate sec^{-1}	Viscosity 10^3 cP
355RA P 30	210	0.830	2.81
	210	1.66	2.74
	210	3.32	2.66
	230	1.66	1.18
	230	3.32	1.14
	230	8.30	1.07
	270	3.32	0.393
	270	8.30	0.333
	270	16.61	0.308
355RB P 45	210	0.830	2.38
	210	1.66	2.23
	210	3.32	2.05
	230	1.66	1.14
	230	3.32	1.03
	230	8.30	0.907
	270	3.32	0.460
	270	8.30	0.347
	270	16.61	0.294
356RA P 47	210	2.04	0.495
	210	4.08	0.460
	210	10.20	0.423
	210	20.40	0.390
	230	4.08	0.262
	230	10.20	0.222
	230	20.40	0.199
	270	10.20	0.099
	270	20.40	0.089

TABLE 9 (Continued)

Run No. DOE	Temperature °F	Shear Rate sec^{-1}	Viscosity cP
356RB P 73	210	0.510	7.48x10^3
	210	1.02	7.32x10^3
	210	2.04	6.64x10^3
	230	1.02	3.18x10^3
	230	2.04	3.03x10^3
	230	4.08	2.82x10^3
	270	2.04	1.05x10^3
	270	4.08	8.60x10^2
	270	10.20	7.26x10^2
	270	20.40	6.13x10^2
357A P 13	210	15.86	17.0
	210	39.64	14.1
	210	79.28	13.3
	230	39.64	10.7
	230	79.28	9.85
	270	39.64	6.90
	270	79.28	6.25
357B P 31	210	15.86	16.5
	210	39.64	14.3
	210	79.28	13.6
	230	39.64	10.9
	230	79.28	10.0
	270	39.64	7.30
	270	79.28	6.60

TABLE 9 (Continued)

Run No. DOE	Temperature °F	Shear Rate sec^{-1}	Viscosity cP
	210	7.93	37.5
	210	15.86	32.8
	210	39.64	29.3
	210	79.28	27.9
357C P 34	230	15.86	24.0
	230	39.64	21.0
	230	79.28	19.5
	270	39.64	12.2
	270	79.28	11.0

a) Brookfield Model LV viscometer
Spindle No. 28 for run DOE 355RA, 355RB
Spindle No. 31 for run DOE 356RA
Spindle No. 34 for run DOE 356RB
Spindle No. 18 for run DOE 357A, 357B, 357C
Procedure: 45 minute initial warmup and equilibration;
20-30 minute equilibration after temperature change.
10 minute equilibration after shear rate change.

TABLE 10

Feed Slurry Viscosities[a]
Runs DOE 355R and 356R, Wadge Seam Coal

Run No. DOE	Temperature °F	Shear Rate sec^{-1}	Viscosity 10^3 cP
355RA[b] P30	210	0.166	14.1
	210	0.415	7.71
	210	0.830	4.74
	210	1.66	3.13
	210	3.32	2.15
	230	0.415	7.45
	230	0.830	4.63
	230	1.66	3.01
	230	3.32	1.93
	230	8.30	1.26
	270	0.830	3.90
	270	1.66	2.70
	270	3.32	1.81
	270	8.30	1.05
355RB[b] P 45	210	0.083	47.9
	210	0.166	36.4
	210	0.415	19.0
	210	0.830	10.9
	230	0.083	58.8
	230	0.166	37.3
	230	0.415	18.4
	230	0.830	10.8
	270	0.166	28.3
	270	0.415	17.5
	270	0.830	10.4
	270	1.66	5.96

TABLE 10 (Continued)

Run No. DOE	Temperature °F	Shear Rate sec^{-1}	Viscosity 10^3 cP
355RB[c] P 45	210	0.083	98.3
	210	0.166	70.9
	230	0.083	67.7
	230	0.166	43.9
	230	0.415	71.1
	270	0.083	76.8
	270	0.166	48.5
	270	0.415	20.8
	270	0.830	12.4
356RA P 47	210	0.166	17.6
	210	0.415	10.2
	210	0.830	6.10
	210	1.66	4.43
	210	3.32	3.34
	230	0.415	7.76
	230	0.830	4.62
	230	1.66	2.94
	230	3.32	2.09
	230	8.30	1.35
	270	1.66	1.52
	270	3.32	1.08
	270	8.30	0.718
	270	16.61	0.555
356RB[d] P 73	320	0.083	189

a) Brookfield Model LV viscometer
Spindle No. 28 for run DOE 355RA, 356RB
Spindle No. 34 for run DOE 356RA, 356RB
Procedure: 45 minute initial warmup and equilibration;
20-30 minute equilibration after temperature change;
10 minute equilibration after shear rate change.

b) Feed slurry samples boiled off volatiles as the temperature increased from 210°F to 230°F. No swelling was noticeable.

c) Product 45 was run again as a check on the original measurements using a modified procedure. The sample was first heated to 270°F for 1 hour to drive off any volatiles. The sample was then cooled to 210°F and the normal procedures followed for making measurements. No boiling of volatiles during the viscosity measurements was noticed using this procedure.

d) Product 73 was the most viscous sample measured to date at this laboratory. Even though the smallest diameter spindle was used, the sample had to be heated to 320°F before a reading was possible.

TABLE 11

Solvent Extraction of Distillation Residues
Runs DOE 351 and 352, Belle Ayr Coal

	DOE 351A P 29	DOE 351B P 35	DOE 352 P 22
Solubility of the SRC Product, wt % in			
Hexane	19.3	14.1	11.1
	18.1	14.8	11.0
Toluene	62.4	61.3	54.8
	60.9	58.4	53.7
Pyridine	99.5	99.6	98.3
	99.7	99.4	99.3
Ratio of Average Solubilities			
Hexane/Pyridine	0.188	0.145	0.113
Toluene Pyridine	0.619	0.602	0.552
Conditions			
Temperature, °C	450	465	445
Pyrite Addition Rate, wt% slurry	1.0	1.0	--

TABLE 12

Solvent Extraction of Distillation Residues
Run DOE 350R, Belle Ayr Coal

	DOE 350RA P 56	DOE 350RB P 86	DOE 350RC-1 P 94	DOE 350RC-1 P 100	DOE 350RC-3 P 114	DOE 350RC-4 P 124	DOE 350RC-5 P 136	DOE 350RC-5 P 141
Solubility of Distillation Residue, wt % in								
Hexane	34.7 35.4	20.4 23.0	21.2 21.2	24.9 24.5	22.2 21.2	12.9 13.8	12.5 11.4	12.7 11.4
Toluene	50.5 49.1	39.3 38.7	43.5 42.6	46.5 45.4	45.9 47.3	43.4 41.9	36.7 35.6	34.5 33.7
Pyridine	55.5 55.5	45.1 44.8	49.7 49.0	52.5 52.7	58.2 58.2	56.3 55.7	51.3 51.0	50.4 50.3
Ratio of Average Solubilities								
Hexane/Pyridine	0.632	0.483	0.429	0.469	0.374	0.238	0.233	0.239
Toluene/Pyridine	0.897	0.867	0.872	0.873	0.801	0.761	0.707	0.677
Conditions								
Temperature, °C	450	465	← 450 →					
Pyrite Addition Rate, Wt % slurry	1.0	1.0	--	--	--	--	--	--

TABLE 13

Solvent Extraction of Distillation Residues
Runs DOE 353R and 354, Kaiparowits Coal

Solubility of the Distillation Residue, Wt % in	DOE 353RA P 60	DOE 353RB P87	DOE 353RC P95	 P103	 P106	 P111	DOE 354A P52	DOE 354B P75
Hexane	27.1 27.4	18.2 18.1	22.3 21.3	16.7 14.7	15.9 15.7	9.9 10.2	25.3 25.9	19.7 20.2
Toluene	47.3 45.2	41.4 39.0	46.8 44.9	44.6 41.8	41.9 40.2	31.6 29.9	63.6 67.2	62.0 --
Pyridine	54.2 54.2	46.8 46.7	54.8 54.7	56.0 55.9	54.9 54.6	45.0 44.8	99.9 99.9	99.7 99.8
Ratio of Average Solubilities								
Hexane/Pyridine	0.503	0.388	0.398	0.280	0.289	0.224	0.256	0.200
Toluene/Pyridine	0.854	0.860	0.838	0.771	0.750	0.685	0.655	0.621
Conditions								
Temperature, °C	450	464	← 450 →				451	450
Pyrite addition Rate, Wt % Slurry	1.0	1.0	--	--	--	--	1.0	--
Mode	← SRC II →		← SRC II →				← SRC I →	

TABLE 14

Solvent Extraction of Distillation Residues
Runs DOE 355R, 356R and 357, Wadge Seam Coal

	DOE 355RA	DOE 355RB	DOE[a] 356RA	DOE 356RB	DOE 356RB	DOE 356RB	DOE 357B
	P 30	P 45	P 42	P 65	P 72	P 73	P 28
Solubility of the Distillation Residue, Wt % in							
Hexane	13.0 13.0	7.7 8.0	16.1	8.9 9.3	6.9 7.2	8.7 9.1	19.3 19.8
Toluene	40.3 39.1	30.4 28.1	38.7	32.0 31.3	30.7 29.2	30.8 29.4	50.2 45.9
Pyridine	58.5 58.3	43.2 42.6	48.1	43.4 43.5	42.8 42.9	43.0 42.7	99.7 99.7
Ratio of Average Solubilities							
Hexane/Pyridine	0.223	0.183	0.334	0.210	0.164	0.208	0.196
Toluene/Pyridine	0.690	0.692	0.805	0.728	0.699	0.703	0.482
Conditions							
Temperature, °C	450	465	450	← 465 →			465
Pyrite Addition Rate, Wt % Slurry	← 1.0 →		← 2.0 →				2.0
Mode	← SRC II →		← SRC II →				SRC I

a) Average of 3 trials using sequential extraction.

TABLE 15

Fractions Isolated from Amax Belle Ayr Coal in Run DOE 350RC

Fraction	How Isolated	Boiling Range, °C	% Carbon	% Hydrogen	% Sulfur	% Nitrogen	% Oxygen	Functional Groups
0	Ether extract of water phase from V-2				0.207	0.19	4.03^f	Carbonyl & Phenolic OH
1	Dist. Prop. Blend	RT - 129	83.08	14.22	0.107	0.05^f 0.32^k	nil 2.32^d	Trace Carbonyl Saturated HC
2	Dist. Prop. Blend	129 - 195	83.04	11.05	0.096	0.244^f 0.38^k	4.06^f 5.43^d	Oxygen as phenolic
3	Dist. Prop. Blend	195 - 219	82.41	9.37	0.017	0.46^f 0.49^k	7.40^f 7.71^d	Oxygen as phenolic
4	Dist. Prop. Blend	219 - 245	83.71	9.22	<0.001	0.54^f 0.66^k	4.72^f 6.41^d	Oxygen as phenolic
5	Dist. Prop. Blend	245 - 268	86.13	9.24	0.022	0.67^f 0.89^k	3.56^f 3.72^d	Oxygen as phenolic
6	Dist. Prop. Blend	268 - 296	86.78	9.16	0.017	0.67^f 0.95^k	2.79^f 3.09^d	Oxygen as phenolic
7	Dist. Prop. Blend	296 - 334	88.22	8.46	0.022	0.58^f 0.90^k	2.07^f 2.40^d	Oxygen as phenolic
8	Vacuum Dist. Prop. Blend	169 - 215	89.47	7.69	0.178	0.47^f 0.92^k	2.15^f 1.74^d	
9	Vacuum Dist. Prop. Blend	215 - 260	89.36	7.51	0.034	0.61^f 1.19^k	2.51^f 1.91^d	
10	Vacuum Dist. Prop. Blend	over 260	89.23	7.19	0.084	0.75^f 1.44^k	2.64^f 2.06^d	
11	Hexane Extract of Dist. Residue		89.98	6.16	0.084	1.40^k	2.38^d	
12	Toluene Extract of Dist. Residue		89.32	5.08	0.117	1.90^k	3.58^d	
13	Pyridine Extract of Dist. Residue		85.30	4.36	0.116	3.14^k	7.08^d	
14	Pyridine Insoluble from Dist. Residue^e		49.68 85.17	1.88 3.22	1.916	0.87 1.49	10.12	

Notes: Fractions 1-10 are ten percent distillation cuts of a proportional blend of the distillate oils. Fraction 0 is the organic material found in the product water and comprises less than 1% of the water phase. Fractions 11-14 are made by sequential extraction of the distillation residue by the solvent stated.

d) Oxygen by difference. e) Calculated ash free. f) Functional group titration; nitrogen by $HClO_4$ in acetic acid, oxygen as acid or phenolic by tetrabutylammonium hydroxide in dimethyl sulfoxide. k) Nitrogen by Kjeldahl.

TABLE 16

Elemental Balance for Belle Ayr Coal Product Array; Run DOE 350R, Product 124

SUBSTANCE	APPROXIMATE[c] YIELD	C %	H %	S %	N %	O %	C g	H g	S g	N g	O g
Methane	3.95	74.86	25.13				2.96	0.89			
Ethane	2.61	79.89	20.11				2.09	0.52			
Propane	2.13	81.71	18.29				1.74	0.39			
Butanes	0.86	82.66	17.34				0.71	0.15			
C_5 & C_6	0.25	83.23 83.62	16.76 16.37				0.21	0.04			
CO_2	5.19	27.29				72.71	1.41				3.77
CO	0.88	42.89				57.11	0.38				0.50
Water	14.78		11.19			88.81		1.65			13.13
Ammonia	0.53		17.75		82.24			0.04		0.44	
H_2S	0.53		5.91	94.09				0.03	0.50		
RT - 129	3.06	83.08	14.22	0.107	0.32	2.32	2.54	0.44	0.0033	0.009	0.71
129 - 195	3.45	83.04	11.05	0.096	0.38	5.43	2.86	0.38	0.0036	0.013	0.187
195 - 219	3.30	82.41	9.37	0.017	0.49	7.71	2.72	0.31	0.0001	0.016	0.254
219 - 245	3.30	83.71	9.22	0.001	0.66	6.41	2.76	0.30	0.0000	0.022	0.211
245 - 268	3.30	86.13	9.24	0.022	0.89	3.72	2.84	0.30	0.0007	0.029	0.123
268 - 296	3.30	86.78	9.16	0.017	0.95	3.09	2.86	0.30	0.0006	0.031	0.102
296 - 334	3.30	88.22	8.46	0.022	0.90	2.40	2.91	0.28	0.0007	0.030	0.079
169 - 215[a]	3.30	89.47	7.69	0.178	0.92	1.74	2.95	0.25	0.0058	0.030	0.057
215-260[a]	3.30	89.36	7.51	0.034	1.19	1.91	2.95	0.25	0.0011	0.039	0.063
Over 260[a]	3.30	89.23	7.19	0.084	1.44	2.06	2.94	0.24	0.0027	0.047	0.068
Hexane Sol.	8.47	89.98	6.16	0.084	1.40	2.38	7.62	0.52	0.0071	0.119	0.202
Toluene Sol.	11.02	89.32	5.08	0.117	1.90	3.58	9.84	0.56	0.0128	0.209	0.395
Pyridine Sol.	3.43	85.30	4.36	0.116	2.25	7.08	2.92	0.15	0.0039	0.077	0.242
Insol. Org.	9.23	85.17	3.22	0.12[b]	1.49	10.00	7.86	0.30	0.0111	0.138	0.923
					TOTALS		66.07	8.29	0.55	1.28	21.02
	INPUT:				GRAMS ELEMENT/100 GM COAL		63.30	5.28	0.57	1.11	22.05
					EXCESS HYDROGEN IN PRODUCT			3.01			

NOTES: This is a raw elemental balance using yields as calculated from product weights and using the raw water yield corrected for the carbonate, ammonia, and hydrogen sulfide contents. The second oil fraction has been increased to include the organic matter which is dissolved in the water (since this is principally phenol). The first fraction has been reduced to allow for the water recovered in fraction 1 of the proportional blend on distillation.

a) Vacuum distillation. b) Calculated ash free. c) Preliminary yields, wet coal basis.

TABLE 17

Fractions Isolated from Kaiparowits Coal in Run DOE 353RA

FRACTION	HOW ISOLATED	BOILING RANGE °C	% CARBON	% HYDROGEN	% SULFUR	% NITROGEN	% OXYGEN	FUNCTIONAL GROUPS PRESENT
1	Dist.Prop. Blend	RT-129	81.82	14.23	0.084	0.019^f 0.31^k	3.56^d	a & b
2	Dist.Prop. Blend	129-195	83.81	11.75	0.036	0.287^f 0.49^k	3.06^f 3.91^d	a & b
3	Dist.Prop. Blend	195-222	83.00	9.73	0.005	0.620^f 0.72^k	5.49^f 6.55^d	a & b
4	Dist.Prop. Blend	222-243	83.60	9.63	0.019	0.654^f 0.00^k	4.54^f 5.96^d	a & b
5	Dist.Prop. Blend	243-265	85.60	9.61	0.004	0.662^f 0.91^k	3.27^f 3.88^d	a & b
6	Dist.Prop. Blend	265-294	86.76	9.55	0.002	0.687^f 1.01^k	2.48^f 2.68^d	a & b
7	Dist.Prop. Blend	294-333	87.89	9.24	0.002	0.589^f 0.94^k	1.70^f 1.93^d	a & b
8	Vacuum Dist. Prop. Blend	159-202	89.39	8.25	0.112	0.542^f 1.04^k	1.57^f 1.21^d	a & b
9	Vacuum Dist. Prop. Blend	202-250	89.14	8.08	0.036	0.708^f 1.29^k	2.49^f 1.45^d	a & b
10	Vacuum Dist. Prop. Blend	over 250	87.95	7.81	0.091	1.56^k	2.44^f 2.59^d	a & b
11	Hexane Extract of Dist. Residue		89.28	6.26	0.108	1.60^k	2.75^d	
12	Toluene Extract of Dist. Residue		89.40	5.25	0.102	2.12^k	3.13^d	
13	Pyridine Extract of Dist. Residue		85.12	4.78	0.098	2.42^k	7.68^d	
14	Pyridine Insolubles from Dist. Residue[g]		28.34 83.59	1.06 3.13	5.74	1.33^k 3.92		
15	Acid Washed Pyridine Insolubles[h]		83.42 85.91	2.90 2.99	4.67 4.81	0.45 0.46	5.83^d	

NOTES: a) Those acidic to tetra butyl ammonium hydroxide (mostly phenolic). b) Those basic to perchloric acid (assumed to be nitrogen as amine or in ring as pyridine or quinoline like structure). k) By Kjeldahl. d) By difference. f) By functional group titration. g) Calculated ash free (contained 66.1% ash). h) Calculated ash free (contained 2.48% ash).

TABLE 18

Yield and Whole Product Array; Run DOE 353A, Kaiparowits Coal

SUBSTANCE	APPROXIMATE[a] YIELD	C %	H %	S %	N %	O %	C g	H g	S g	N g	O g
CH_4	4.48	74.86	25.13				3.35	1.13			
C_2H_6	3.01	79.89	20.11				2.40	0.61			
C_3H_8	2.72	81.71	18.29				2.22	0.50			
C_4H_{10}	1.16	82.66	17.34				0.96	0.20			
C_5 & C_6	1.04	83.50	16.50				0.87	0.17			
CO	1.33	42.89				57.11	0.57				0.76
CO_2	4.15	27.29				72.71	1.13				3.02
NH_3	0.49		17.75		82.24			0.09		0.40	
H_2S	0.97		5.91	94.09				0.06	0.91		
H_2O	6.99		11.19			88.81		0.78			6.21
RT-129°C	4.33	81.82	14.23	0.084	0.31	3.56	3.54	0.62	0.0036	0.0134	0.15
129-195°C	4.33	83.81	11.75	0.036	0.49	3.91	3.63	0.51	0.0016	0.0212	0.17
195-222°C	4.33	83.00	9.75	0.005	0.72	6.55	3.59	0.42	0.0002	0.0312	0.28
222-243°C	4.33	83.60	9.63	0.019	0.80	5.95	3.62	0.42	0.0008	0.0346	0.26
243-265°C	4.33	85.60	9.61	0.004	0.91	3.88	3.71	0.42	0.0002	0.0394	0.17
265-294°C	4.33	86.76	9.55	0.002	1.01	2.68	3.76	0.41	0.0001	0.0437	0.12
294-333°C	4.33	87.89	9.24	0.002	0.94	1.93	3.80	0.40	0.0001	0.0407	0.08
159-202°C[b]	4.33	89.39	8.25	0.112	1.04	1.21	3.87	0.36	0.0048	0.0450	0.05
202-250°C[b]	4.33	89.14	8.08	0.036	1.29	1.45	3.86	0.35	0.0016	0.0558	0.06
over 250°C[b]	4.33	87.95	7.81	0.091	1.56	2.59	3.80	0.34	0.0039	0.0675	0.11
Hexane Sol.	15.89	89.28	6.26	0.108	1.60	2.75	14.19	0.99	0.0172	0.2549	0.44
Toluene Sol.	6.90	89.40	5.25	0.102	2.12	3.13	6.17	0.36	0.0070	0.146	0.22
Pyridine Sol.	3.01	85.12	4.78	0.098	2.42	7.58	2.56	0.14	0.0030	0.0728	0.23
IOM	3.60	85.91	2.99	4.81	1.33	4.96	3.09	0.11	0.1732	0.0479	0.18
Ash	8.25								0.40		
TOTALS							74.69	9.39	1.529	1.31	12.51
ELEMENTS FED WITH 100 GRAMS OF COAL (dry basis)							70.69	4.85	0.47	1.43	14.10
ELEMENT FED WITH PYRITE									1.14		
						Hydrogen Reacted		4.54			

a) Weight % based on dry coal, corrected for carbonate, ammonia and hydrogen sulfide in the water.

b) Vacuum distillation.

TABLE 19

Fractions Isolated from a Proportional Blend of Products from Wadge Seam Coal in Run DOE 356RA[a]

Fraction	How Isolated	Boiling Range °C	% Carbon	% Hydrogen	% Sulfur	% Nitrogen	% Oxygen	% Ash
0	From V-2 Water							
1	Dist. Prop. Blend	RT - 112	83.76	14.83	0.37	0.011^f 0.05^k	0.19^f 1.32^d	
2	Dist. Prop. Blend	112 - 180	84.24	12.52	0.24	0.252^f 0.57^k	1.86^f 2.43^d	
3	Dist. Prop. Blend	180 - 213	81.86	9.57	0.10	0.726^f 0.89^k	6.11^f 7.58^d	
4	Dist. Prop. Blend	213 - 234	83.83	9.38	0.005	0.912^f 1.08^k	5.82^f 5.70^d	
5	Dist. Prop. Blend	234 - 255	84.06	9.37	0.007	0.922^d 1.12^k	4.49^f 4.64^d	
6	Dist. Prop. Blend	255 - 275	86.07	9.28	0.027	0.954^f 1.30^k	3.66^f 3.32^d	
7	Dist. Prop. Blend	275 - 299	87.00	9.18	0.026	0.864^f 1.28^k	3.09^f 2.51^d	
8	Vac. Dist. Prop.Blend	140 - 170	88.66	8.69	0.129	0.584^f 0.90^k	2.14^f 1.62^d	
9	Vac. Dist. Prop.Blend	170 - 212	88.75	8.34	0.208	0.702^f 1.32^k	2.02^f 1.38^d	
10	Vac. Dist. Prop.Blend	Over 212	88.28	7.93	0.133	1.039^f 1.81^k	3.26^f 1.85^d	
11	Hexane Extract of Dist.Residue		89.52	6.18	0.16	2.11^k	2.03^d	0.49
12	Toluene Extract of Dist.Residue		88.58	5.52	0.03	2.57^k	3.30^d	
13	Pyridine Extract of Dist.Residue		84.39	4.50	0.14	3.01^{c,k}	7.96^d	0.57
14	Pyridine[b] Insoluble from Dist.Residue		28.76 79.31	1.64 4.52	7.65	0.93^k 2.56		63.74
15	Acid Washed Pyridine Insolubles		80.72	3.38	3.97	2.33^k	7.06^d	2.54

a) Proportional blend based on trial calculation on product 38. b) Calculated ash free. c) Corrected for an estimated 5% pyridine included in the residue. d) Oxygen by difference. f) Determined by functional group titration. k) Nitrogen determined by Kjeldahl.

TABLE 20

Elemental Balance for Wadge Seam Coal Products Based on Run DOE 356R, Product 38

Substance	Approximate Yield[a]	C %	H %	S %	N %	O %	C g	H g	S g	N g	O g
CH_4	4.79	76.86	25.13				3.68	1.11			
C_2H_5	3.00	79.89	20.11				2.40	0.60			
C_3H_8	2.54	81.71	18.29				2.08	0.46			
C_4H_{10}	1.02	82.66	17.34				0.84	0.18			
C_5 & C_6	0.25	83.50	16.50				0.21	0.04			
CO_2	2.64	27.29				72.71	0.72				1.92
CO	0.77	42.89				57.11	0.33				0.44
H_2S	1.54		5.91	94.09				0.09	1.45		
NH_3	0.63		17.75		82.24			0.11		0.52	
H_2O	13.04		11.19			88.81		1.46			11.58
<u>OILS</u>											
RT - 112°C	3.42	83.73	14.83	0.37	0.05	1.32	2.86	0.51	0.013	0.0017	0.05
112 - 180°C	3.42	84.24	12.52	0.24	0.57	2.43	2.88	0.43	0.008	0.0195	0.08
180 - 213°C	3.42	81.86	9.57	0.10	0.89	7.58	2.80	0.33	0.003	0.0304	0.26
213 - 234°C	3.42	83.83	9.38	0.005	1.08	5.70	2.87	0.32	0.000	0.0369	0.19
234 - 255°C	3.42	84.86	9.37	0.007	1.12	4.64	2.90	0.32	0.000	0.0383	0.16
255 - 275°C	3.42	86.07	9.28	0.027	1.30	3.32	2.94	0.32	0.001	0.0445	0.11
275 - 299°C	3.42	87.00	9.18	0.026	1.28	2.51	2.98	0.31	0.001	0.0438	0.09
140 - 170°C[b]	3.42	88.66	8.69	0.129	0.90	1.62	3.03	0.30	0.004	0.0308	0.06
170 - 212°C[b]	3.42	88.75	8.34	0.208	1.32	1.38	3.04	0.29	0.007	0.0451	0.05
Over 212°C[b]	3.42	88.28	7.93	0.133	1.81	1.85	3.02	0.27	0.005	0.0619	0.06
Hexane Sol.	8.92	89.52	6.18	0.16	2.11	2.03	7.99	0.55	0.014	0.1882	0.18
Toluene Sol.	12.59	88.58	5.52	0.03	2.57	3.30	11.15	0.69	0.004	0.3236	0.32
Pyridine Sol.	5.21	84.39	4.50	0.14	3.90	7.96	4.39	0.23	0.007	0.2032	0.41
IOM	4.66	80.72	3.38	3.97	2.33	7.06	3.76	0.16	0.158	0.1086	0.33
Ash	9.29	from coal & 4.96% from pyrite							1.289		
						TOTALS	66.87	9.08	2.96	1.70	16.29
INPUT (Coal)	8.83 grams of ash plus elements as follows						65.50	5.45	0.51	1.82	17.78
INPUT (Additive)	6.6 grams pyrite per 100 grams of coal @ 53.0% sulfur.								3.50		
	Hydrogen reacted by difference							3.63%			

a) Weight % based on wet coal. The hydrogen by difference is less than hydrogen from the measurements of gas input less gas output, perhaps as a result of hydrogen solubility in some of the products. Sulfur output seems low compared to the input and again loss by solubility in the light oil during high pressure separations seems probable.

b) Vacuum distillation.

TABLE 21

Polar and Neutral Oil Fractions Isolated from Wadge Seam Coal in Run DOE 356RB[a]

Fraction	How Isolated	Boiling Range °C	% Carbon	% Hydrogen	% Sulfur	% Nitrogen	% Oxygen
Bases	Sulfuric Acid Extraction[b]	Whole Boiling Range	73.11	9.63		7.74[f] 8.90[k]	
Acids	NaOH Extraction	Whole boiling range	74.26	8.89		0.155[f] 0.42[k]	
Neutral Oils 1	Dist. Prop. blend	RT - 84	83.92	15.17	0.062	0.04[f]	0.132[f]
2	Dist. Prop. blend	84 - 145	85.65	13.37	0.133	0.05[f]	0.194[f]
3	Dist. Prop. blend	145 - 202	86.63	12.06	0.170	0.21[f]	0.237[f]
4	Dist. Prop. blend	202 - 231	88.55	10.70	0.083	0.46[f]	0.368[f]
5	Dist. Prop. blend	231 - 251	88.70	9.82	0.055	0.58[f]	0.557[f]
6	Dist. Prop. blend	251 - 272	88.92	9.56	0.012	0.68[f]	0.766[f]
7	Dist. Prop. blend	272 - 295	88.73	9.48	0.015	0.68[f]	0.55[f]
8	Dist. Prop. blend	295 - 317	89.26	9.18	0.064	0.61[f]	0.52[f]
9	Dist. Prop. blend	317 - 347	89.72	8.44	0.188	0.60[f]	0.72[f]
10	Vac. Dist. Prop. blend	Ends @ 210 @ 2 mm.	90.75	7.96	0.181	0.70[f]	1.23[f]

a) Basic and Acidic fractions by aqueous extraction - residual oil is neutral oil.
b) Neutral equivalent weight = 180.
f) Determined by functional group titration.
k) Nitrogen determined by Kjeldahl.

FIGURE 1

PARTICLE SIZE DISTRIBUTION OF ROBENA PYRITE II

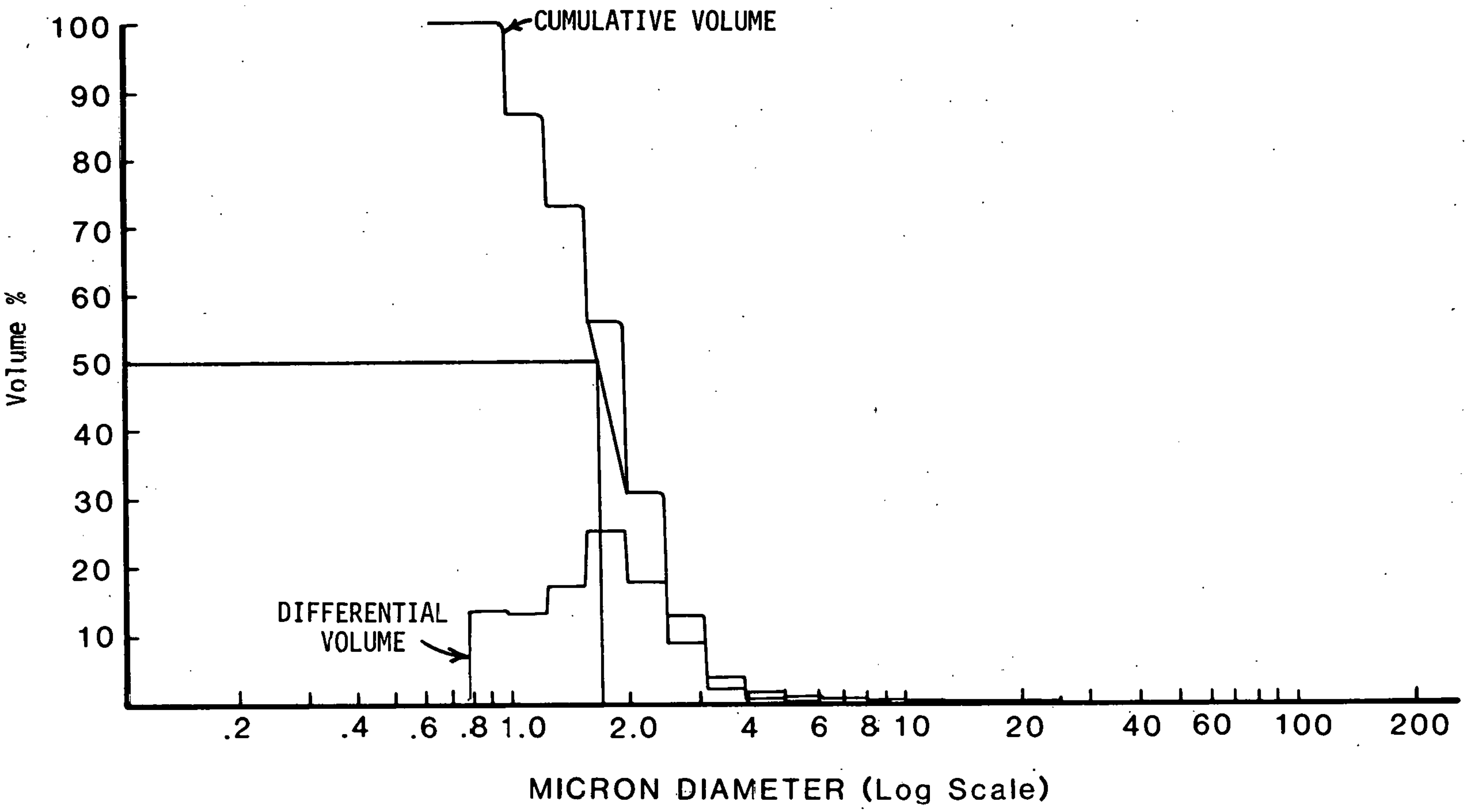


Figure 2

Effect of Iron Level on Yields
Run DOE 350RC, Belle Ayr Coal

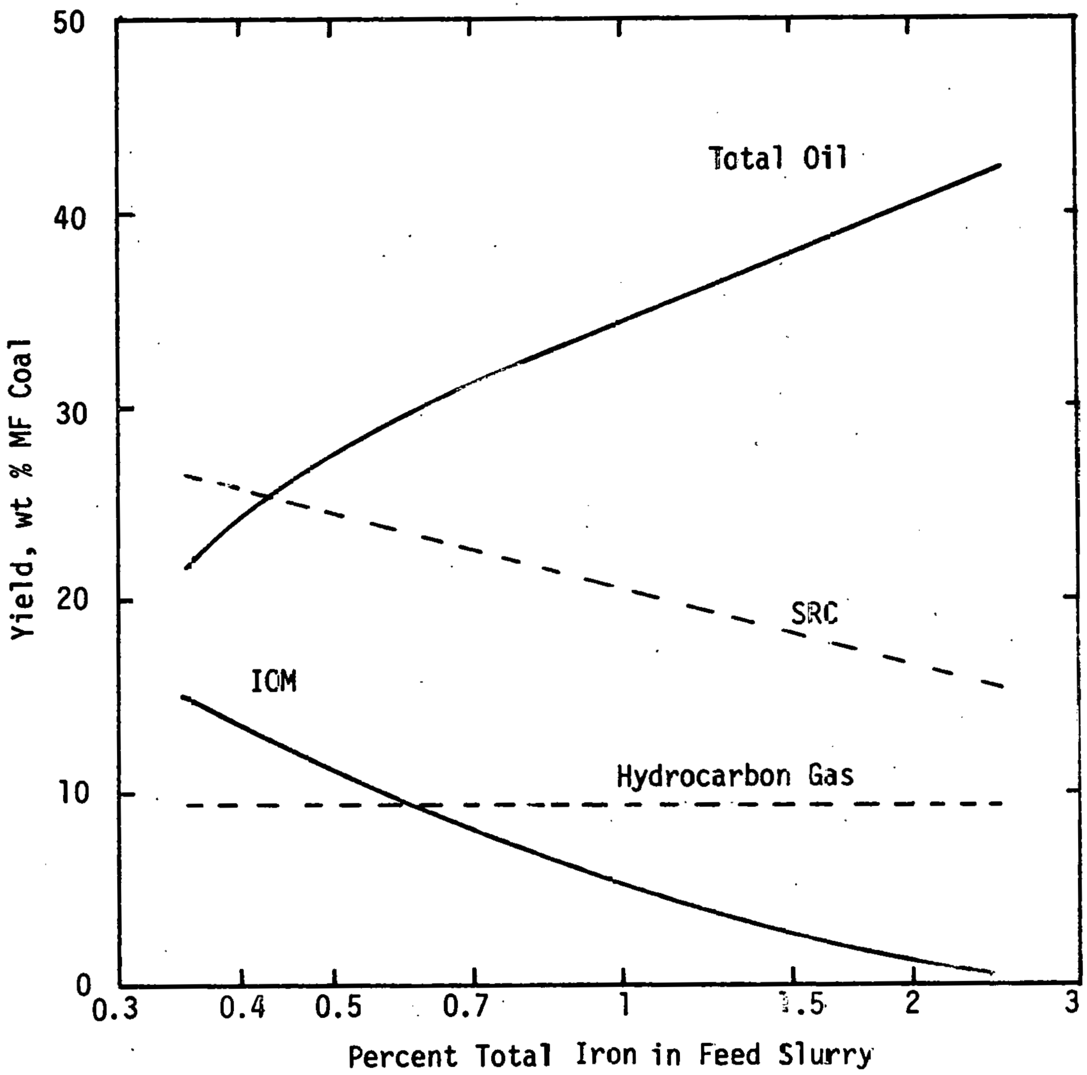


FIGURE 3

UNFILTERED COAL SOLUTION VISCOSITIES-COMPARISON OF RUNS DOE 354A AND 357A

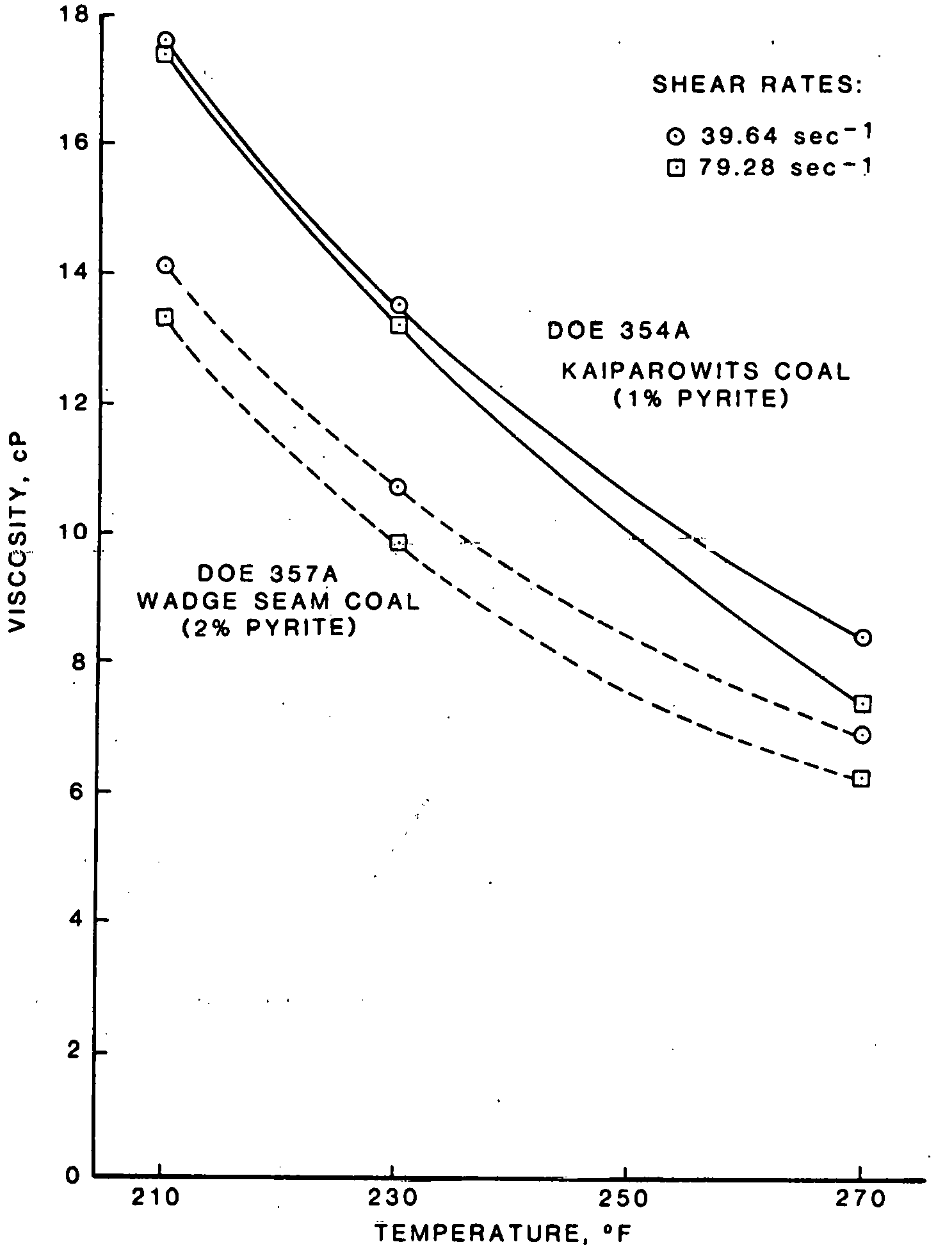


FIGURE 4

UNFILTERED COAL SOLUTION VISCOSITIES-COMPARISON OF RUNS DOE 350RA, 353RA AND 356RA

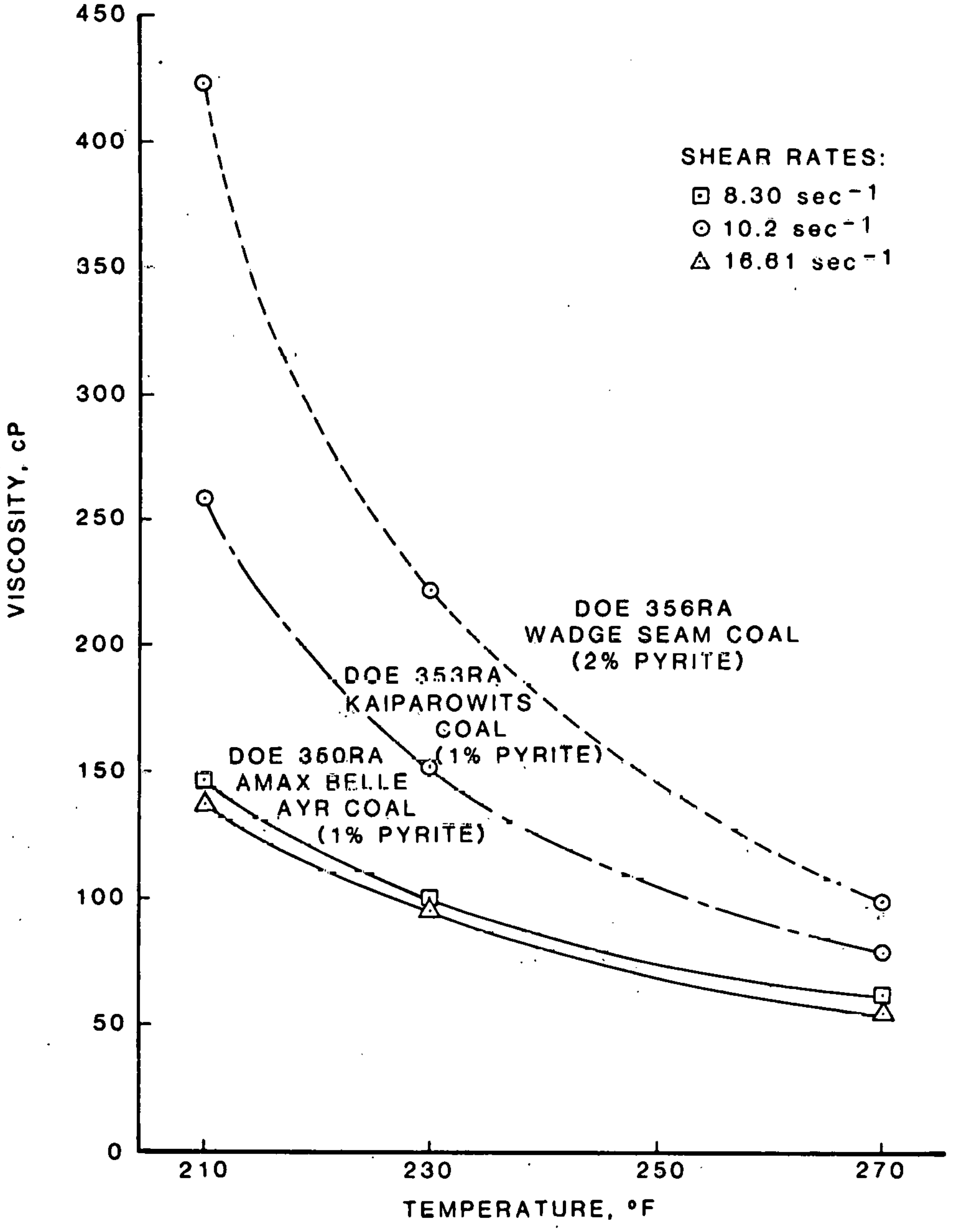


FIGURE 5

FEED SLURRY VISCOSITIES-COMPARISON OF RUNS DOE 353RA AND 356RA

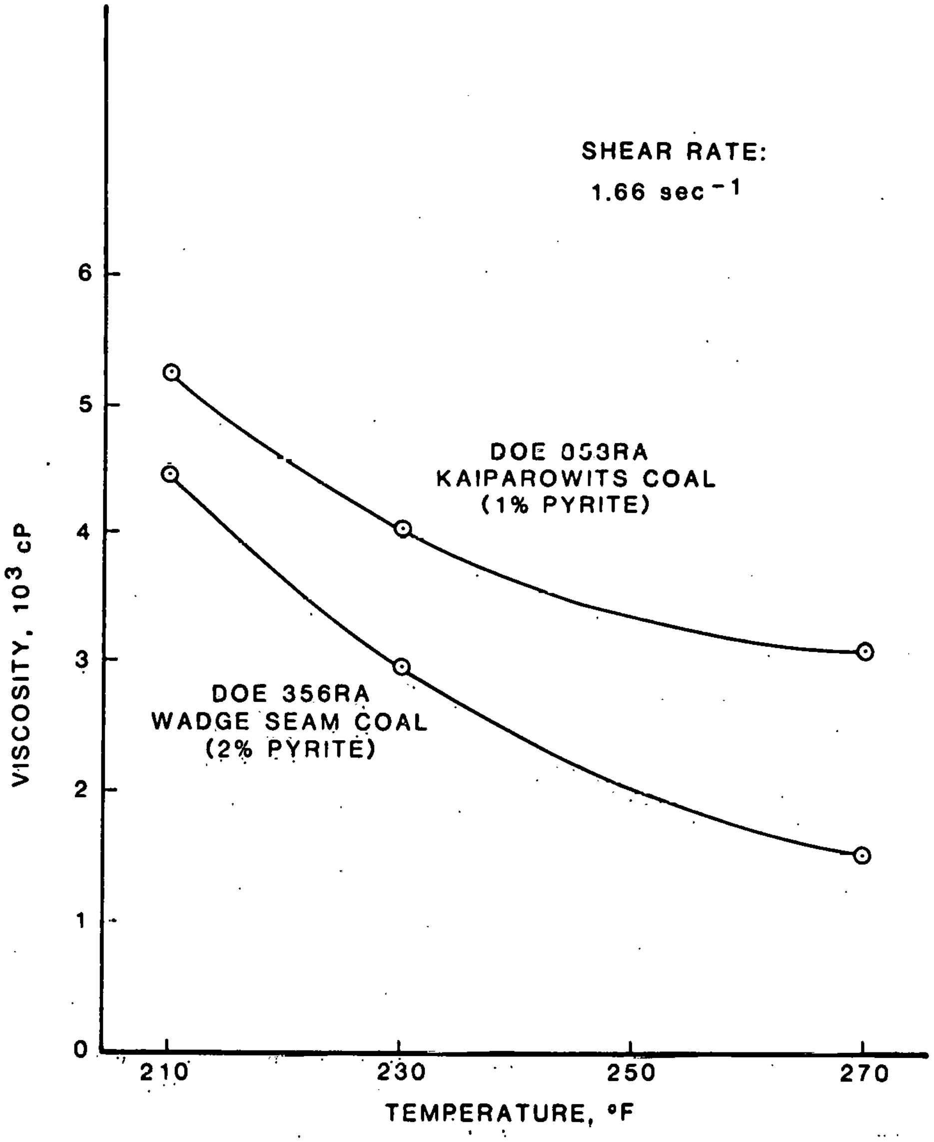


FIGURE 6

UNFILTERED COAL SOLUTION VISCOSITIES-RUNS DOE 349, 351 AND 352-BELLE AYR COAL

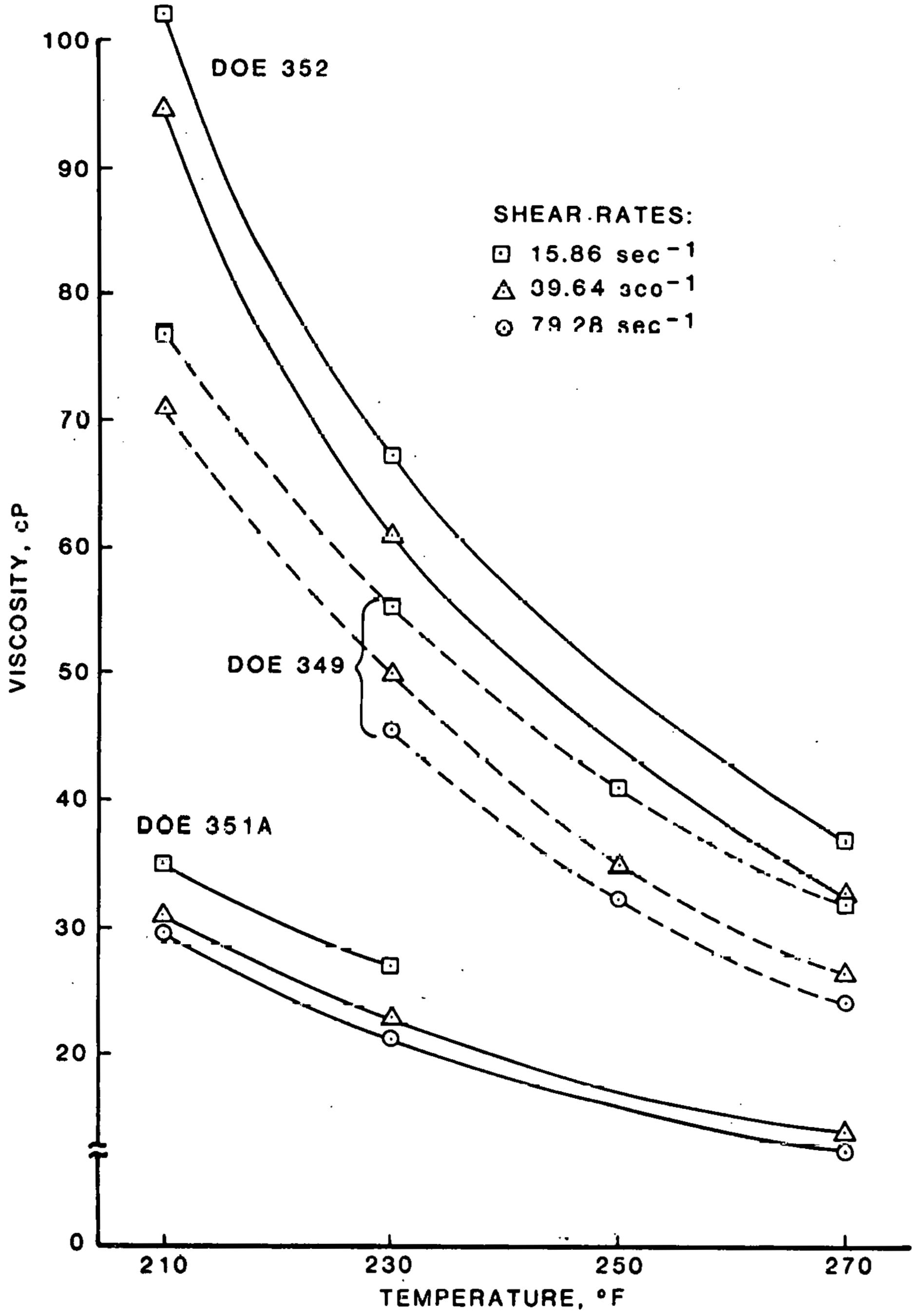


FIGURE 7

UNFILTERED COAL SOLUTION VISCOSITIES
RUN DOE 350R, BELLE AYR COAL

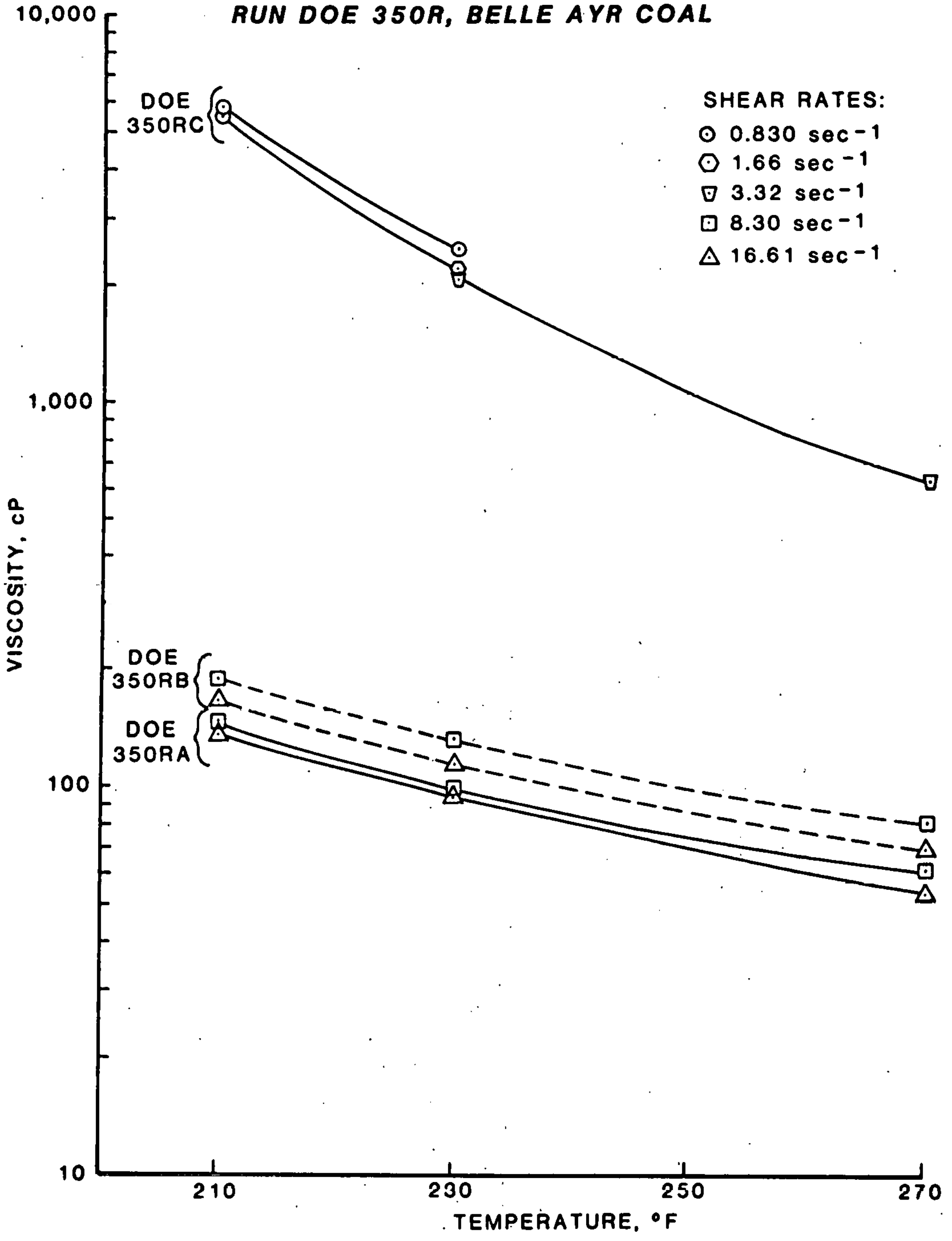


FIGURE 8

FEED SLURRY VISCOSITIES-RUN DOE 350R-BELLE AYR COAL

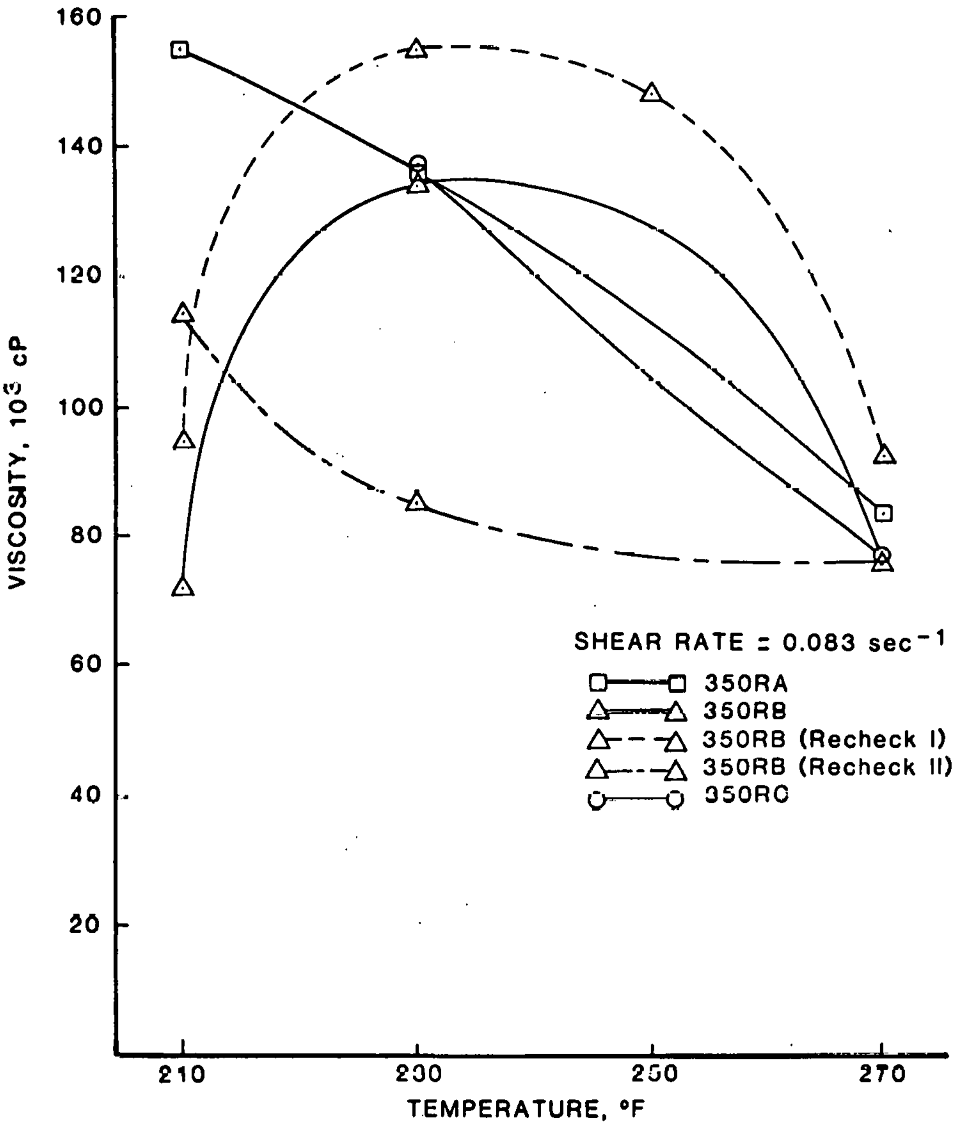


FIGURE 9

UNFILTERED COAL SOLUTION VISCOSITIES
RUN DOE 354-KAIPAROWITS COAL

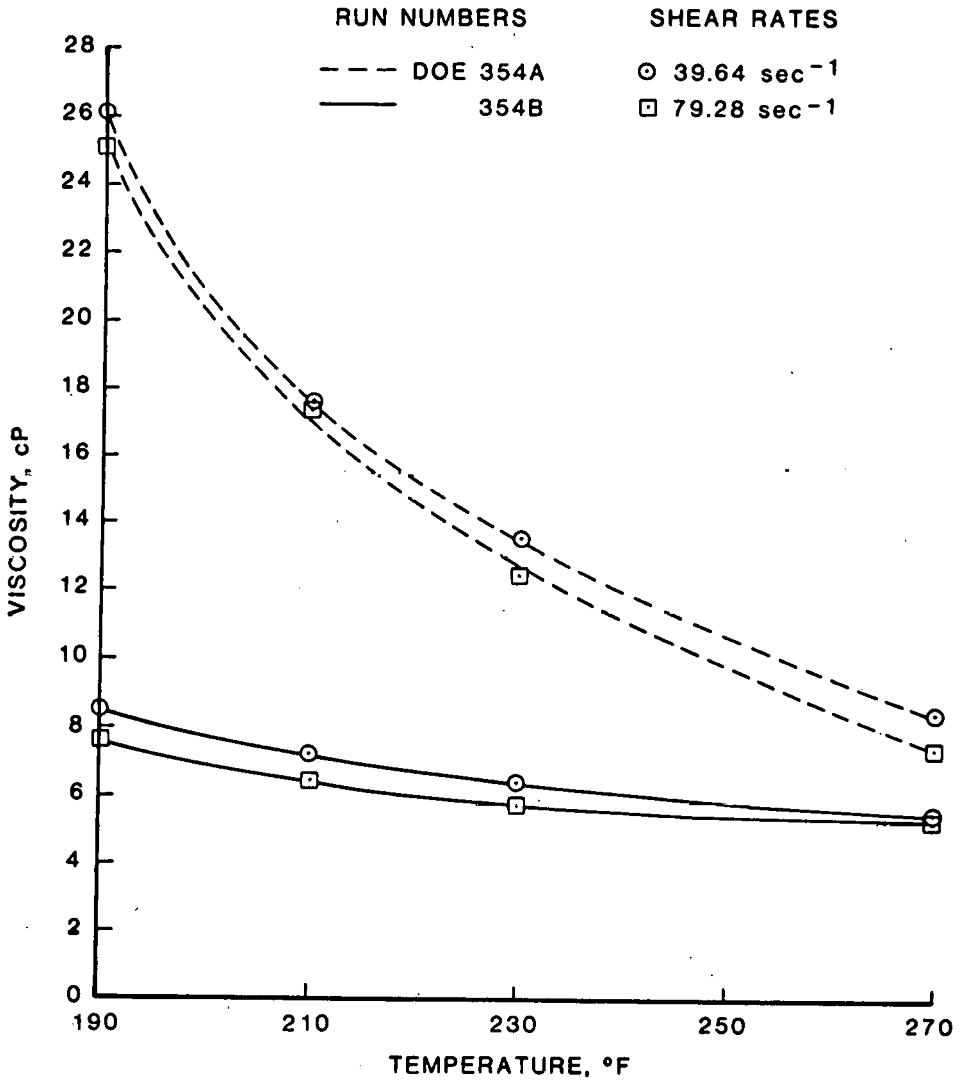


FIGURE 10

UNFILTERED COAL SOLUTION VISCOSITIES RUN DOE 353R-KAIPAROWITS COAL

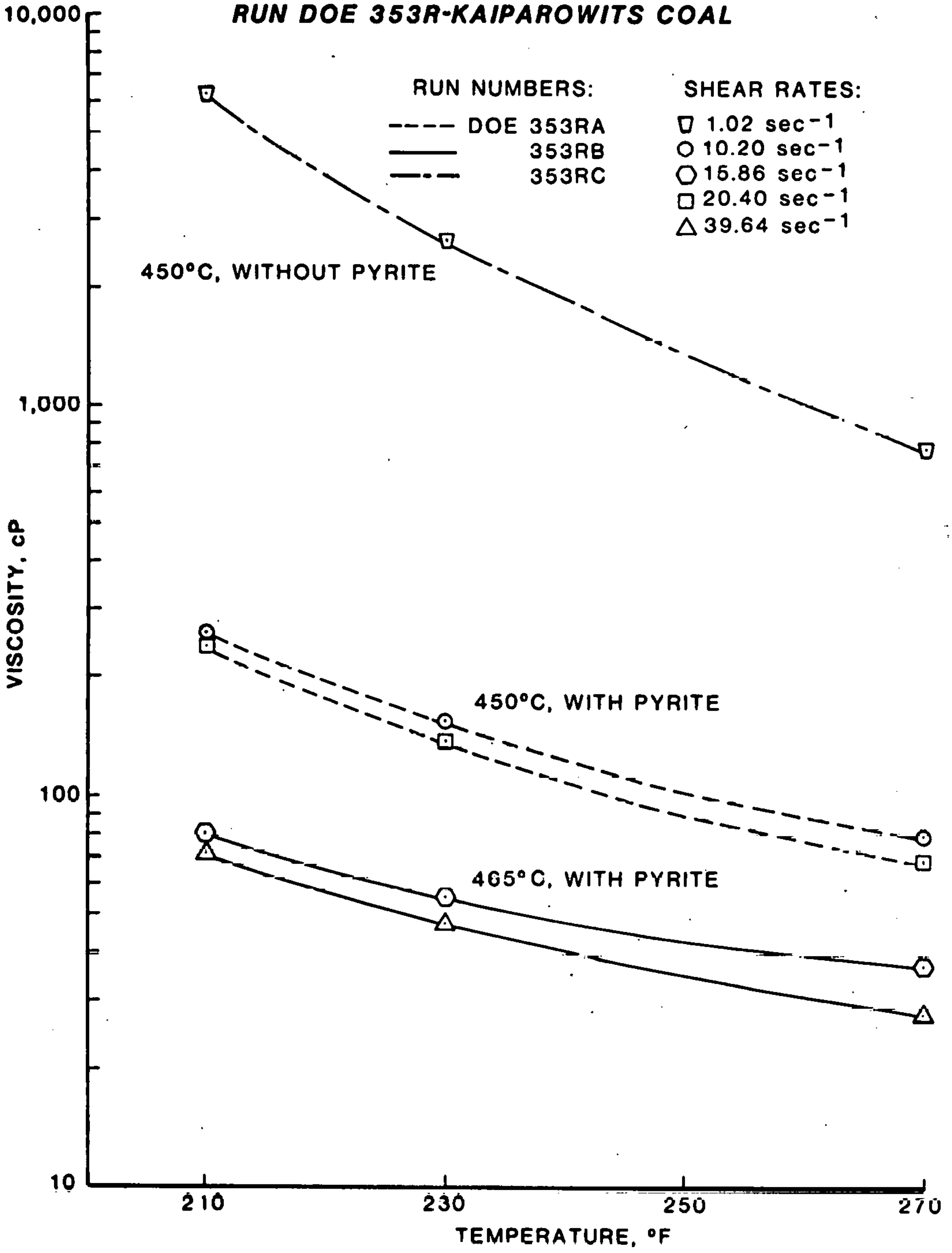


FIGURE 11

FEED SLURRY VISCOSITIES
RUN DOE 353R-KAIPAROWITS COAL

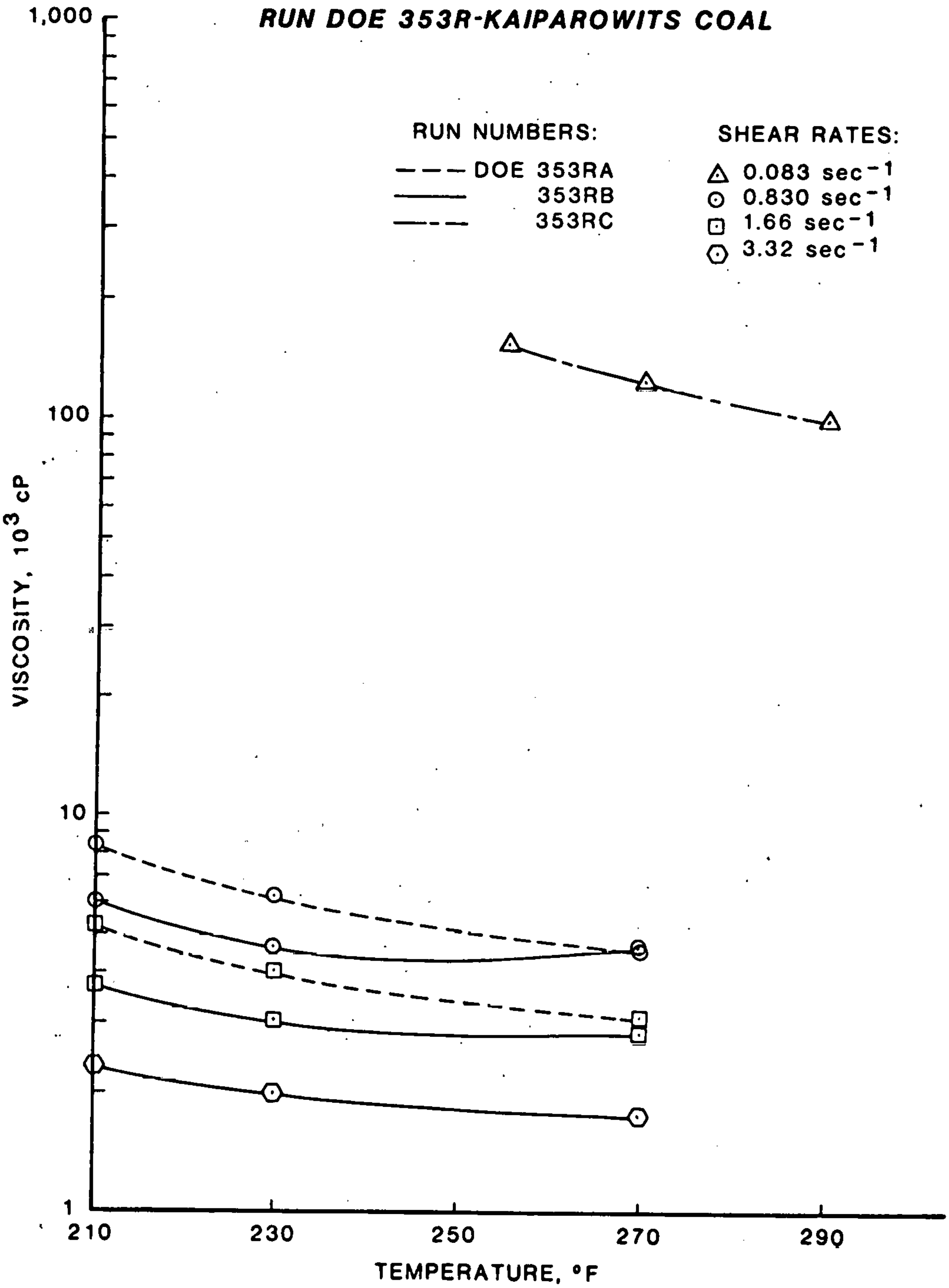


FIGURE 12

UNFILTERED COAL SOLUTION VISCOSITIES-RUN DOE 357, WADGE SEAM COAL

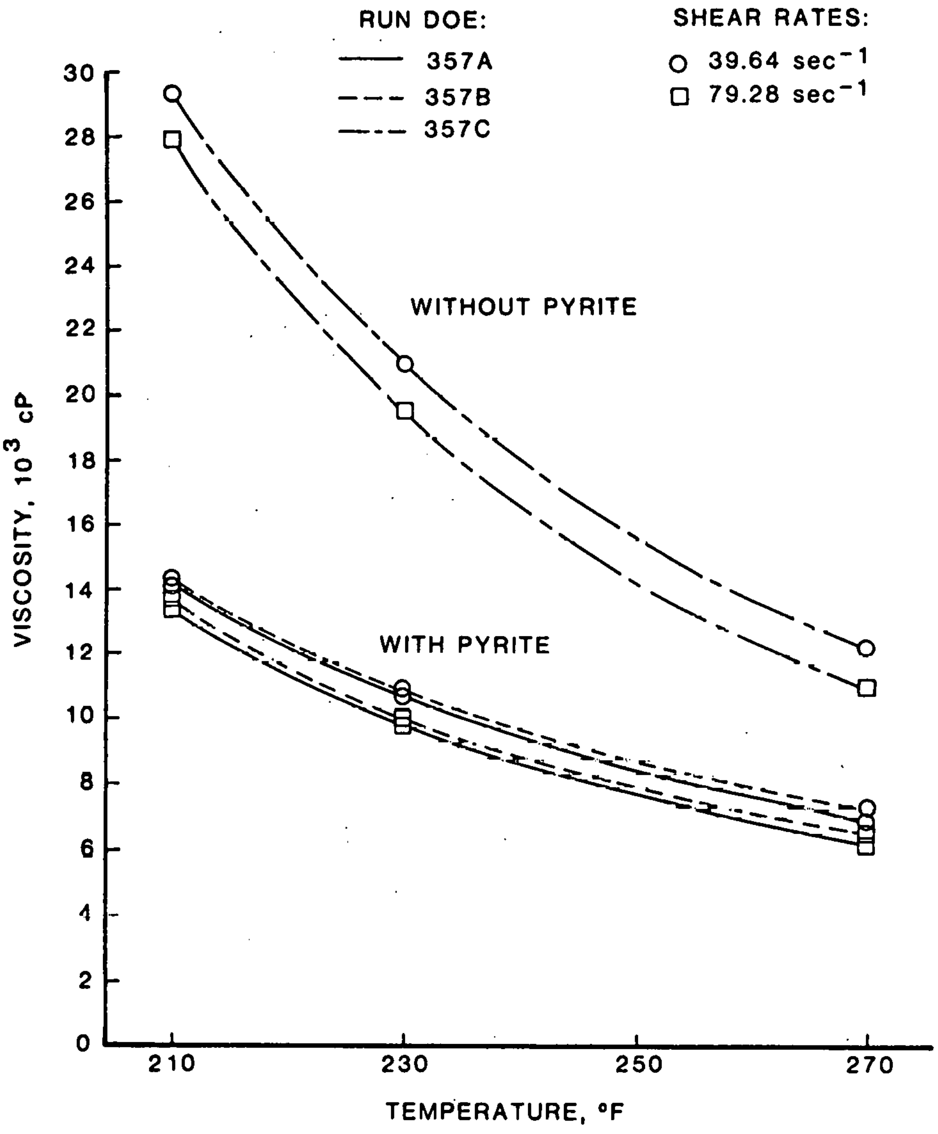


FIGURE 13

UNFILTERED COAL SOLUTION VISCOSITIES
RUNS DOE 355R AND-356R WADGE SEAM COAL

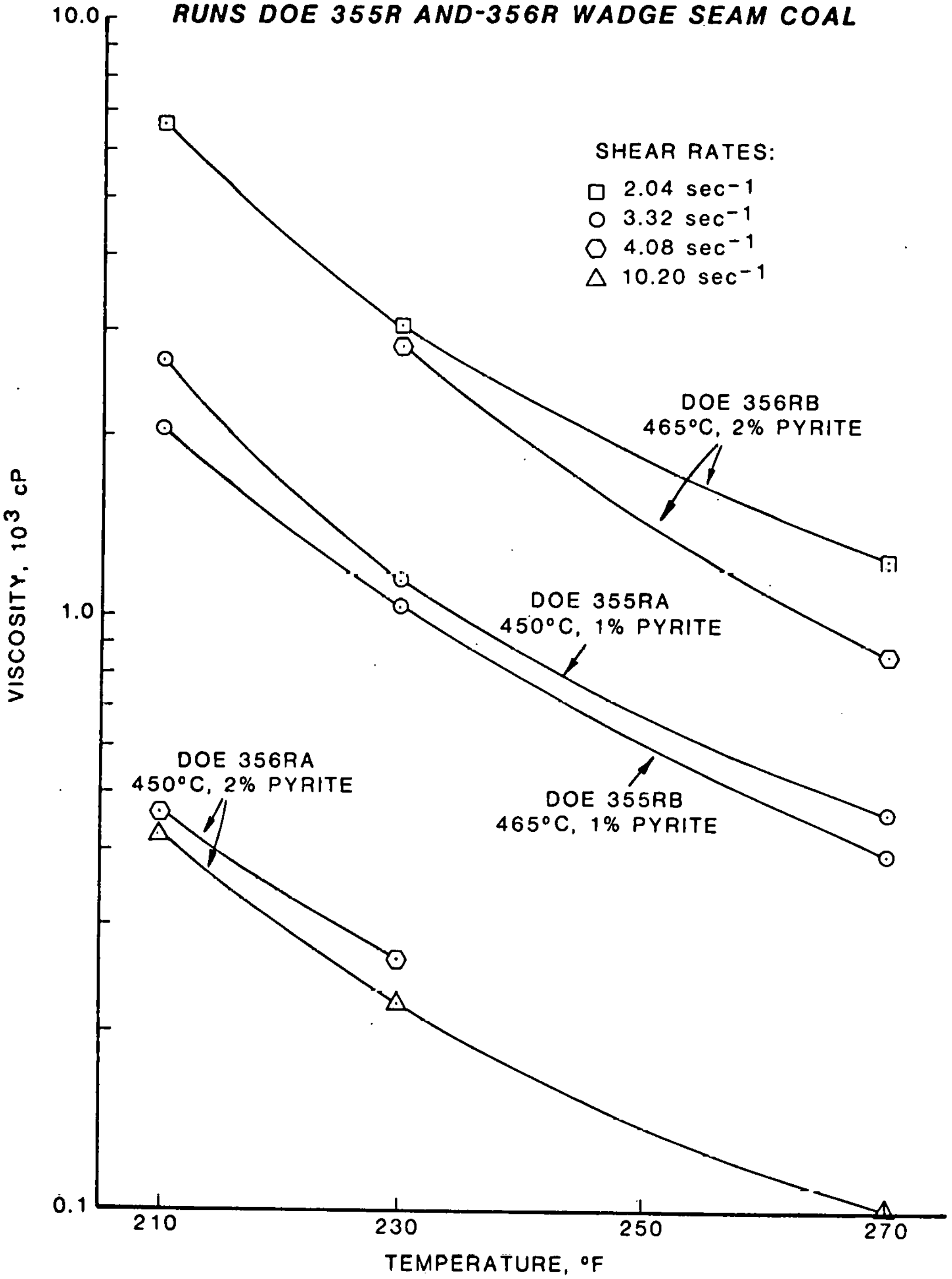


FIGURE 14

FEED SLURRY VISCOSITIES-RUNS DOE 355R AND 356R-WADGE SEAM COAL

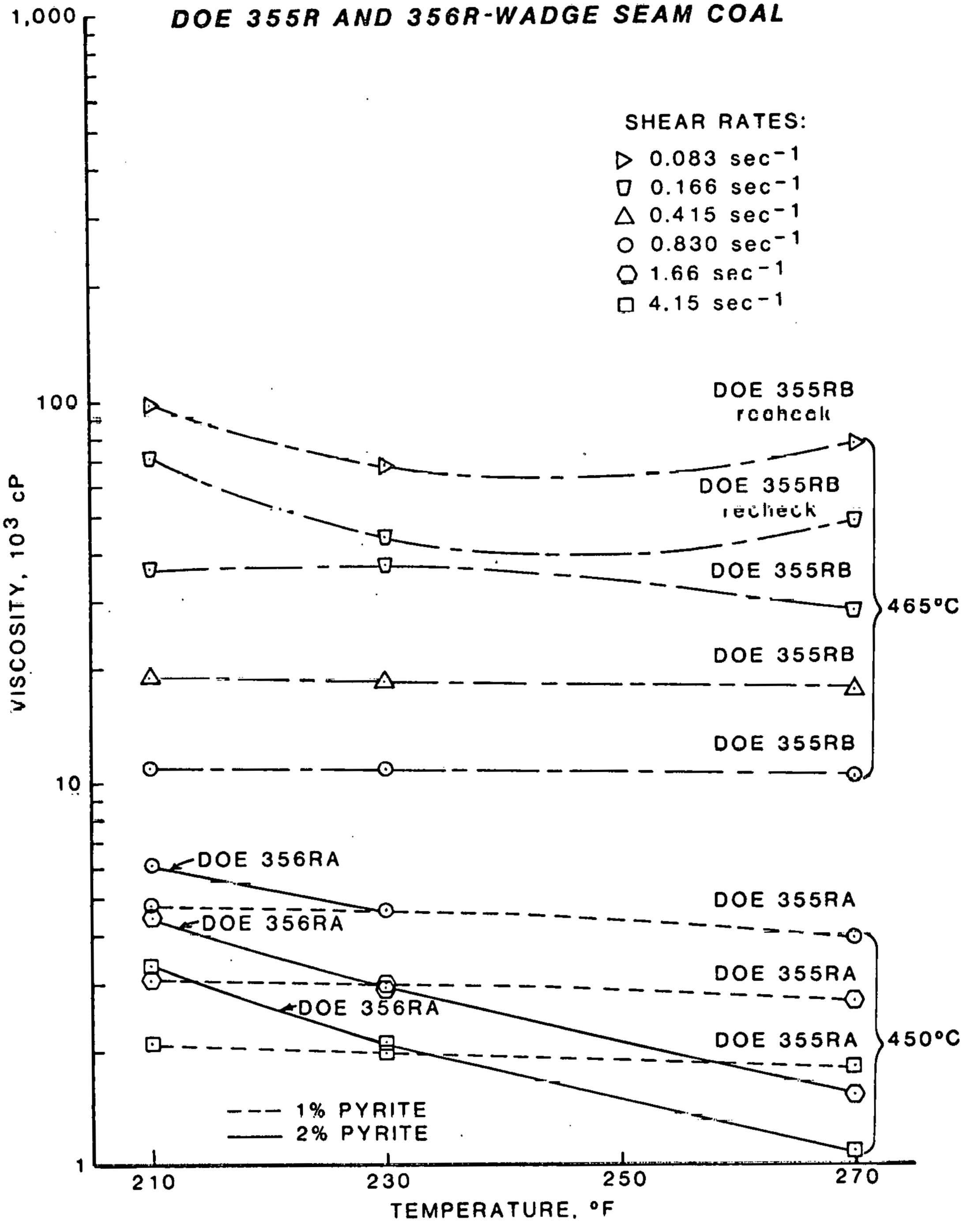
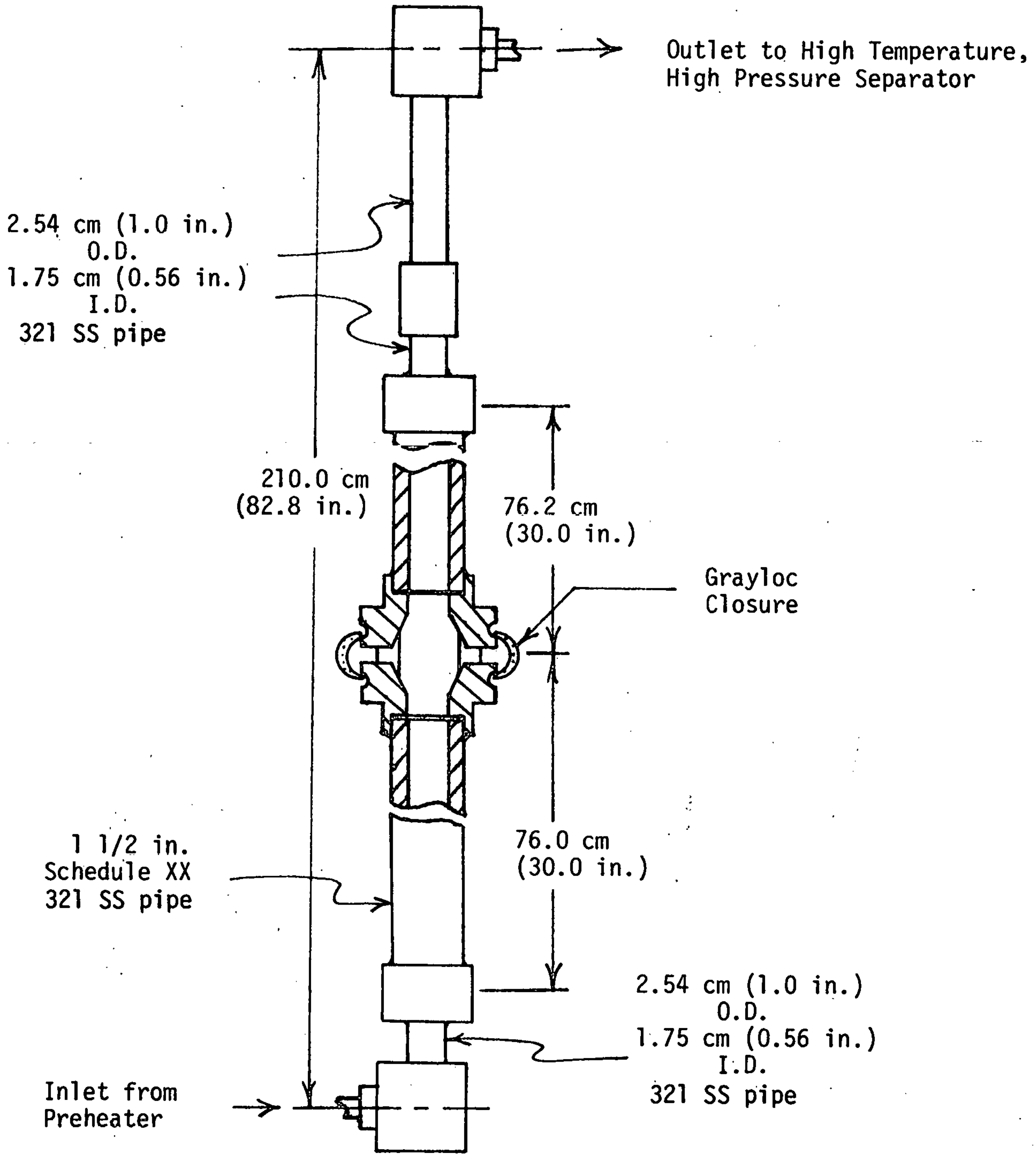


FIGURE 15

The DOE 3 Dissolver
(used in Run DOE 357)



Volume = 1064 cm^3

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APPENDIX A

INSPECTION OF PRODUCTS BY INFRARED SPECTROSCOPY AND SIMULATED DISTILLATION

I. INTRODUCTION

A number of analyses were made to determine what materials could be isolated from the light oils from Amax Belle Ayr coal (run DOE 350RA) by conventional means. A 100 ml sample of the vessel 2 (ambient temperature separator bottoms) oil was extracted with aqueous caustic to remove acidic materials, followed by an extraction with aqueous sulfuric acid to isolate basic substances. The resulting neutral oil was reacted with concentrated sulfuric acid to isolate the saturates. These procedures were done in a way which permitted measurement of the amount of material extracted and allowed isolation of these characteristic fractions for further examination. The original oil and the fractions available for examination were then analyzed by infrared spectroscopy and simulated distillation gas chromatography (GC). This gives considerable insight into the kinds of functional groups present and the number of substances present in given boiling ranges and product categories. A similar procedure was used for the vessel 4 (atmospheric distillation overhead) condensate as well. Raw vessel 3 (atmospheric distillation bottoms) and unfiltered coal solution (UFCS) distillates were also examined.*

II. INSPECTION BY INFRARED SPECTROSCOPY

A. Inspection of Distillates from UFCS

Unfiltered coal solution (UFCS) products were distilled at 2 mm pressure with a preliminary cut taken from room temperature up to 108°C and the major fraction of the oil recovered in a second cut taken from 108°C to a final vapor temperature of 270°C (cut 2). The behavior during the distillation was normal with pot temperatures in the vicinity of 335°C and pressures holding between 2 and 5 mm at the end of the distillation. Figure A-1 shows the IR spectrum of the cut 2 oil from the second phase of the experiment (DOE 350RB) in which the reactor temperature was 465°C. Figure A-2 shows a typical sample of the oil distilling from room temperature to 108°C. Neither of these appear to have any unusual characteristics which can be observed by infrared although the oil is a little more hydrogenated than would normally be the case at this temperature. It must be remembered that the pressure is higher than normal and that considerable iron in the form of pyrite is present. The spectrum tended to show even more hydrogenation of the product from the 450°C portion of the run.

B. Inspection of Vessel 3 Oil

The vessel 3 oil was inspected by infrared and appeared to be quite similar to the cut 2 oil although there was a characteristic skew in the product distribution favoring higher concentrations of substances in the low molecular weight end of the product distribution. This is inferred from the increased hydrogenation evident in the IR spectrum and has been confirmed by simulated distillation. Figure A-3 shows the spectrum of the vessel 3 oil.

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* During this particular run, the net (not recycled) yield of oil collected in vessel 2 was 24.1% of the dry feed coal while that collected in vessel 4 was 3.9%. Oil amounting to 12.7% of the dry feed coal was collected in vessel 3 but was recycled.

C. Inspection of Vessel 2 Oil

The vessel 2 oil was analyzed by infrared and evidence for a considerable amount of phenolic material was obtained. The spectrum of the crude vessel 2 oil is presented as Figure A-4. Upon extraction with caustic, it was found that about 35% of the oil dissolved. Extraction with aqueous sulfuric acid reduced the residual oil to about 60% of the original sample. Such values are not much different than those obtained with similar materials from other coals.

When the neutral oil fraction was examined, it was found that the two extractions had removed much of the aromatic material. This means that much of the aromatic material originally present was associated with a functional group which would react either with an acid or a base. The spectrum of the neutral oil is given as Figure A-5. The only remarkable feature is a trace of carbonyl function (probably) which remains from a considerably more concentrated mixture of this material (or materials) observed in the raw vessel 2 oil. Compare Figure A-4 and Figure A-5 at about 5.8 microns.

A portion of the neutral oil was then extracted in a Babcock bottle using concentrated sulfuric acid to dissolve the aromatic material (this is a rather mild reagent and quantitative extraction of aromatic material requires complete remixing and extended contact times). The clear oil which came to the top was about 56% of the neutral oil sample taken, by volume. After the oil was separated from the acid, a spectrum was run to confirm that the acid had indeed reacted with most of the aromatic material. The spectrum of the acid insoluble product is presented as Figure A-6. This shows the presence of only trace amounts of aromatic material. It was estimated that the saturates accounted for approximately 34% of the original vessel 2 oil, by volume.

The aqueous caustic solution was made acidic to release the dissolved acidic material extracted from the vessel 2 oil. The insoluble oil was separated from the water and the water phase was then extracted with diethyl ether to recover any material which remained dissolved. Figure A-7 is the infrared spectrum of the water insoluble material. The ether extract was warmed on a hot plate to distill any ether away. Figure A-8 is the infrared spectrum of the ether extract. Both materials are predominantly phenolic in functionality. The water insoluble material probably consists of substituted phenols such as methyl or dimethyl phenol, while the water soluble product is dominated by phenol itself. The latter can be readily seen as a major component in the infrared spectrum. Both spectra show only trace amounts of carbonyl function. Since the volume shrinkage of the vessel 2 oil was about 35%, and the water insoluble phenolic material was estimated to comprise about 20% by volume, it is suggested that simple phenol was a substantial component of this product.

The acid extract was treated with excess caustic to release any basic material present. The volume of water insoluble material was

was warmed on the hot plate until ether was removed. The spectrum of the material obtained is shown as Figure A-9. Based on this spectrum, ether removal seems complete. It appears that one of the main basic functions must be an amine, since considerable N-H absorbance is present. The product had a quinoline-like odor.

D. Inspection of Vessel 4 Oil

The vessel 4 oil is qualitatively similar to material distilled from UFCS between room temperature and 108°C at 2 mm Hg. The spectrum of the vessel 4 oil is given as Figure A-10 which should be compared to Figure A-2 to see the similarity. The vessel 4 oil was analyzed in the same way as that from vessel 2. A 100 ml sample of the oil shrank down to approximately 65 ml upon extraction with aqueous caustic. This material, upon extraction with aqueous sulfuric acid, sustained a small additional shrinkage and the neutral oil again accounted for about 60% of the original sample, by volume. The spectrum of the neutral oil is given as Figure A-11. This material is appreciably more aromatic than was the vessel 2 neutral oil fraction. Compare Figure A-11 with Figure A-5.

The neutral oil was extracted in a Babcock bottle with concentrated sulfuric acid. The volume of unreactive clear oil which remained accounted for 29% of the neutral oil (or about 17.5% of the original vessel 4 oil). The spectrum of the saturates isolated by this procedure is presented as Figure A-12 and inspection of this spectrum shows that the procedure completely reacted the aromatics.

The aqueous caustic extract was acidified to release the materials dissolved in the caustic. An insoluble oil was obtained which was separated from the aqueous phase. The aqueous phase was then extracted with diethyl ether to recover as much of the water soluble material as possible. The ether extract was evaporated on the hot plate to obtain an ether free residue. The infrared spectrum of the water insoluble material is presented as Figure A-13 and the material recovered from the ether extract is shown in Figure A-14. Again, the spectra indicate substituted phenols as the dominant species in the water insoluble phase and simple phenol as one of the main components of the water soluble phase.

The aqueous acid extract was made basic by the addition of excess caustic. This caused the separation of a small amount of oil which was recovered by shaking the mixture with diethyl ether. The ether phase was transferred to a beaker and the ether was evaporated on a hot plate in the hood. It was possible to remove the ether quantitatively. The product was examined by infrared and this spectrum is given as Figure A-15. The spectrum resembles substituted aromatic amines for the most part, although the product had a pronounced odor resembling quinoline.

E. Conclusions from Examination of IR Spectra

Similar separations have been conducted on light oil fractions made from bituminous coals. In general, the fractions derived from a subbituminous coal appear to be quite similar to those materials which have been obtained from bituminous coals. The only new functional group observed is a minor amount of carbonyl observed in the spectrum of the raw vessel 2 oil. This was not well accounted for in the separation scheme, with significant reductions in the intensity of the band in fractions which were later isolated. This is probably too small an amount of material to be of much interest, and probably it is a material which is quite water soluble. No workup of the water phase in contact with the vessel 2 oil has been done and perhaps some new substance will turn up when this material is inspected. When water phases from the usual bituminous coals are analyzed, the principal components have been ammonium bicarbonate, ammonium sulfide, and about a percent of phenol.

The present examination has failed to show the presence of any obviously different material from reaction of subbituminous coal. The amount of functional groups present seem to be about the same from cuts of similar boiling range from subbituminous and bituminous coal derived products since caustic and acid extractions gave similar yields of material.

III. INSPECTION BY GAS CHROMATOGRAPHY

One of the objectives of this study has been development of qualitative ~~information on the number and kind of substances in coal derived products.~~ The simulated distillation chromatograph was used to develop rough boiling range data, and at least a minimum count of the number of compounds represented in each of the samples previously discussed. Copies of the spectra are presented in order to indicate the complex nature of the oils in question.

A. Inspection of Vessel 2 Oil

Figure A-16 presents the spectrum for the simulated distillation of the neutral oil fraction from run DOE 350R vessel 2 oil. Counting well defined peaks and shoulders indicates at least 50 substances in this chromatogram (which is run with a column deliberately made to resolve poorly). The instrument uses a flame ionization detector and the response is therefore proportional to the carbon content of the peak being detected. Inspection of the data shows that the largest area percentage reported is 8.47% of the total area detected. Retention times are given for the peaks in hundredths of minutes. The atmospheric boiling range of the sample is presented at the bottom of the page in degrees centigrade. Because the peaks are merged throughout most of the chart area, percentages are reported at constant time increments and the areas reported are only loosely associated with the peaks in the area of the time print. Large peaks may be cut up into several time slices while several small sharp peaks may fall within one time interval. This operating mode is required to produce the boiling range data but is not convenient for estimating the contribution of single peaks.

Figure A-17 presents the spectrum for the simulated distillation of the saturates which were isolated by sulfuric acid extraction of the neutral oil from run DOE 350R vessel 2 oil. Counting well defined peaks and shoulders indicates that a minimum of 50 substances are resolved. A regular pattern is observed which is characteristic of a homologous series of hydrocarbons. This material is separated from the neutral oil, therefore the spectrum presented as Figure A-16 must have contained all of the peaks shown here at a reduced concentration. Some of the peaks for lighter compounds match well in retention time on both spectra while the major peaks on the neutral oil spectrum are not represented on the spectrum of the saturates. This is good qualitative support for the observation that lighter products tend to be saturated while products with higher molecular weights are more aromatic. Resolution is too poor to allow identification of specific peaks. As would be expected, the boiling range of the saturates tends to be lower than that of the aromatic substances present (compare the simulated distillation data at the bottom of charts A-16 and A-17). Unfortunately, the sulfuric acid consumes the aromatic material with this separation procedure and it is not possible to develop a spectrum for only the aromatic fraction.

The caustic extractable material in the vessel 2 oil was separated into two fractions. One fell out of solution as an oil which could be separated from the aqueous phase when the caustic extract was neutralized and made slightly acid. The water insoluble oil was analyzed by the simulated distillation procedure which produced the spectrum presented as Figure A-18. Counting well defined peaks and shoulders gives an indication of about a dozen compounds. These are bunched together and may obscure the presence of many more. These are higher boiling materials corresponding to the aromatic part of the neutral oil distillation curve and run quite a bit higher than the boiling range of the saturates.

The water phase from the procedure above was then extracted with ether to recover as much of the phenolic material as possible. This includes material which is soluble and some which was suspended as fine droplets or stuck to the separatory funnel. After removal of the ether, a sample of the recovered material was analyzed by simulated distillation. The spectrum for this sample is presented as Figure A-19. It can be seen that the lower boiling (lower molecular weight) material tends to be water soluble and that the first compounds to emerge have driven the recorder off scale. From the infrared spectrum it is clear that the main component of this is phenol while other substances such as methyl phenol would be significantly less soluble but still present. Some of the heavy material probably was stuck to the separatory funnel.

The sulfuric acid extract of the vessel 2 oil was made basic and then the released material was recovered by extraction with ether. After evaporation of the ether, a sample of the recovered material was analyzed by simulated distillation. The spectrum for this material is presented as Figure A-20. At least 30 peaks or shoulders on peaks can be counted. The distribution of substances in this array of materials is skewed towards the high boiling end of the chromatogram. Most of these are likely amine compounds so retention of nitrogen by aromatic and more complex molecules is suggested by the shape of the distillation.

B. Inspection of Vessel 4 Oil

The same sequence of separations and analyses was repeated for the vessel 4 oil. This product is separated on the DOE reactor system by distillation of the bottoms from the intermediate temperature, high pressure separator. It is the overheads from distillation of the oil which boils just higher than that collected in vessel 2. This is a poorly rectified oil with an average boiling range between the vessel 2 oil and process solvent. The spectrum of the neutral oils separated from the vessel 4 product is presented as Figure A-21. The major part of the material falls in a fairly narrow band but minor amounts of lower and higher boiling material are present over a considerable range.

As previously observed, the water phase separated from the water insoluble phenolic substances still contained an appreciable amount of material which could be reclaimed by extraction with ether. The simulated distillation of the reclaimed material is presented as Figure A-22. These results show an enhancement in the concentration of the lower boiling (and presumably lower molecular weight) phenols. This spectra should be compared to that for the water insoluble phenolic products which is presented as Figure A-23. Indications of about 20 substances are found on Figure A-23 and a similar number with a different distribution on Figure A-22. These appear to be pretty much the same materials, but a higher concentration of the lower molecular weight materials was obtained from the water extraction.

The bases in the vessel 4 oil were recovered in the same manner as previously described. The spectrum for the simulated distillation is presented as Figure A-24. When this chart is compared to the simulated distillation of the bases in the vessel 2 oil, the lower boiling range substances appear to be similar. The vessel 4 sample has an array of higher boiling substances and appears to represent a larger number of materials.

A portion of the vessel 4 neutral oil was reacted with concentrated sulfuric acid to dissolve the aromatic materials. A clear saturated hydrocarbon sample was isolated and the simulated distillation of this material is presented on Figure A-25. The spectrum shows a regular pattern of complex peaks. At least 57 peaks and shoulders can be counted on this chart and it is quite likely that with reasonable resolution this number could be increased substantially. The simulated distillation apparatus is calibrated by means of a mixture of known saturated hydrocarbons ranging from C_5 to C_{40}. A spectrum of this mixture with known compounds indicated is presented as Figure A-26. It can be seen that certain peaks in the vessel 4 sample coincide closely with some of the known peaks. Many peaks are present between those in the calibration standard and the presence of various branched and naphthenic hydrocarbons must be presumed from the complexity of the display.

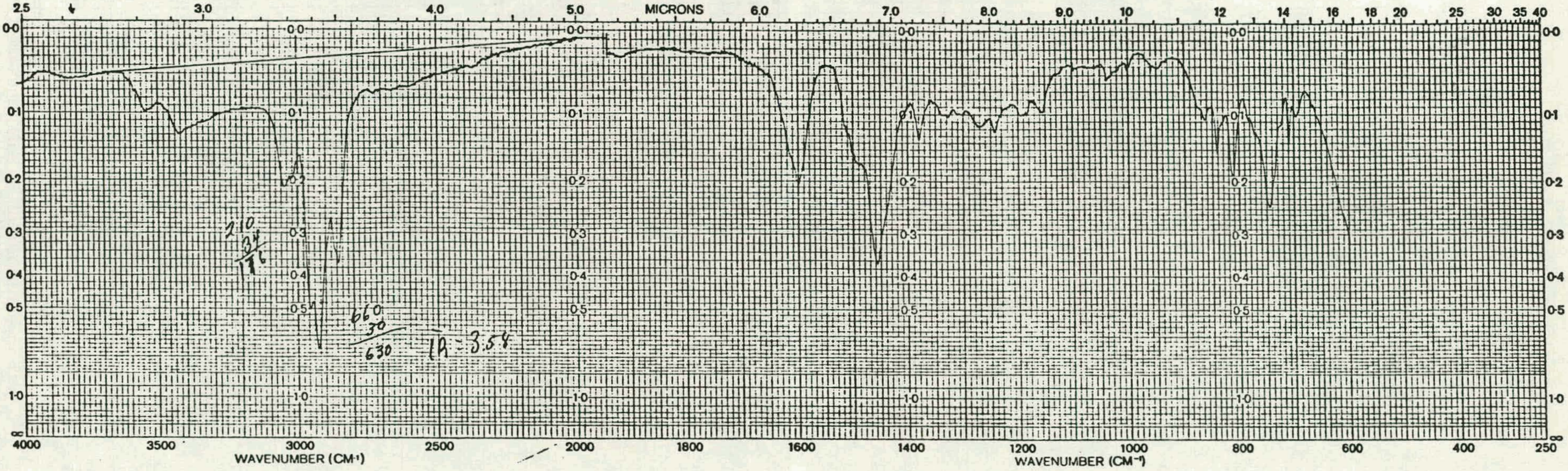
IV. ELEMENTAL ANALYSIS

The separation was done with enough starting material to give an ample amount of separated material for elemental analysis in most cases. The results of elemental analysis are tabulated below:

ELEMENTAL ANALYSES; RUN DOE 350R

SAMPLE	CARBON	HYDROGEN	SULFUR	NITROGEN	OXYGEN
Vessel 2 Neutral Oil	87.17	11.80	0.069	0.17	0.79
Vessel 2 Saturates	86.37	13.79	0.003	0.00	--
Vessel 2 Phenols (insol)	74.53	8.36	0.003	0.28	16.83
Vessel 2 Phenols (soluble)	76.98	7.28	nil	0.09	15.85
Vessel 2 Bases	79.99	9.57	nil	7.99	2.45
Vessel 4 Neutral Oil	88.91	9.91	0.161	0.29	0.73
Vessel 4 Saturates	86.12	13.39	0.019	0.00	0.47
Vessel 4 Phenols (insol)	76.04	7.83	0.006	0.50	15.62
Vessel 4 Phenols (soluble)	77.50	7.81	0.005	0.46	14.23
Vessel 4 Bases	75.12	8.88	0.003	7.19	8.81

Figure A-1 Run DOE 350R, Product 74, Cut 2 Oil (108-270°C at 2mm)

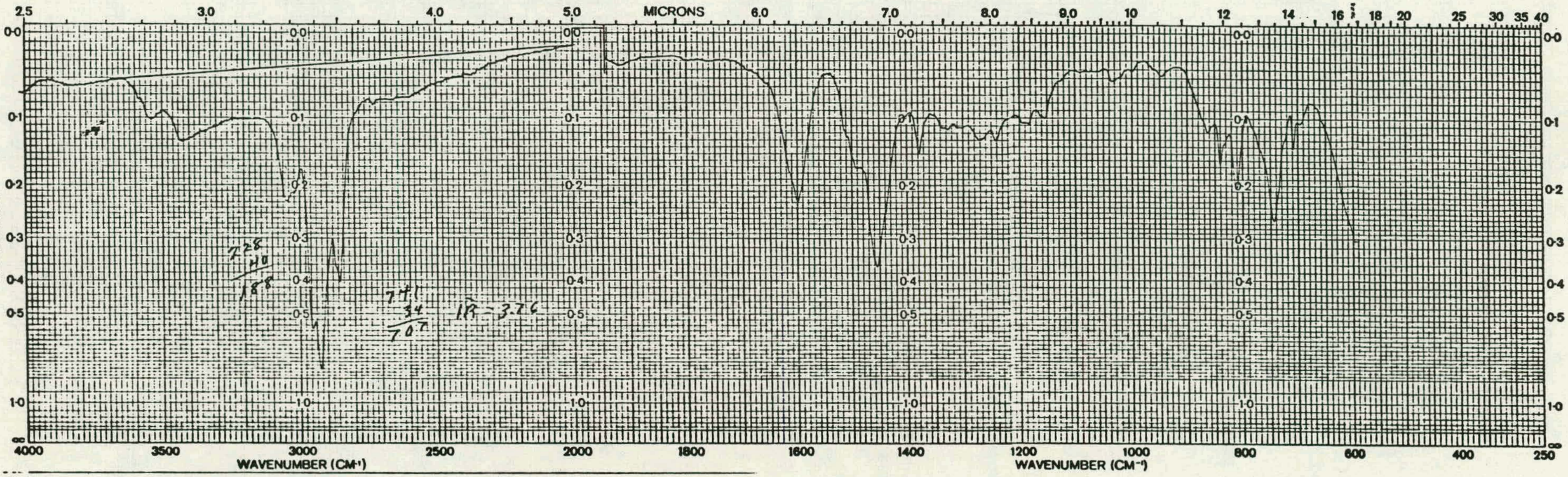


210
34
176

660
30
630

IR = 3.58

Figure A-2 Run DOE 350R, Product 68, Cut 2 Oil, RT ⟶ 108°C at 2mm



228
40
188

741
34
707

IR = 3.76

Figure A-3 Run DOE 350R, Products 1-21, Vessel 3 Oil

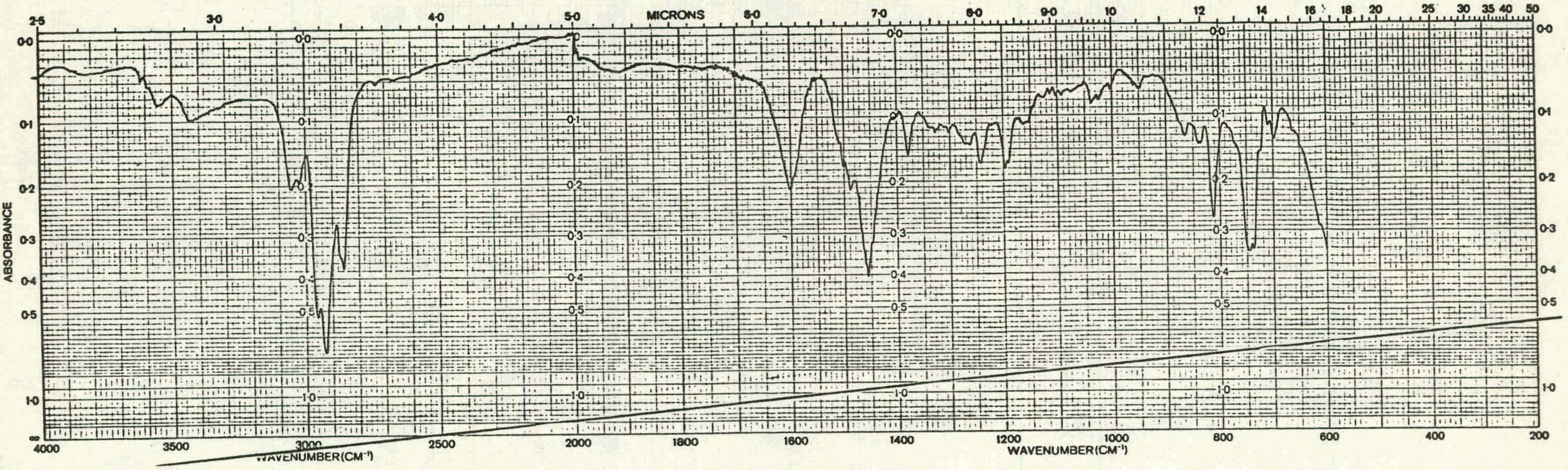


Figure A-4 Run DOE 350R, Vessel 2 Oil

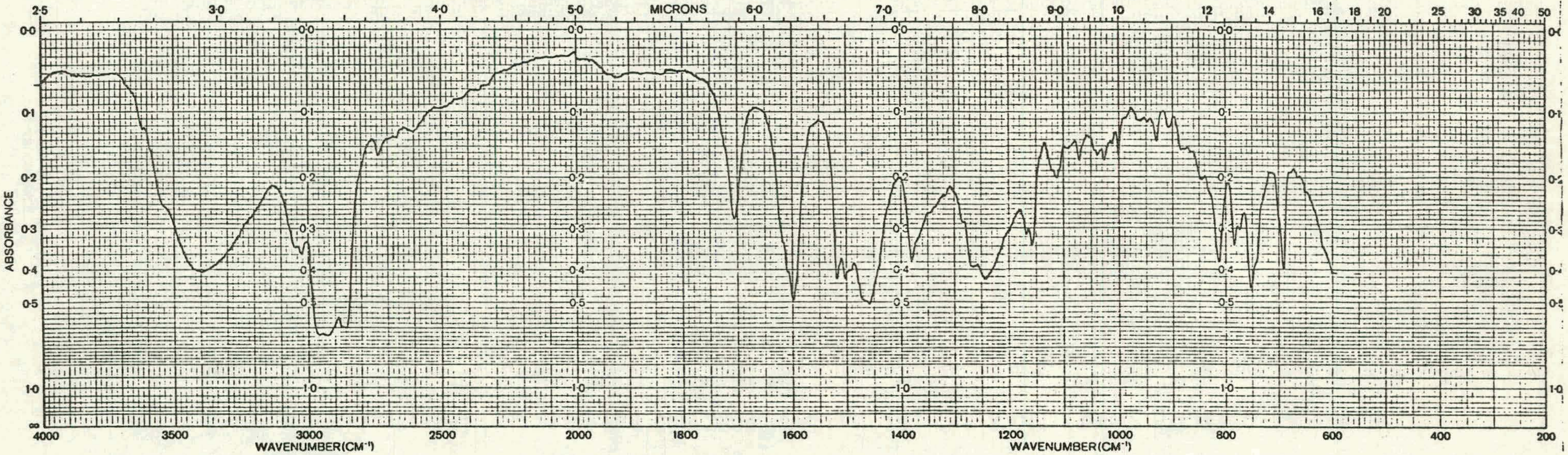


Figure A-5 Run DOE 350R, Vessel 2 Oil Extracted by NaOH then H_2SO_4 Solution (Neutral Oil Fraction)

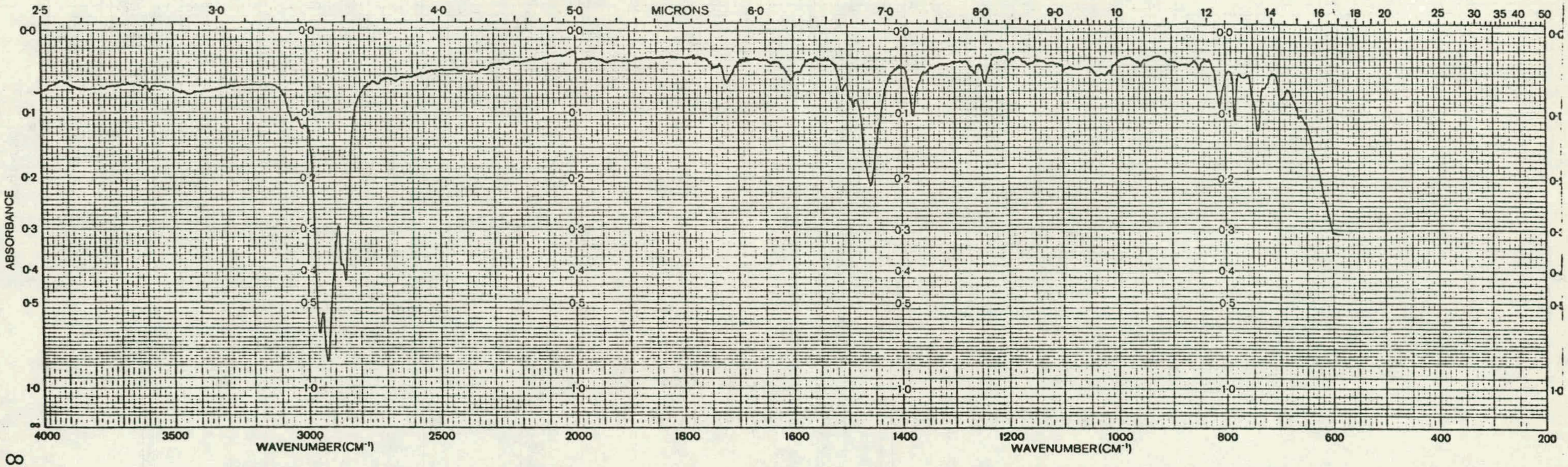


Figure A-6 Run DOE 350R Vessel 2 Oil, Neutral Oil Sample - Fraction Insoluble in Concentrated H_2SO_4 (≈36% of Original V2 Oil)

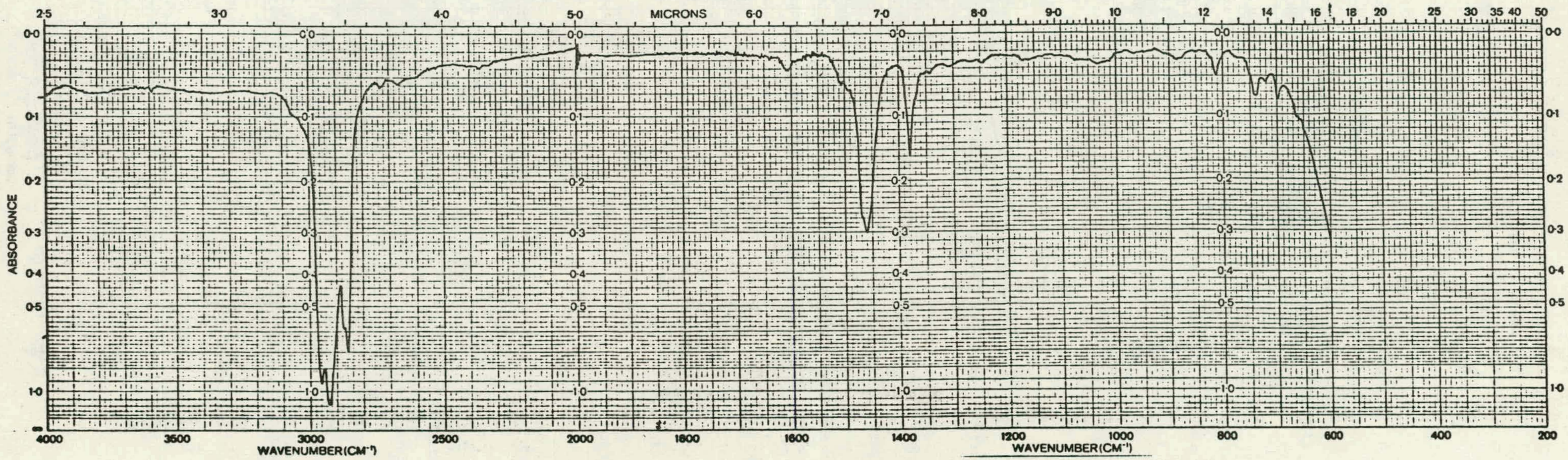


Figure A-7 Run DOE 350R Vessel 2 Oil, Caustic Soluble Product Reclaimed by HCl Acidification Water Insoluble

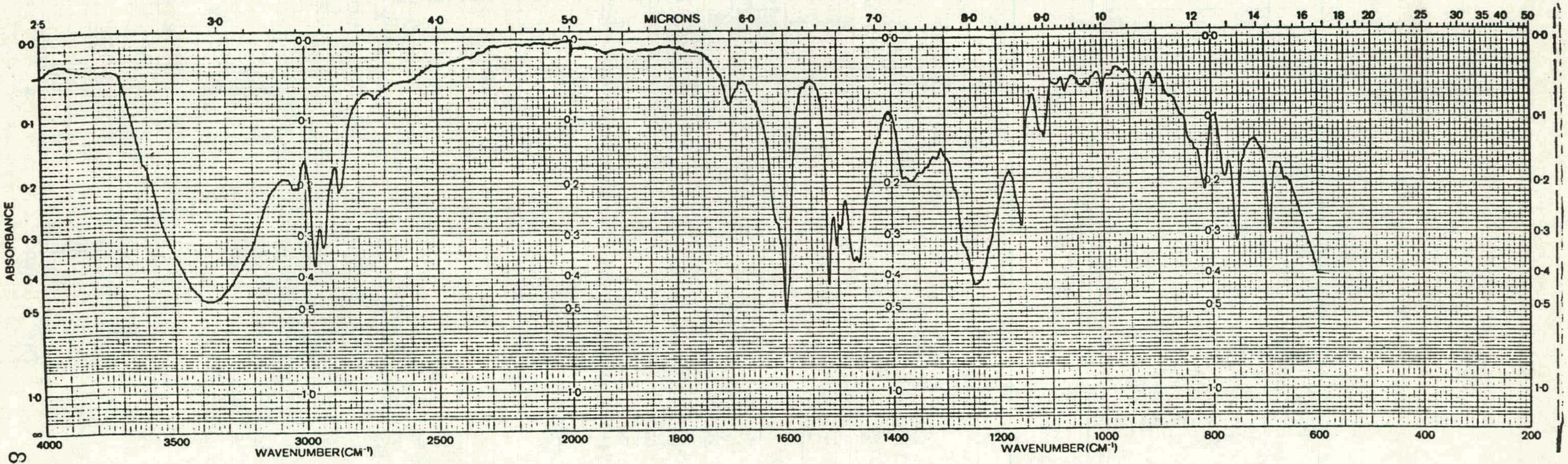


Figure A-8 Run DOE 350R Vessel 2 Oil, Ether Extract of Acidic Material

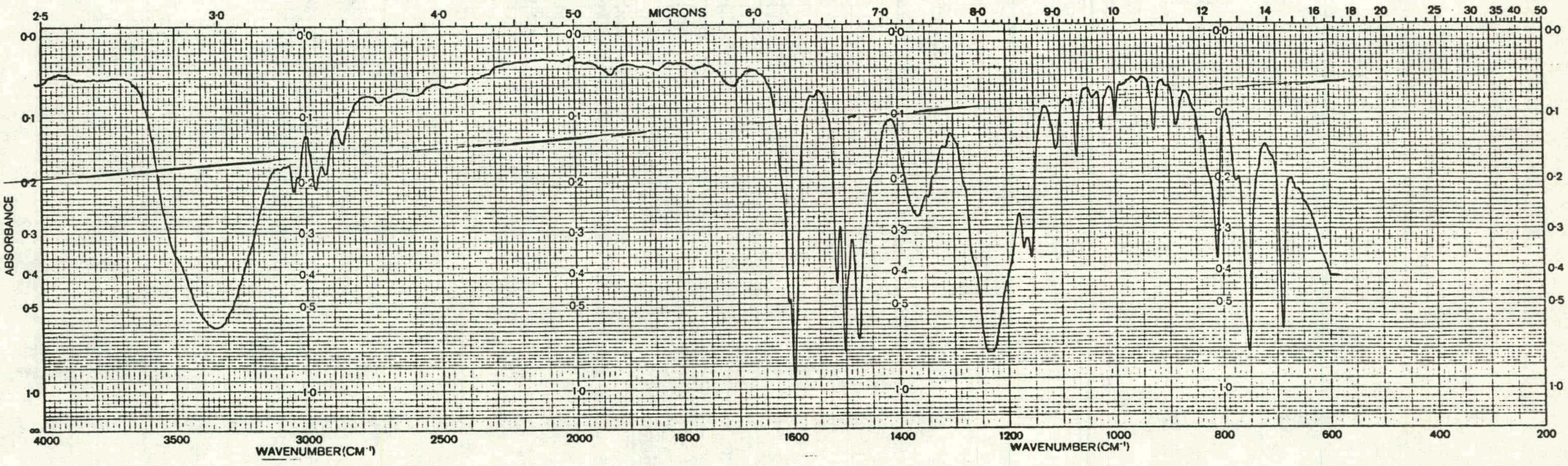


Figure A-9 Run DOE 350R Vessel 2 Oil, Acid Soluble Material - Reprecipitated with Caustic and Extracted with Ether

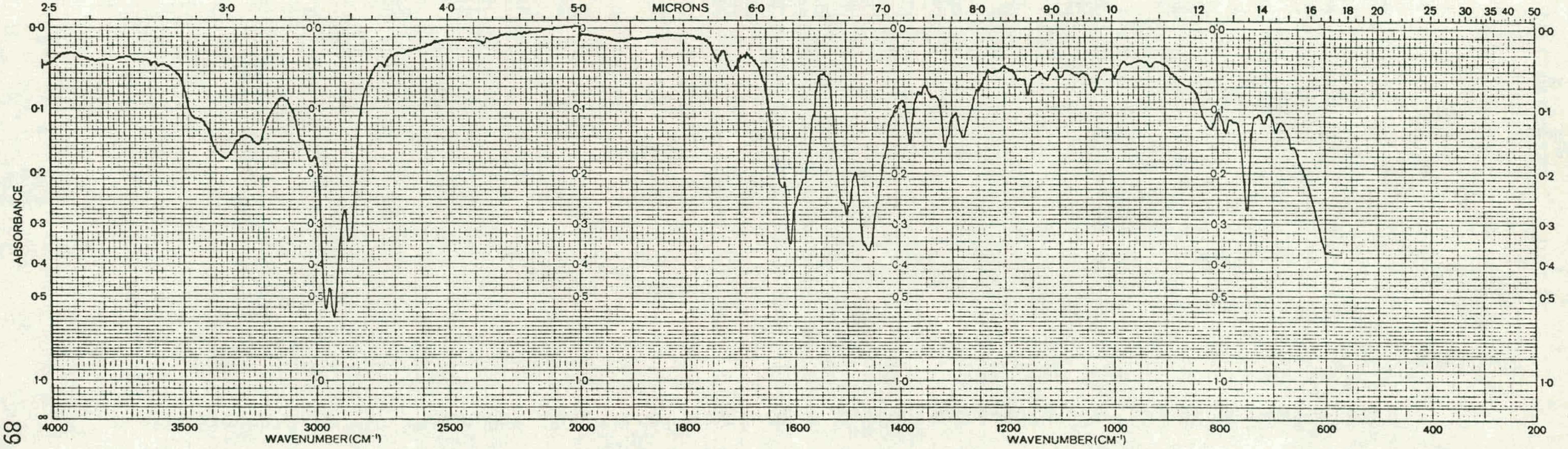


Figure A-10 Run DOE 350R, Product 1-37, Vessel 4 Oil

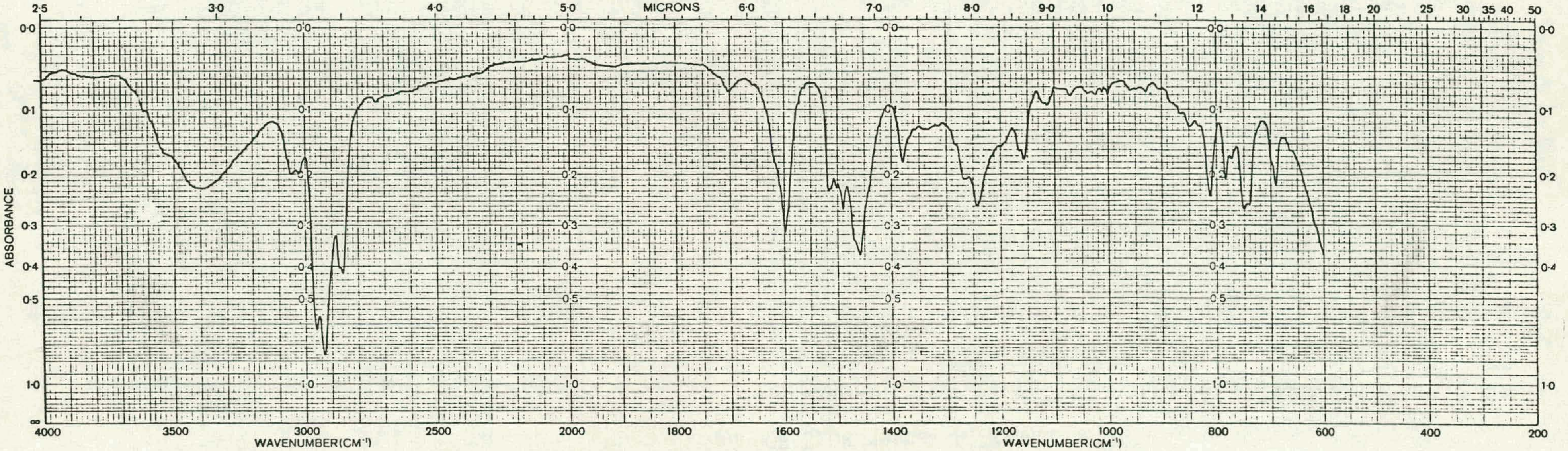


Figure A-11 Run DOE 350R Vessel 4 Neutral Oils

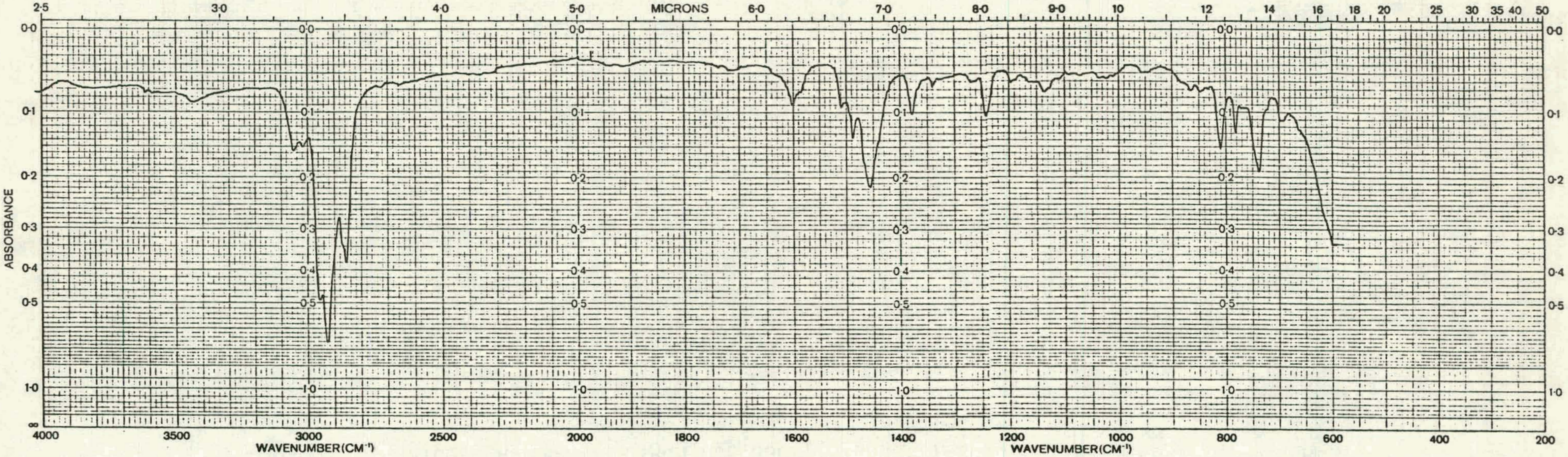


Figure A-12 Run DOE 350R Vessel 4 Saturates by Concentrated H_2SO_4 (29% of Neutral Oils)

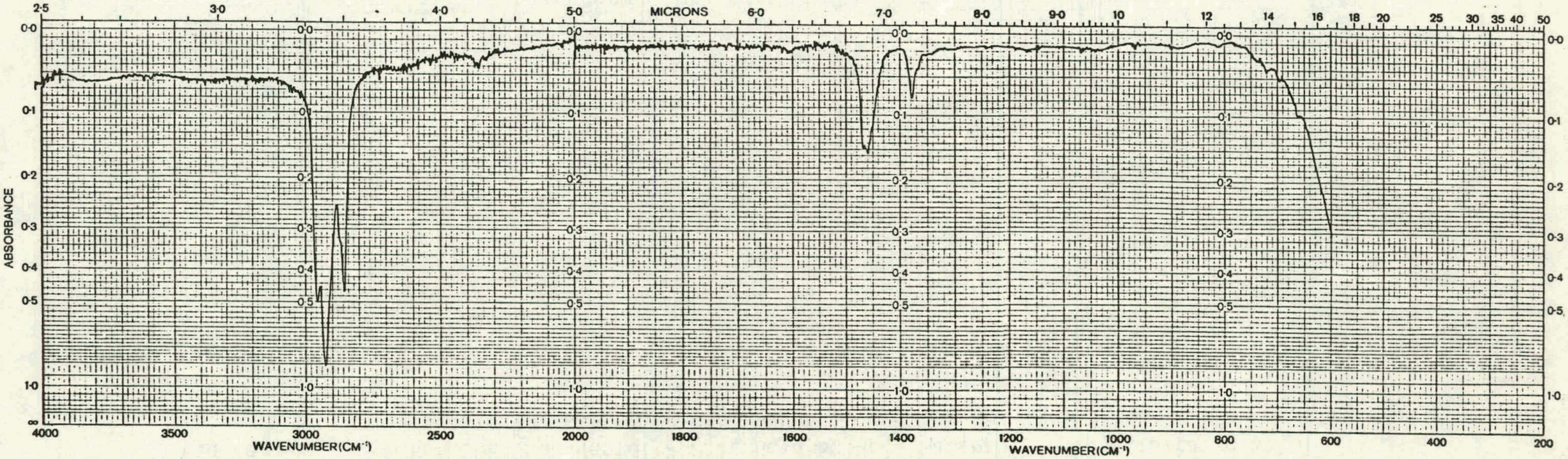


Figure A-13 Run DOE 350R Vessel 4 Oil, Phenolic Material Extracted by NaOH and Made Acid by HCl (Water Insoluble Product)

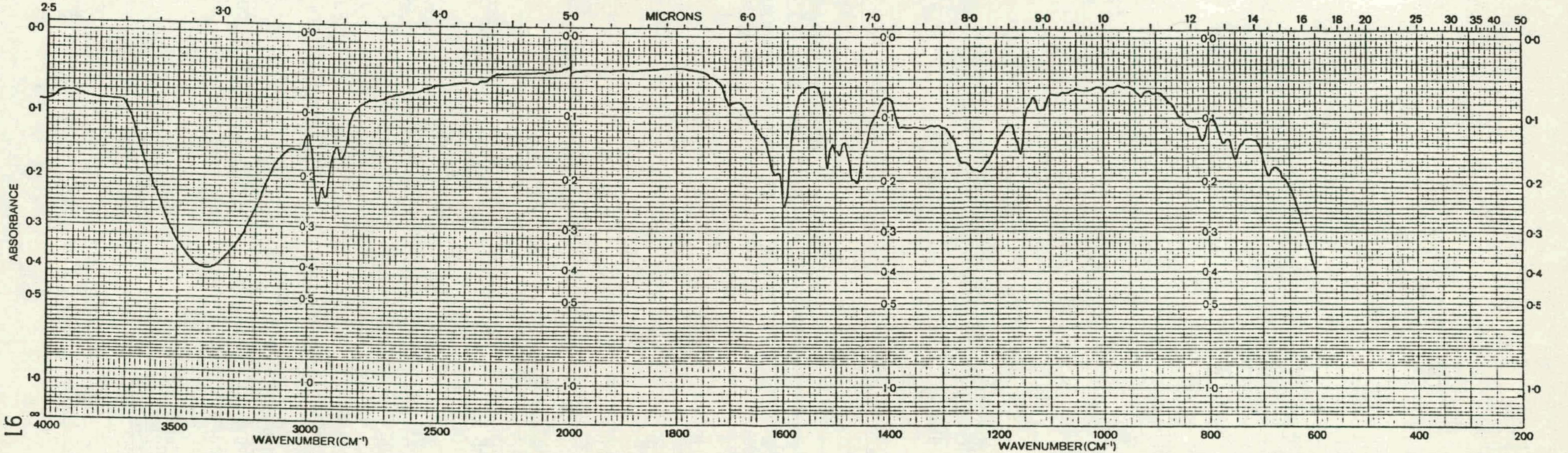


Figure A-14 Run DOE 350R Vessel 4 Oil, Extracted with Caustic and Acidified (Ether Extract of Water Phase)

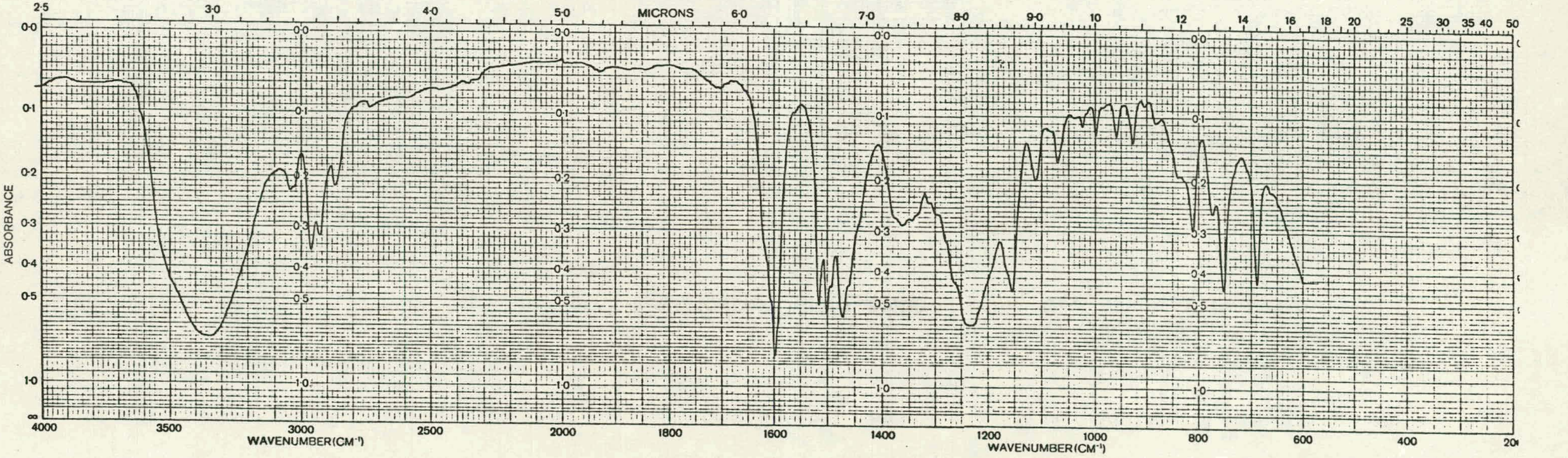


Figure A-15 Run DOE 350R Vessel 4 Bases - Extracted by H_2SO_4. Reprecipitated by Caustic and Extracted with Ether

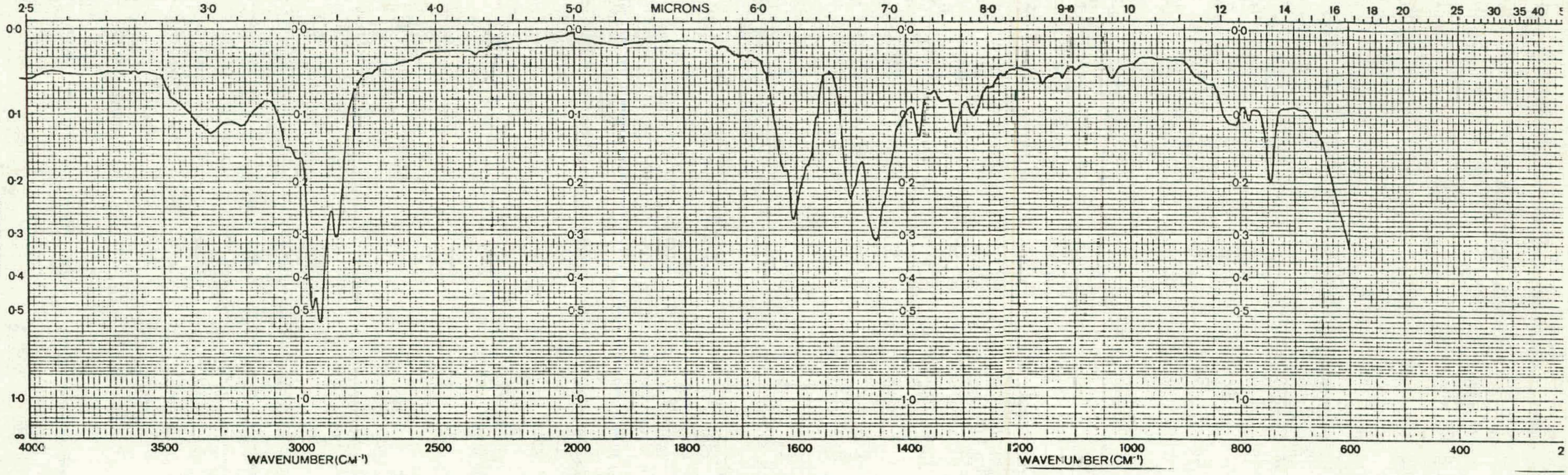
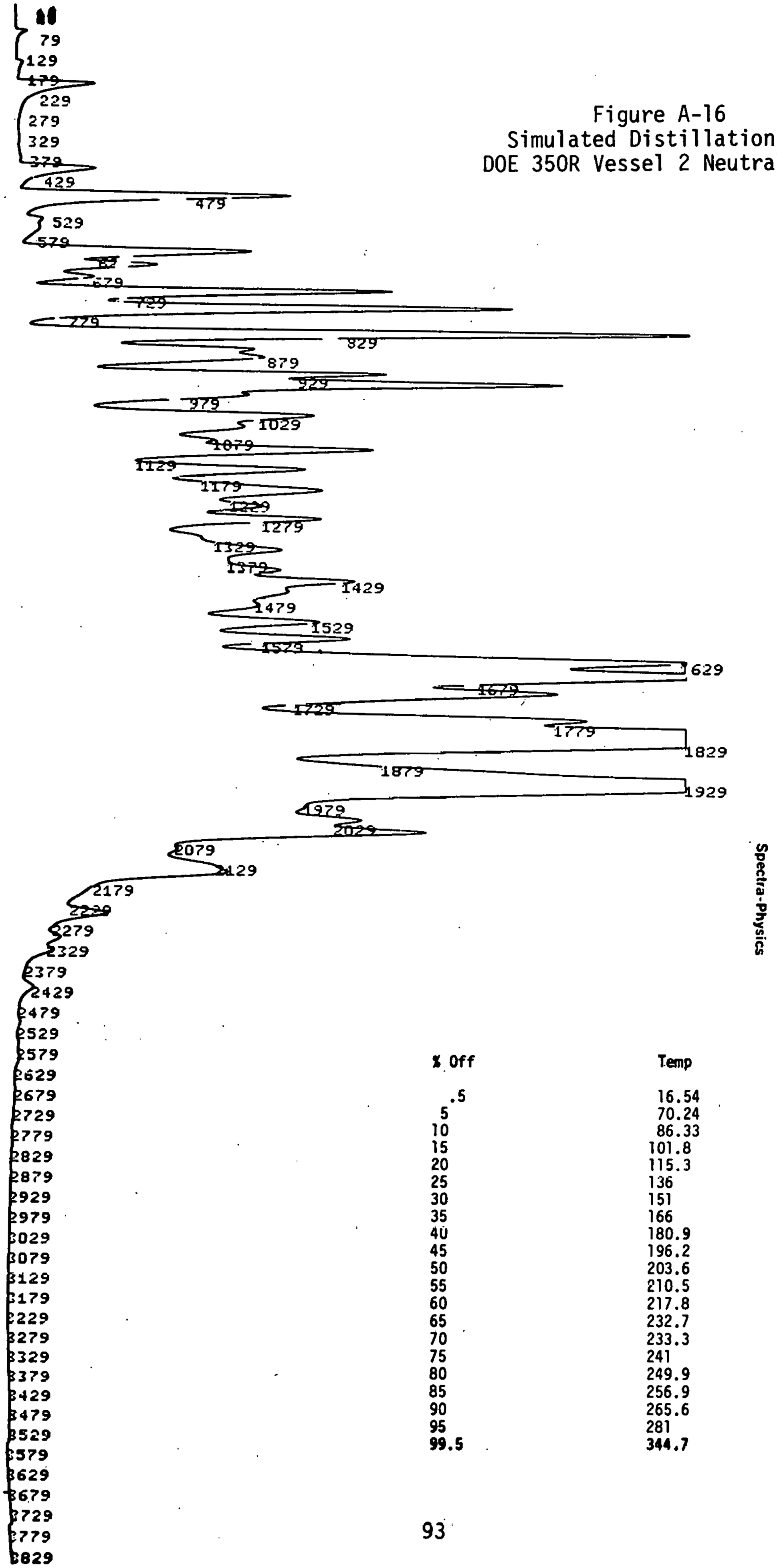
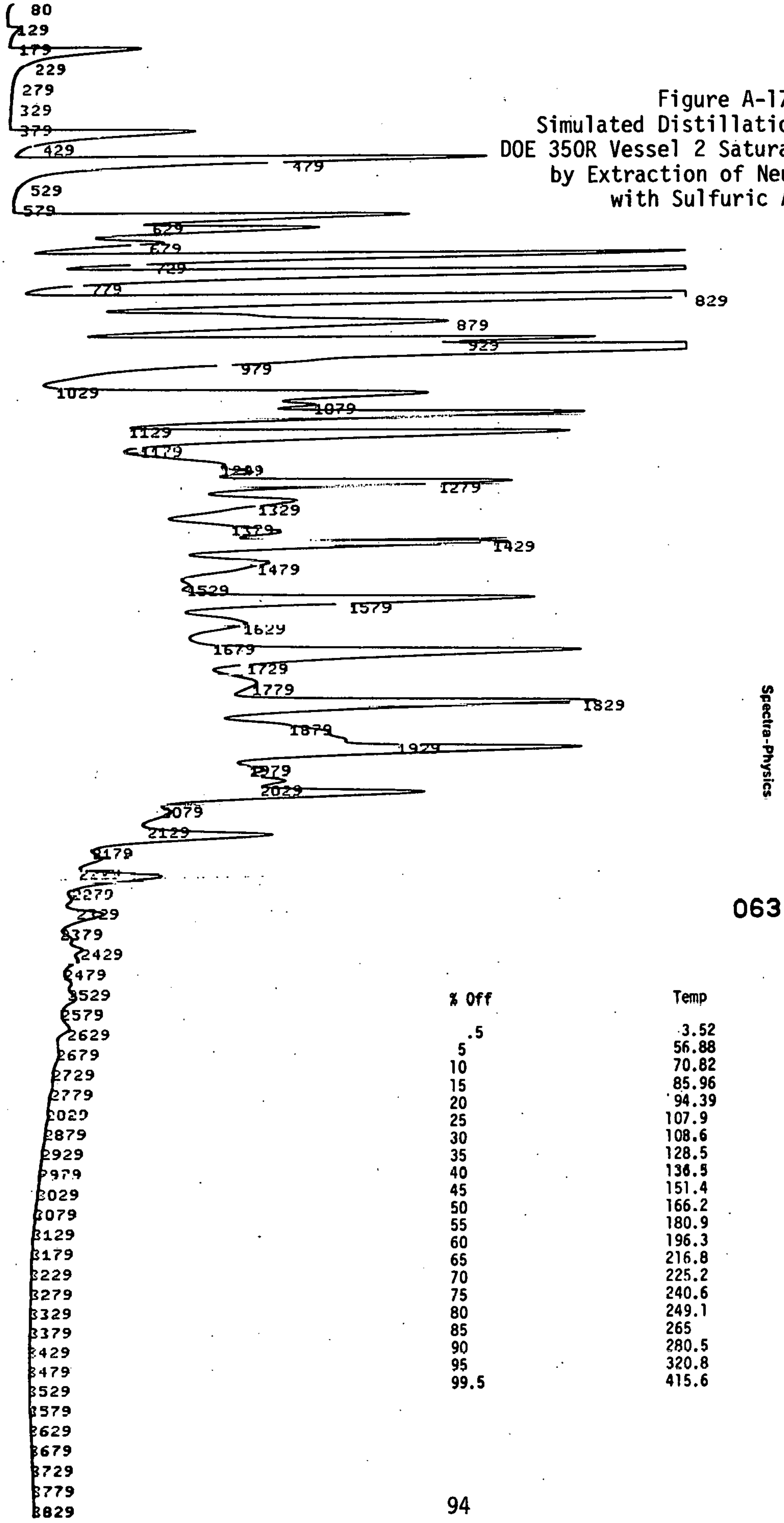


Figure A-16
Simulated Distillation GC
DOE 350R Vessel 2 Neutral Oil



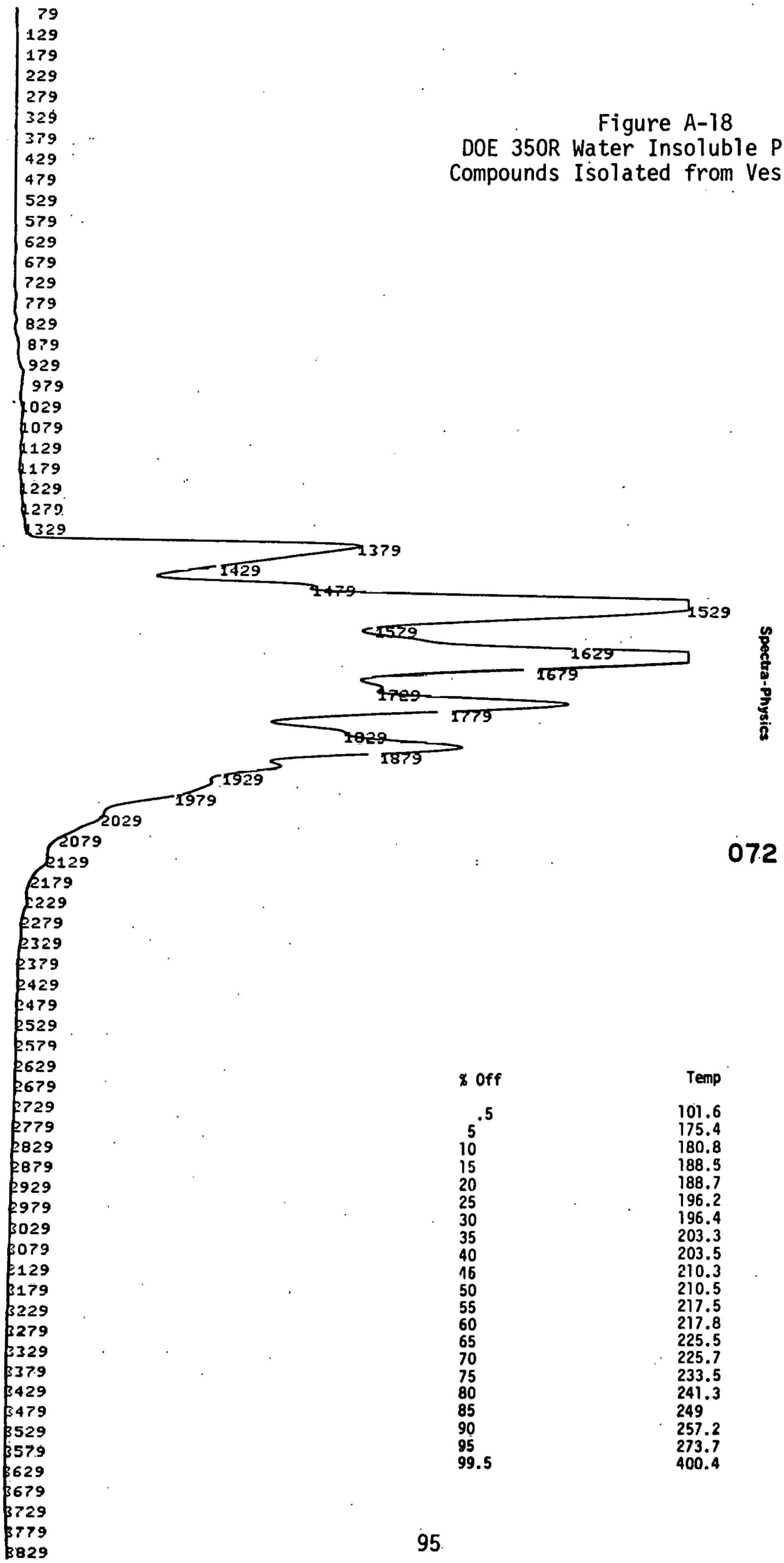
% Off	Temp
.5	16.54
5	70.24
10	86.33
15	101.8
20	115.3
25	136
30	151
35	166
40	180.9
45	196.2
50	203.6
55	210.5
60	217.8
65	232.7
70	233.3
75	241
80	249.9
85	256.9
90	265.6
95	281
99.5	344.7

Figure A-17
Simulated Distillation GC
DOE 350R Vessel 2 Saturates Isolated by Extraction of Neutral Oil with Sulfuric Acid



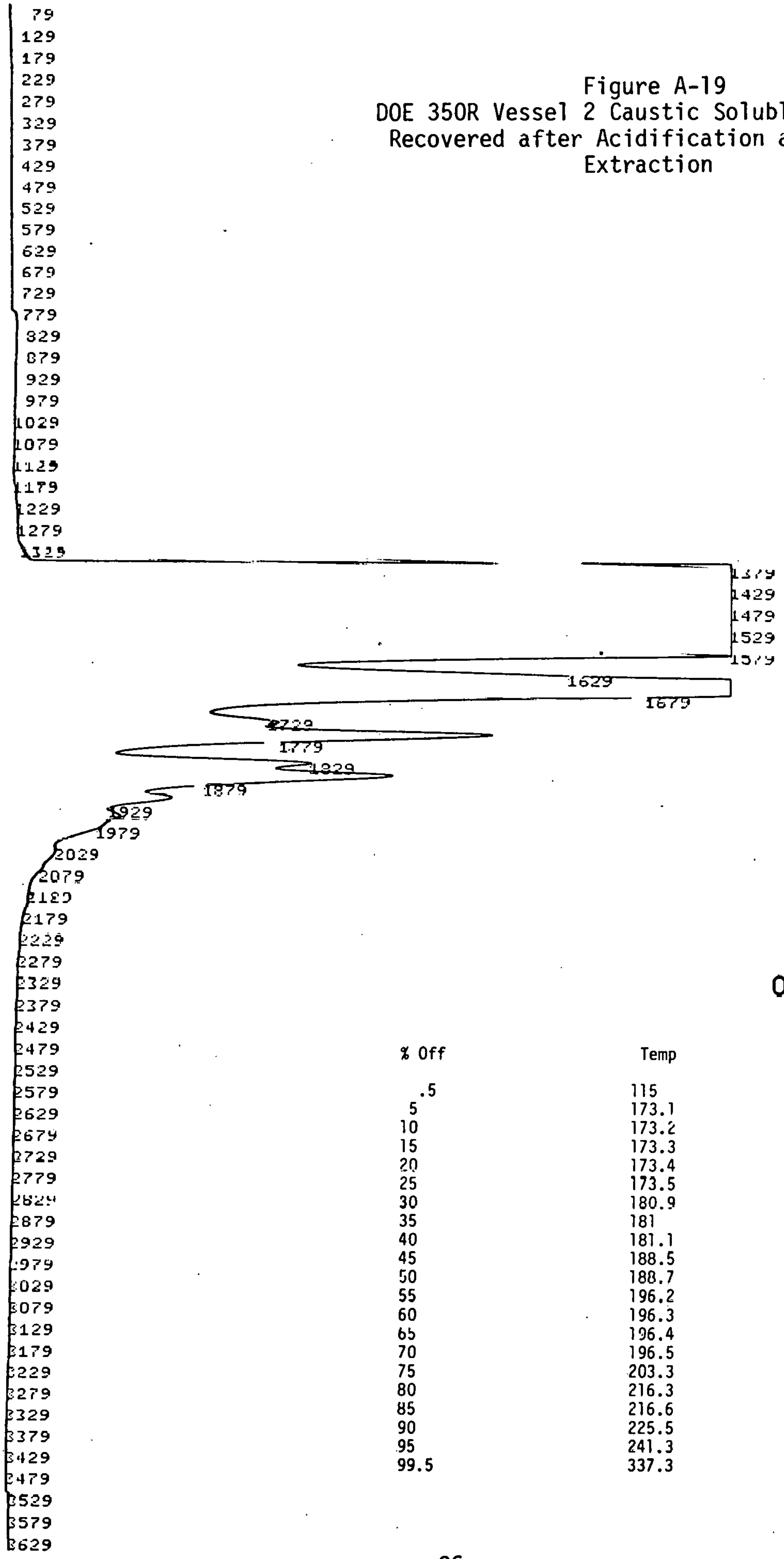
% Off	Temp
.5	3.52
5	56.88
10	70.82
15	85.96
20	94.39
25	107.9
30	108.6
35	128.5
40	136.5
45	151.4
50	166.2
55	180.9
60	196.3
65	216.8
70	225.2
75	240.6
80	249.1
85	265
90	280.5
95	320.8
99.5	415.6

Figure A-18
DOE 350R Water Insoluble Phenolic
Compounds Isolated from Vessel 2 Oil



% Off	Temp
.5	101.6
5	175.4
10	180.8
15	188.5
20	188.7
25	196.2
30	196.4
35	203.3
40	203.5
46	210.3
50	210.5
55	217.5
60	217.8
65	225.5
70	225.7
75	233.5
80	241.3
85	249
90	257.2
95	273.7
99.5	400.4

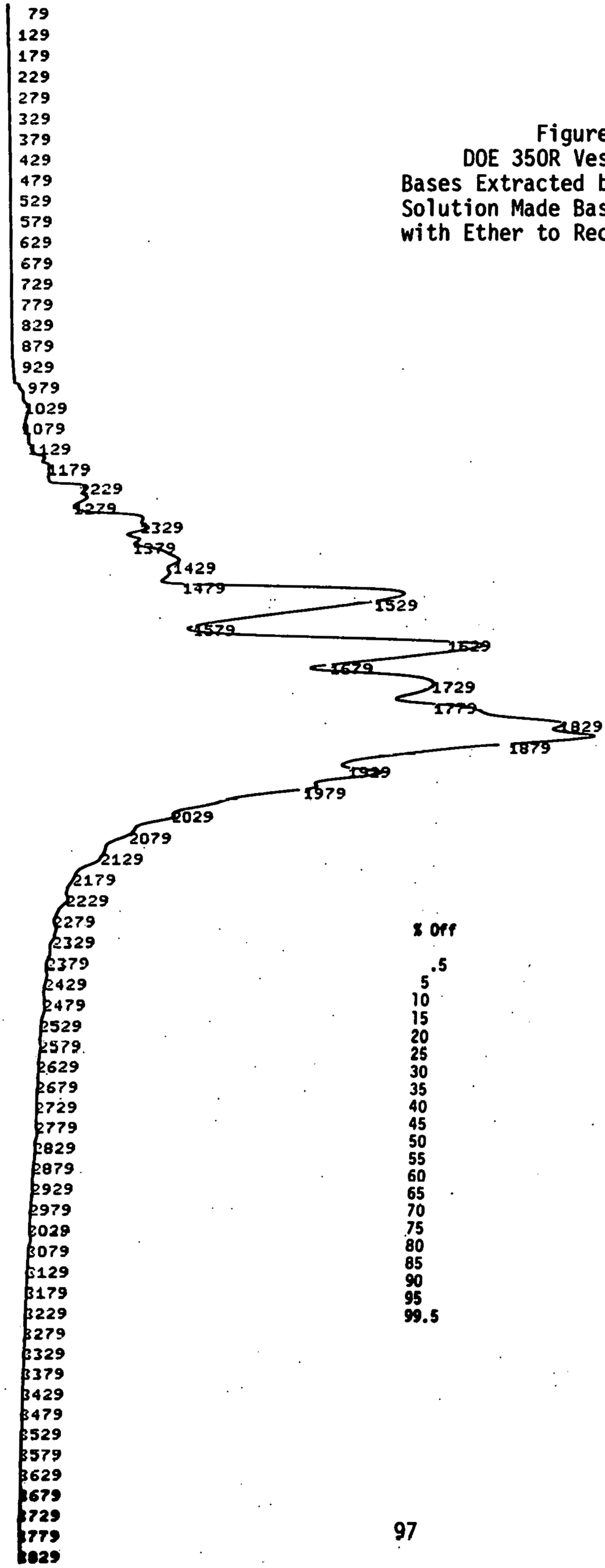
Figure A-19
DOE 350R Vessel 2 Caustic Soluble Product
Recovered after Acidification and Ether
Extraction



066

% Off	Temp
.5	115
5	173.1
10	173.2
15	173.3
20	173.4
25	173.5
30	180.9
35	181
40	181.1
45	188.5
50	188.7
55	196.2
60	196.3
65	196.4
70	196.5
75	203.3
80	216.3
85	216.6
90	225.5
95	241.3
99.5	337.3

Figure A-20
DOE 350R Vessel 2 Oil
Bases Extracted by Aqueous Acid
Solution Made Basic & Extracted
with Ether to Recover Bases

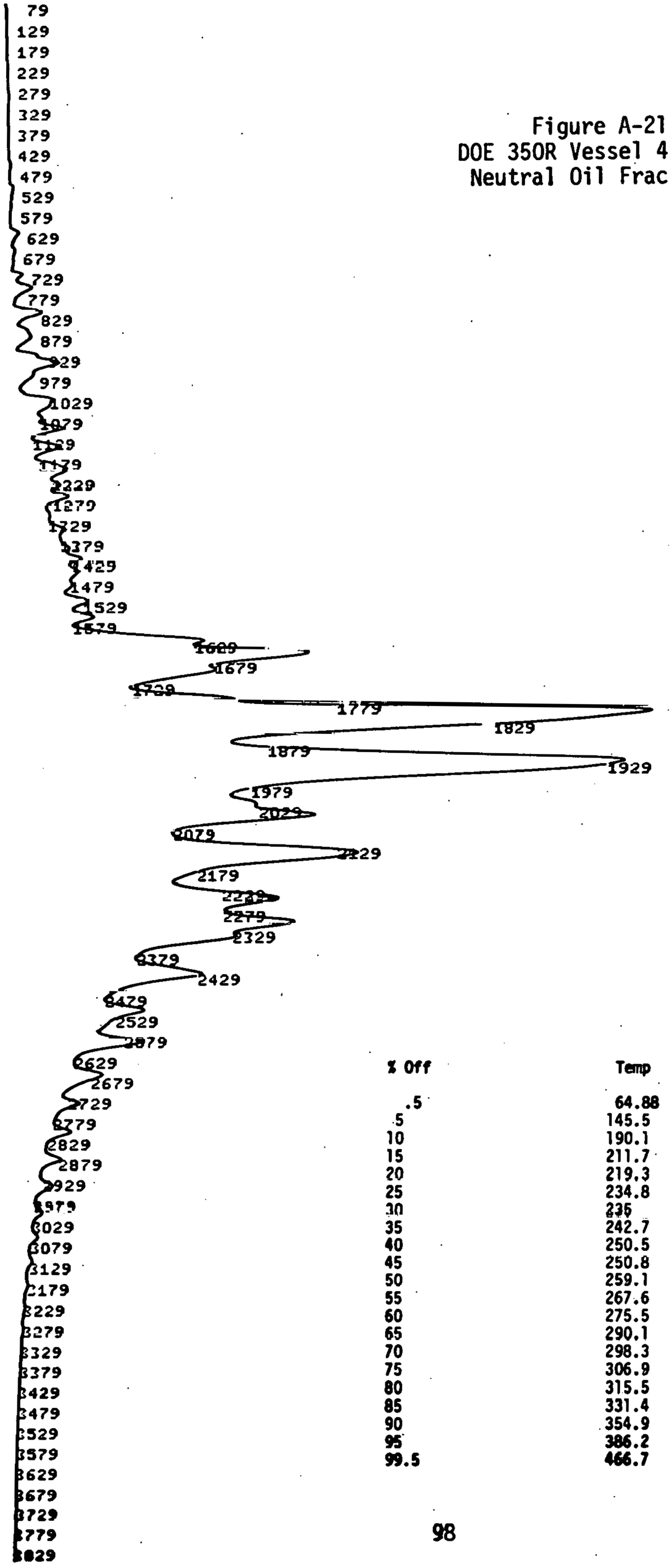


% Off	Temp
.5	96.18
5	160.2
10	174.9
15	190.1
20	197.6
25	204.6
30	211.7
35	211.9
40	219.2
45	227
50	227.3
55	235
60	242.6
65	242.9
70	250.5
75	250.9
80	259.2
85	267.8
90	290.2
95	339.4
99.5	466.3

Spectra-Physics

077

Figure A-21
DOE 350R Vessel 4 Oil
Neutral Oil Fraction



Spectra-Physics

080

% Off	Temp
.5	64.88
5	145.5
10	190.1
15	211.7
20	219.3
25	234.8
30	235
35	242.7
40	250.5
45	250.8
50	259.1
55	267.6
60	275.5
65	290.1
70	298.3
75	306.9
80	315.5
85	331.4
90	354.9
95	386.2
99.5	466.7

Spectra-Physics

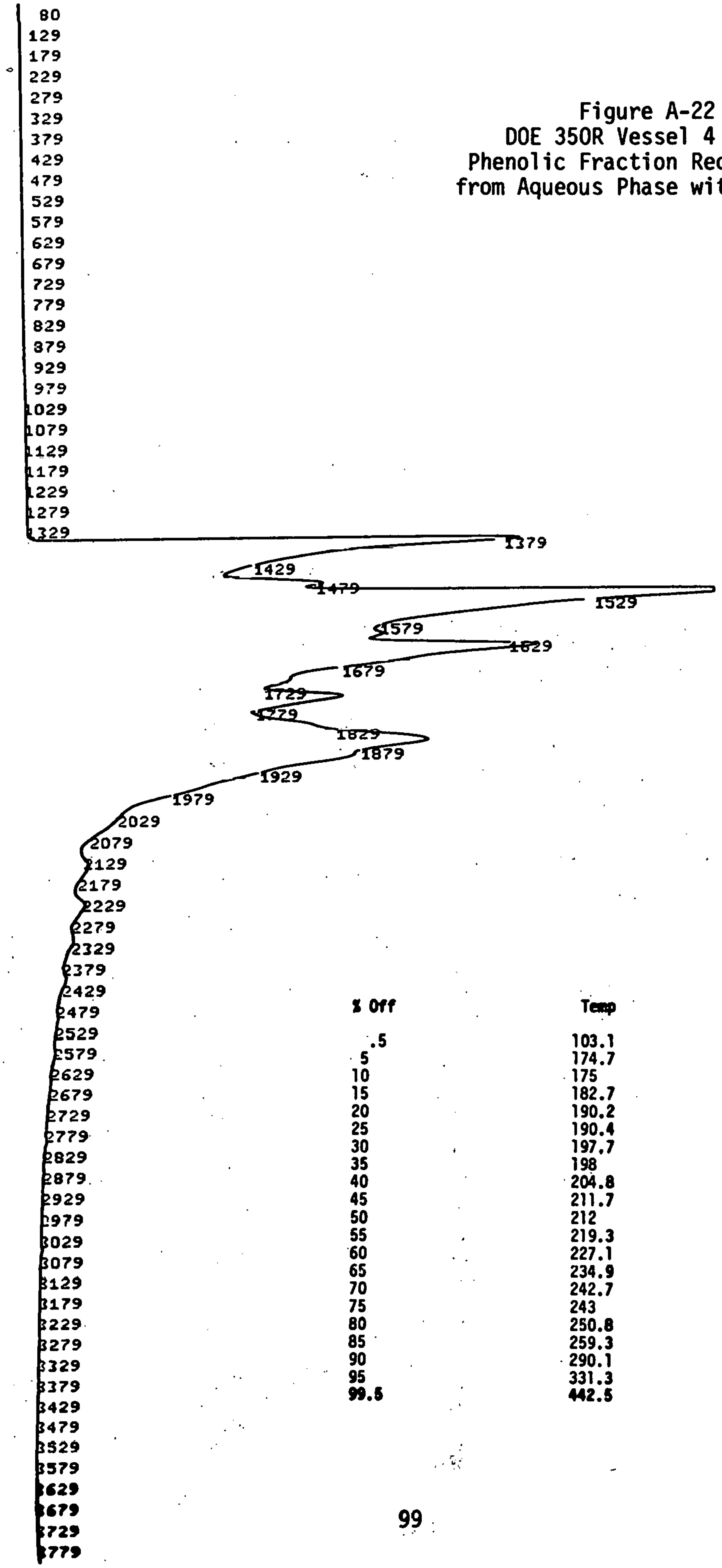


Figure A-22
DOE 350R Vessel 4 Oil
Phenolic Fraction Reclaimed
from Aqueous Phase with Ether

% Off	Temp
.5	103.1
5	174.7
10	175
15	182.7
20	190.2
25	190.4
30	197.7
35	198
40	204.8
45	211.7
50	212
55	219.3
60	227.1
65	234.9
70	242.7
75	243
80	250.8
85	259.3
90	290.1
95	331.3
99.5	442.5

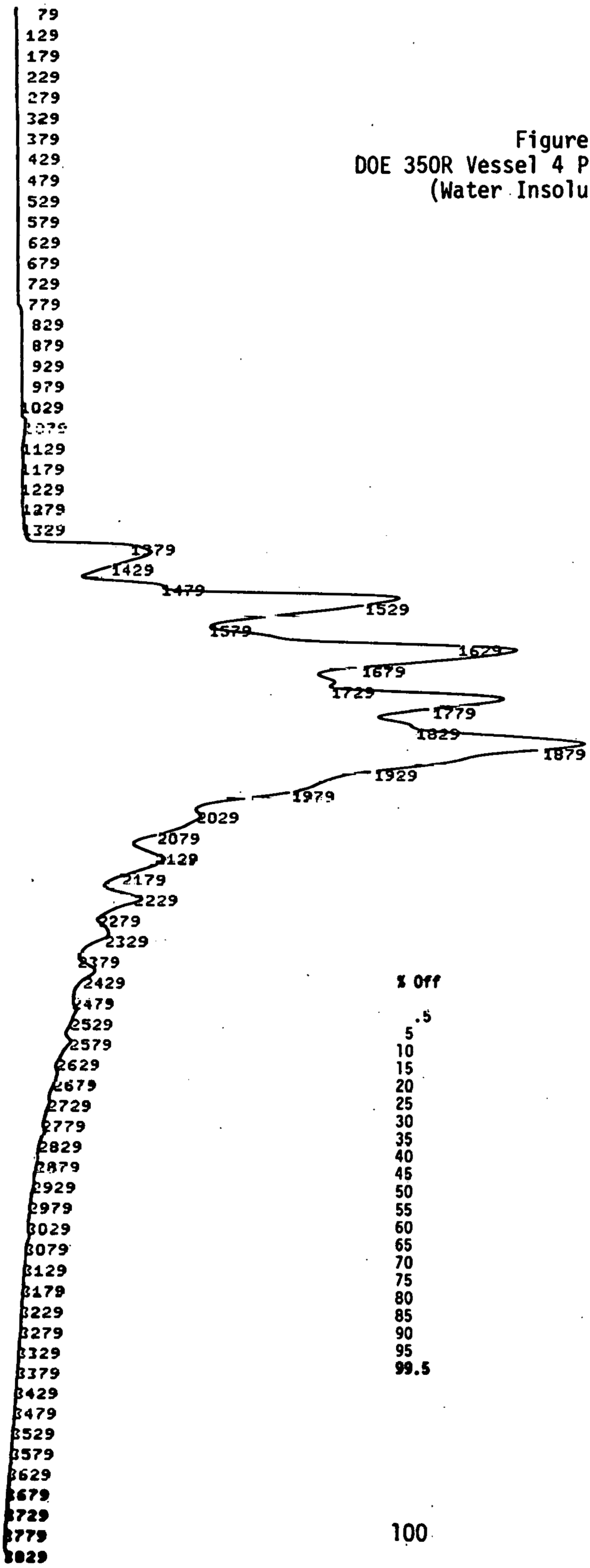


Figure A-23
DOE 350R Vessel 4 Phenolic Fraction
(Water Insoluble Product)

% Off	Temp
.5	65.08
5	182.3
10	190.3
15	197.9
20	204.9
25	211.8
30	219.1
35	226.9
40	227.2
45	234.9
50	242.7
55	242.9
60	250.6
65	258.8
70	259.3
75	275.3
80	290.3
85	307
90	339.3
95	386.2
99.5	496.8

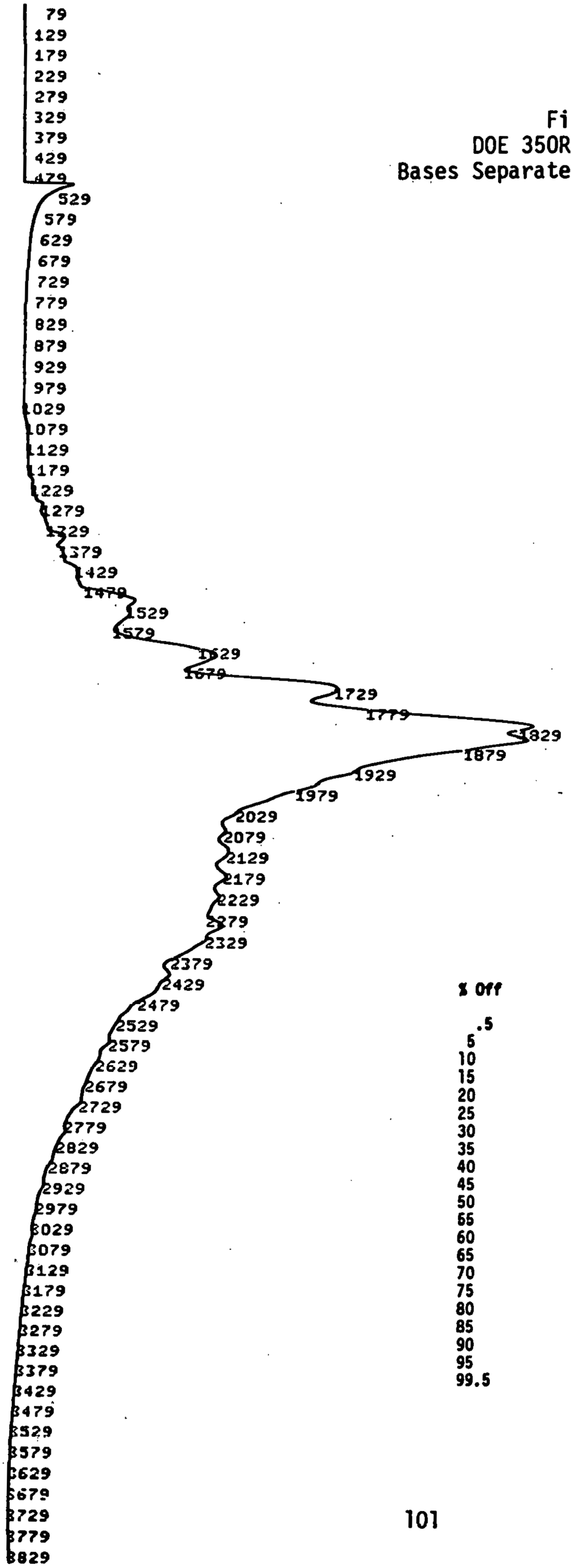


Figure A-24
DOE 350R Vessel 4 Oil
Bases Separated by Acid Extraction

% Off	Temp
.5	45.2
5	182.6
10	204.8
15	219
20	226.9
25	234.8
30	235
35	242.7
40	243
45	250,8
50	259
55	267.6
60	275.5
65	290.1
70	298.4
75	307
80	323.3
85	339.1
90	355.1
95	386.4
99.5	466.7

Spectra-Physics

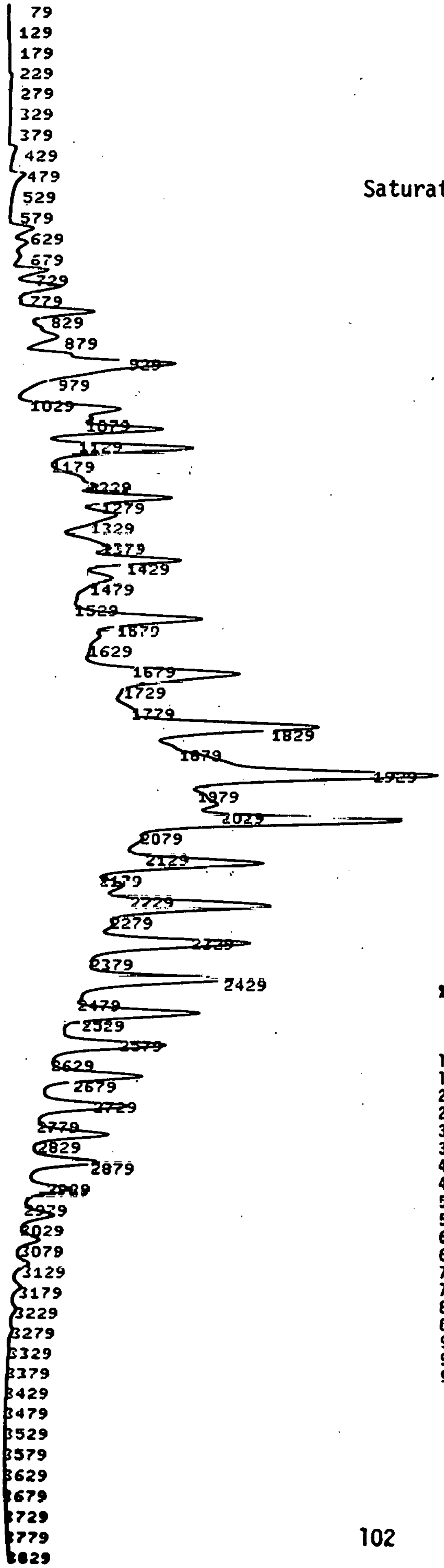
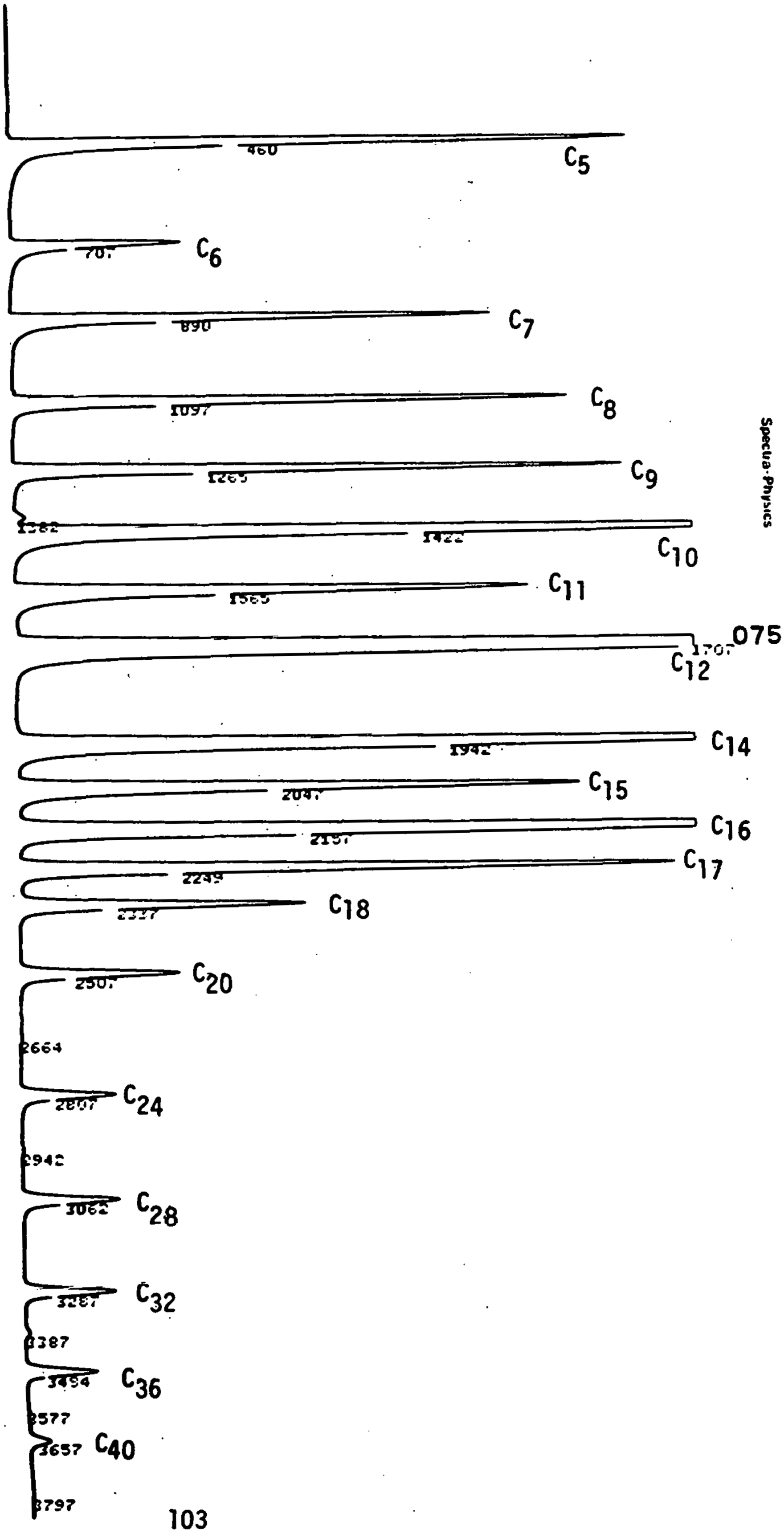


Figure A-25
DOE 350R Vessel 4 Oil
Saturates by Sulfuric Acid Extraction

% Off	Temp
.5	43.79
5	100.4
10	130
15	148.6
20	165.9
25	184.9
30	207.3
35	216.9
40	233.6
45	237
50	244.4
55	251.5
60	264.1
65	275.8
70	283.5
75	305.1
80	319.9
85	338
90	356.1
95	383.3
99.5	445

Spectra-Physics

FIGURE A-26
Calibration Mixture of Known Saturated Linear Hydrocarbons



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APPENDIX B

THE CHEMISTRY OF AMAX BELLE AYR COAL IN THE SRC II PROCESS

I. INTRODUCTION

Run DOE 350R has been used as a model experiment to define an SRC II process using a feed coal (Amax Belle Ayr) of considerably different composition than the coals which were studied in the original development of the process. It was expected that operating problems would develop as a result of the substantial absence of iron in this coal, and this was avoided by the addition of finely ground pyrite. Without knowledge of the kind of operating conditions required, it was decided to use higher than standard hydrogen pressure and to retain the nominal one hour retention time of the standard process. The initial slurry formulation called for use of 30% coal (dry basis) plus 2.35% pyrite based on the feed slurry. After some time, the slurry ash became too high and conversion was also high, so reduction in the rate of pyrite addition seemed justified. The experiment was then continued with pyrite added at a level of 1% based on feed slurry. The reactor was operated at 450°C with hydrogen fed at a level of 4% based on feed slurry at 2250 psig. These conditions allowed a well defined steady state to be developed and a yield structure was determined. The temperature was then increased to 465°C and a second steady state and yield structure was developed. Finally, the temperature was reduced to 450°C and the experiment was continued without addition of pyrite. Over a period of time the composition of the recycle stream changed from iron rich to iron poor and a conversion versus catalyst concentration curve was determined. As the composition of the ash in the feed slurry approached the composition of the ash in the coal, the process produced less and less oil and more and more SRC and IOM. The experiment was ended by plug formation in the reactor, suggesting inoperability with uncatalyzed coal under these conditions.

The experiment was continued for a total of 144 products, each taken for a 2.5 hour time interval, for a total of 360 hours on stream. During this time about 130 kilograms of the Belle Ayr coal were processed without plug formation due to calcium carbonate recrystallization. It is hoped that the SRC II process can be used for coals of this type without calcium carbonate deposition as is reported for the SRC I process.

II. STUDIES

Several studies of a qualitative nature were undertaken using materials from this run. In one study, the light oil products were submitted to chemical separation procedures to isolate and characterize the several kinds of functional groups which could be identified and followed by infrared spectroscopy. The separated materials were further characterized by means of simulated distillation and analyzed to determine the composition of each fraction isolated. This study is detailed in Appendix A.

In a second study, the oils produced in a selected portion of the run were composited in a proportional blend based on the yield structure. The proportional blend was then distilled into ten equal weight fractions. The water produced was also extracted to recover the dissolved organic matter present. Finally, the distillation residue was extracted in sequence with hexane, toluene and pyridine to yield the substances soluble in each of these solvents in turn. These were recovered by evaporation of the solvent and together with the pyridine insoluble fraction comprise a qualitative scan of the products in the vacuum bottoms. Taken in total, these materials comprise the organic matter made from the coal in the SRC II process except for the various gaseous products already described in good detail by the infrared and gas chromatographic analyses normally used. These materials have been characterized by means of infrared and by means of elemental analysis; certain other procedures have been used as opportunity presented itself, including functional group analysis and various physical tests. This work is described in section V-E in the body of the report.

During the operation with iron systematically declining in concentration, the yield structure changed in an orderly way from high conversion to oil to a much lower conversion. The yields of various products and characterization of the distillation residue by solvent extraction as well as other usual analytical procedures form the basis for a study relating yields and other properties to the amount of iron in the reacting system (using the fixed reactor conditions of 2250 psig and 450°C).

III. AMAX BELLE AYR COAL

The run was started using an old sample of coal and when this was used up a switch was made to a new one from the same source. Both samples were supplied by the Wilsonville Pilot Plant and were originally used in studies of the SRC I process at that location. A detailed analysis of both lots is shown in Table 2 in the body of the report. No change in run characteristics could be observed when the change from one lot to the other was made.

The coal contains about 7-8% ash and a similar amount of moisture when checked on each 5 gallon pail as fed. The dry basis oxygen content was 16-18%. The coal ranks as subbituminous B and is nonagglomerating (free swelling index 0).

The ash of this coal is almost pure white and when analyzed is found to contain only 5.06% iron as ferric oxide. The sulfur content is 0.56% of which only 0.12% is attributed to pyrite. This leaves 0.44% organic sulfur as no sulfate sulfur was found. This small amount of iron is not considered to be enough to facilitate SRC I production at normal rates or conditions (as confirmed by Wilsonville Pilot Plant studies) and is clearly insufficient to allow SRC II operation without added catalyst. We have confirmed both statements in SRC I and SRC II studies with this coal.

When coals of this kind are reacted in either the SRC I or the SRC II mode, much of the oxygen is eliminated as carbon dioxide. A corresponding tendency to make a little more carbon monoxide is also observed. The probable source of the added carbon dioxide is a carboxylic acid functional group in the coal generally present as a salt with calcium, magnesium, sodium, or potassium. These coals will exchange ions and may be converted from salts to acids by acid washing or from salt to salt by washing with solutions of the salt to be exchanged into the coal. The water/gas shift reaction attempts to equilibrate carbon dioxide, water, carbon monoxide and hydrogen in the reactor. This accounts for the tendency for carbon monoxide to increase as carbon dioxide increases.

The coal was fed wet and slurry analysis for water was done on a regular basis to account for water fed through the process and to allow calculation of water yields directly.

IV. OBSERVATIONS DURING THE EXPERIMENTS

The usual measurements by infrared and visible range spectroscopy were done. The solutions were well hydrogenated and light colored (low blackness† values) as long as pyrite addition was continued. The feed slurry was not viscous and could be operated with quite high burdens of total solids (due to coal, catalyst and insoluble material in the recycle stream). When operating at 450°C no return of cut 2 solvent* was needed to maintain workable slurry feed consistency. After raising the temperature to 465°C, the gas formation rate increased and it appeared that little or no increase in conversion to oil was produced. The slurry became thicker and return of cut 2 oil was started to maintain a readily pumpable feed slurry. The blackness of the slurry increased a bit and an appreciable drop in the hydrogen content of the liquid part of the system was indicated by the drop in IR ratio ($\overline{IR}$).**

When the temperature was reduced to 450°C and addition of pyrite discontinued, the blackness of the UFCS increased and the unfiltered coal product solution first gained hydrogen (in response to lowering the temperature) then slowly lost hydrogen (in response to the decline in iron as pyrite was slowly worked out of the system).

Because the slurry had to be maintained within workable viscosity limits by the addition of different amounts of return oil and UFCS in different parts of the experiment, the yields are influenced by these variations in feed slurry formulation. It can be argued that such changes are inherent in operation over a wide range of conditions (as far as catalyst concentration is concerned, at least) and that the qualitative results to be reported are valid within this framework.

V. OBSERVATIONS DURING THE TIME IRON WAS DECLINING

Pyrite addition was stopped just after the end of the 86th product interval. The temperature was not immediately changed and a few products were made at 465°C without adding fresh pyrite to the feed. A supply of slurry containing pyrite was still in the feed pot, however, so it is reasonable that no particular change in the operation developed promptly. The temperature was reset to 450°C and by product interval 96 the product had become well hydrogenated again ($\overline{IR}$ increased to 3.4). After that the blackness increased slowly from about 9 or 10 to about 20 while $\overline{IR}$ values dropped slowly from over 3 to the vicinity of 2.0 to 2.3. Addition of cut 2 oil was increased from 4% to 8% at product interval 130 to extend the operating time (slurry viscosity was a problem, with rupture disc failure on the pump system necessitating a reduction in slurry viscosity). An attempt to increase temperature to 465°C during product intervals 143 and 144 resulted in a plugged reactor--not in production of more oil.

---

† Calculated absorbance for a solution of 1 gm unfiltered coal solution (UFCS)/100 ml pyridine measured in a 1/2" cell at 550 nanometers.

* Material recovered between 108°C and 270°C during distillation of UFCS at 2 mm Hg.

** Absorbance at 2920 cm^{-1} divided by absorbance at 3050 cm^{-1} in the infrared spectrum of UFCS.

These qualitative observations indicated clearly that a considerable change in yield pattern was induced by gradual removal of iron from the system. It was therefore decided to work up each of the distillation samples available during this period separately and to assume that each represents a small time interval look at the chemistry as a function of the iron prevalent in the reactor at the time. The slurry ash samples were saved and were analyzed for iron. In addition, UFCS samples were saved to measure pyridine insolubles and for viscosity determinations. It is necessary to average input and output measurements over a short span (several product intervals) so the results may not have the usual precision. This is mitigated by the rather rapid changes in a number of yield parameters and by the observation that a systematic change is being observed. Thus we are in a position to relate a number of product properties and yields to the concentration of iron in the feed slurry.

Slurry ash samples were available for much of the region of declining ash concentration in the later part of the run and were coded with the time at which the slurry was sampled. The results of iron analyses were then plotted on a time scale and the time at which samples were taken for distillation was used to relate feed slurry iron concentration to the samples in question. For the early part of the run, ash samples from the pyridine insolubles were available for iron analysis and between these two kinds of samples it is possible to assign an iron concentration to any part of the experiment which is to be studied.

Iron concentrations may then be assigned to any of the distilled samples which were produced during these operations. These samples are listed together with the iron content determined for the sample of ash at that time period or from the pyridine insolubles residue ash, as the case may be.

IRON CONTENT ASSIGNED TO ASH AT PRODUCT INTERVALS FOR DISTILLED SAMPLES

Product Interval	% Iron	% Slurry Ash
6	--	7.82
21	--	16.06
31	15.18	18.08
40	14.46	17.84
49	14.02	17.92
56	13.86	17.89
Temp. to 465°C		
68	13.27	19.20
74	12.96	18.55
79	12.87	17.90
86	--	18.10
94	10.15	15.93
100	9.00	13.96
104	8.26	13.18
110	7.40	12.10
114	6.50	11.86
124	5.70	10.65
136	4.90	9.30
141	4.35	8.65
Temp. to 460°C		
144	3.60	8.48

Notes: Products 6 through 56 are initial lineout and steady state operation at 450°C.
Products 68 through 86 are from the study at 465°C.
Products 94 through 140 are from the ash decline (no pyrite addition) part of the experiment and are at 450°C. The final sample, 144, was at 460°C and the ash is near the iron content of pure coal ash from the coal in use.

The experiment was done in three sections with a careful attempt to produce a steady state yield structure at 450°C in the first section (run DOE 350RA), at 465°C in the second section (run DOE 350RB) and with a continually changing yield pattern in the third section (run DOE 350RC). All of the samples which were worked up by distillation were also represented by a UFCS sample which could be used for viscosity measurements and for isolation of pyridine insolubles. These provided the data on insoluble organic matter resulting from the process and allowed determination of the ash and iron content of the ash in particular samples.

The main results to be discussed are presented in Figures B-1 through B-4. These are somewhat different than those based on the usual averaging and correction procedures used in preparation of the results presented in the body of the report. Oil yields are presented as raw yields from various separators or operations and are redistributed in the body of the report. These results are sufficient to estimate total oil, SRC and insoluble organic matter (IOM) yields with reasonable accuracy, however.

It is helpful to select a few components of the product array and to plot these versus the concentration of iron in the feed slurry. Units and scales are somewhat arbitrary; however, the plots seem more nearly linear when the iron concentration (in grams per kilogram of feed slurry) is put on a logarithmic scale and the other argument is on a linear scale.

Plots have been made showing that total oil yield increases with increasing iron in the feed slurry and that the total organic residue (SRC + IOM) decreases with increasing iron in the feed slurry (Figure B-1). The total organic residue has been broken into SRC and IOM yields on Figure B-2. Another interesting observation is made in the comparison of yields of carbon monoxide and carbon dioxide (Figure B-3). The carbon dioxide yields are not corrected for the amount of material reacted with ammonia and found dissolved in the water phase, so the decline in yield may not be as marked when corrected. The probability is good, however, that the increase in carbon monoxide yield with increasing iron is real.

Some extraction data is now available showing how the solubility of various components of the organic residue changes as the iron in the system changes. These are expressed as the ratio of the solubility in hexane or in toluene to the solubility in pyridine in Figure B-4. The increase in solubility observed would force the conclusion that a lower average molecular weight product is made in the presence of the higher iron concentrations. This view is supported by noting the considerable range of fusion point values with the lower melting material corresponding to the higher iron concentrations (Figure B-4). These observations are consistent with a mechanism in which free radicals are rapidly formed and quenched with product characteristics determined by the balance struck between rates of formation and rates of quenching. It is necessary to break bonds and to form free radicals in order to reduce the coal from a cross linked (polymeric) condition to a distillate. In order for the material to remain at a lower molecular weight, it is of course necessary to terminate these free radicals frequently by addition of hydrogen.

FIGURE B-1

EFFECT OF IRON LEVEL IN THE SLURRY ON TOTAL OIL, SRC AND IOM YIELDS; RUN DOE 350R, BELLE AYR COAL

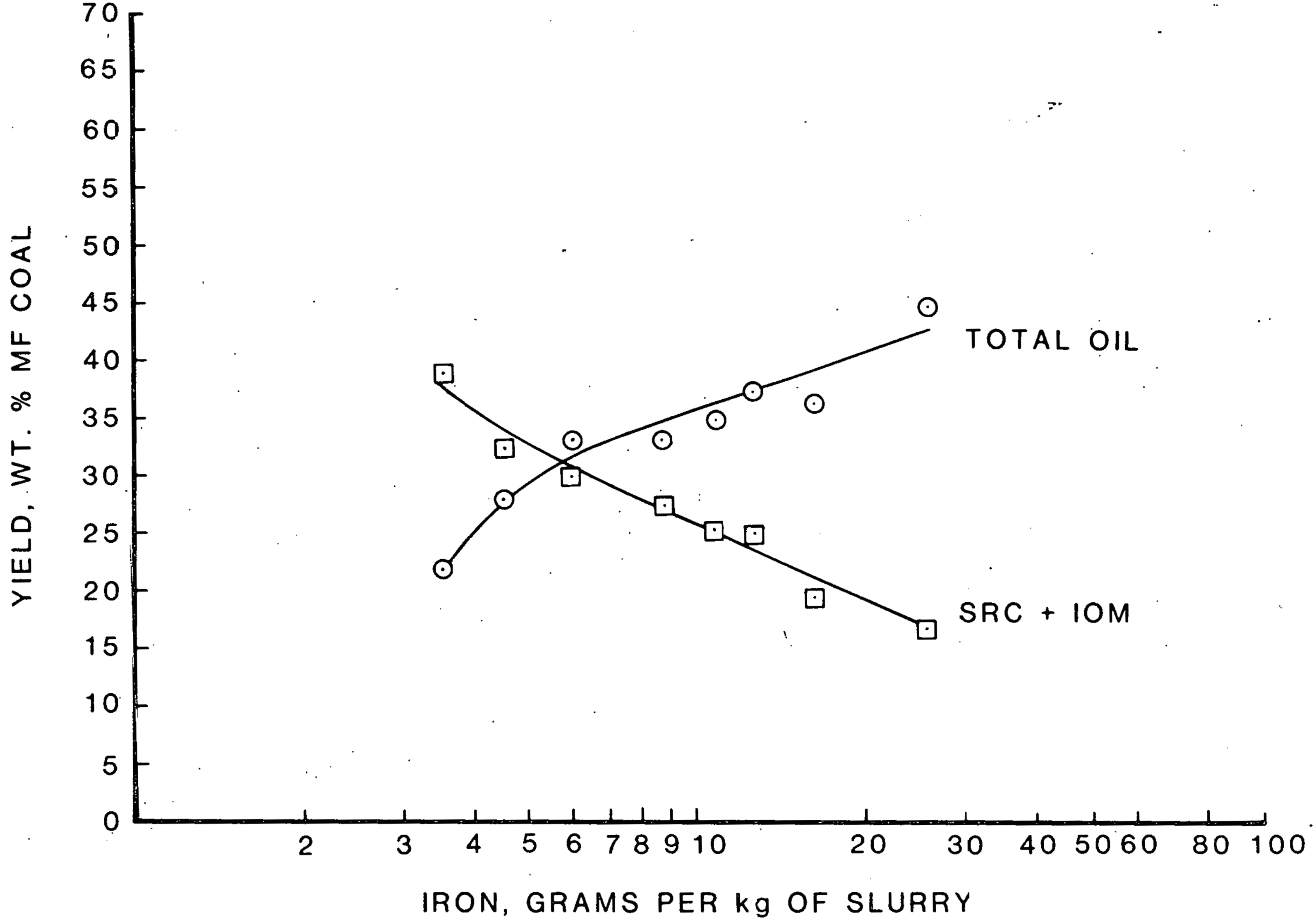


FIGURE B-2

EFFECT OF IRON LEVEL IN THE SLURRY ON SRC AND IOM YIELDS; RUN DOE 350R, BELLE AYR COAL

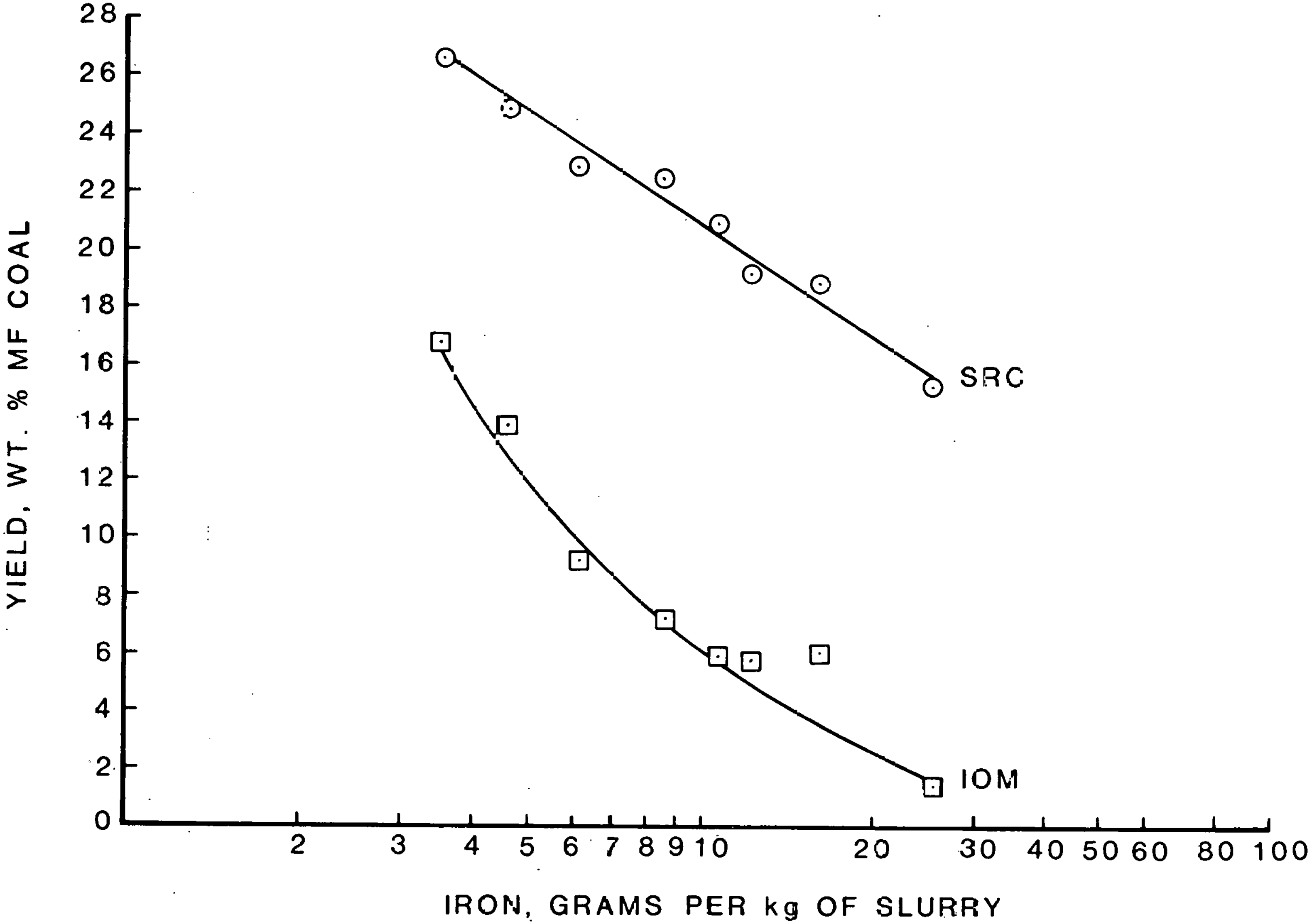


FIGURE B-3

EFFECT OF IRON LEVEL IN THE SLURRY ON CO, CO_2 AND TOTAL HYDROCARBON GAS YIELDS

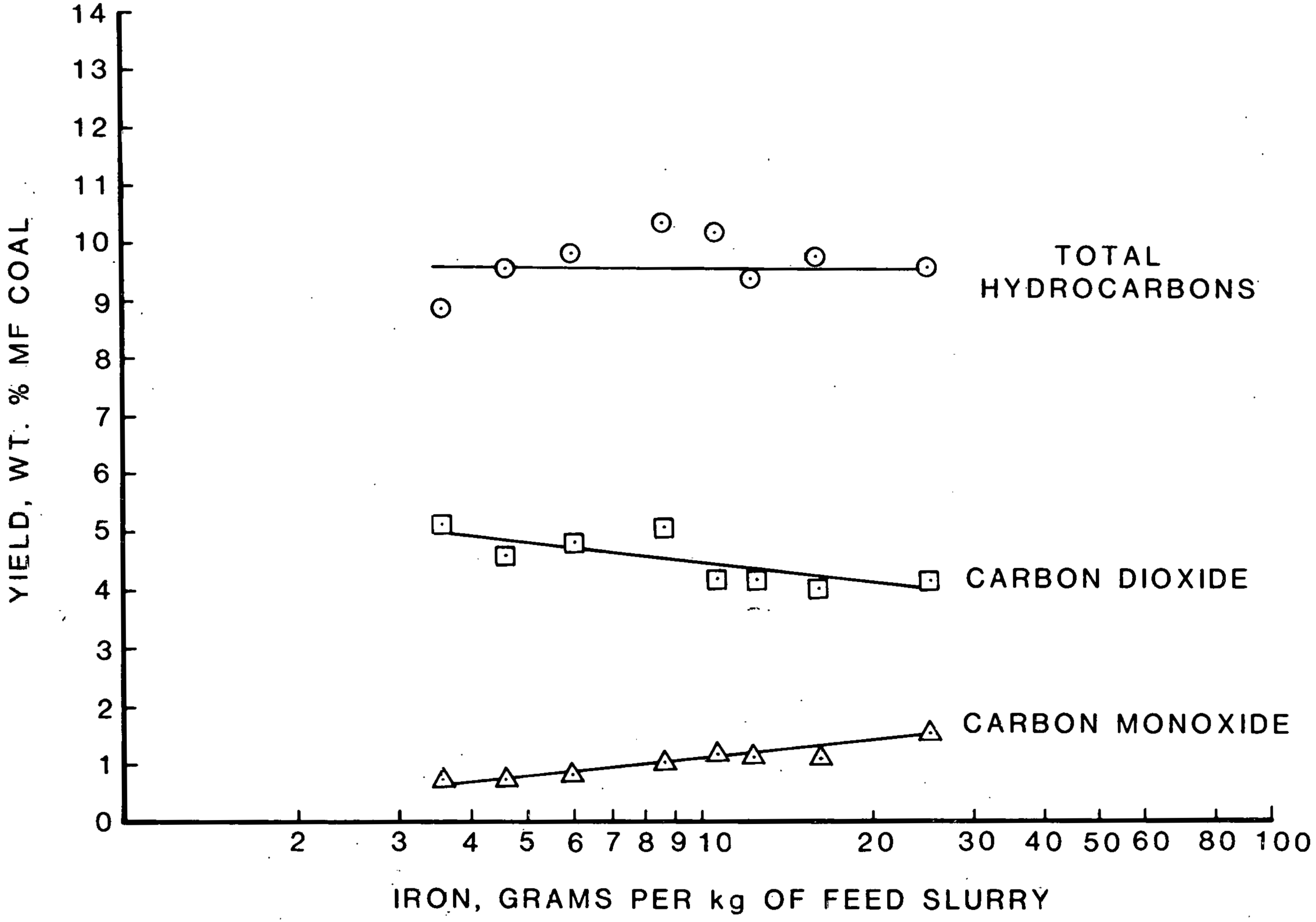
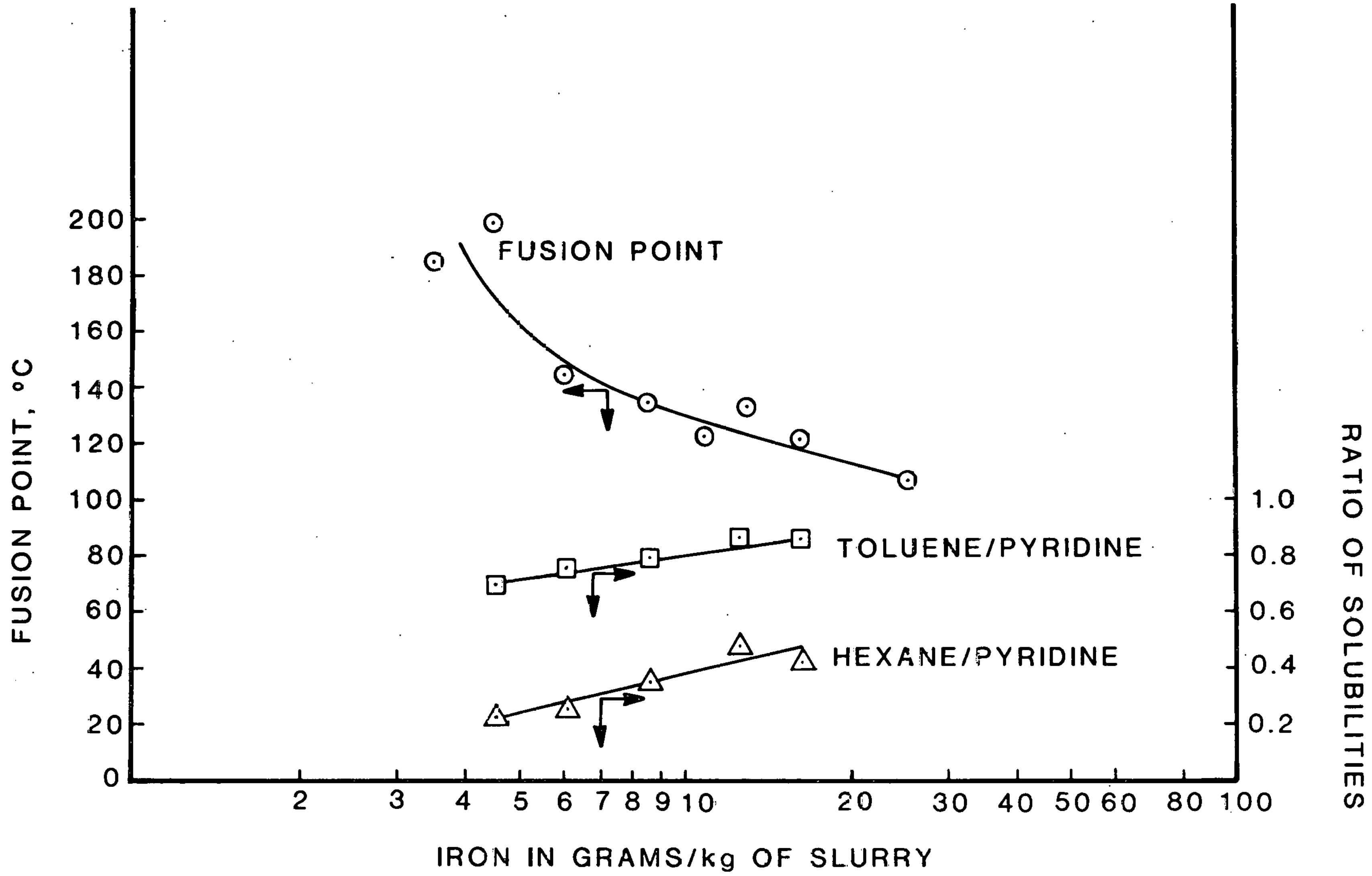


FIGURE B-4

EFFECT OF IRON LEVEL IN THE FEED SLURRY ON THE SOLUBILITY AND FUSION POINT OF THE DISTILLATION RESIDUE: RUN DOE 350R, BELLE AYR COAL



*U.S. GOVERNMENT PRINTING OFFICE: 1981-740-145/2781