DOE/PC/50001-22
(DE84010608)

Energy
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# ADVANCED COAL LIQUEFACTION RESEARCH

## Technical Progress Report for July 1—September 30, 1983

April 1984

Work Performed Under Contract No. AC22-82PC50001

Gulf Research & Development Company
Shawnee Mission, Kansas

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Distribution Category UC-90d

# ADVANCED COAL LIQUEFACTION RESEARCH

## TECHNICAL PROGRESS REPORT
## FOR THE PERIOD
## JULY 1, 1983 THROUGH SEPTEMBER 30, 1983

April 1984

GULF RESEARCH & DEVELOPMENT COMPANY
P. O. BOX 2970
SHAWNEE MISSION, KANSAS 66201

PREPARED FOR THE
U. S. DEPARTMENT OF ENERGY
DIVISION OF COAL CONVERSION AND UTILIZATION
UNDER CONTRACT DE-AC22-82PC50001

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# ABSTRACT

Work this quarter focused on staged liquefaction. The effect of residence time on conversion in single pass experiments was found to be quite different for the subbituminous Belle Ayr Mine and bituminous Illinois No. 6 coals studied. With bituminous coal, conversion to soluble material is quite high and the limit of conversion is approached in only a few minutes. With a subbituminous coal, however, conversion is much lower and the limit of conversion is approached much more slowly.

Short contact time (SCT) dissolution of Belle Ayr coal was studied as a possible first stage in a two-stage process. Conversion, hydrocarbon gas yield and hydrogen consumption were increased as residence time or temperature were increased. Conversion was also significantly increased by partial slurry recycle. Pyrite was found to be the most effective slurry catalyst for increasing conversion, followed by ammonium molybdate emulsion and finally nickel-molybdenum on alumina.

Illinois No. 6 coal was liquefied in two stages. Conditions in the first stage dissolution were varied to determine the effect on upgradability in the second stage. A SCT (6 minute) coal dissolution stage is preferred over one at 30 minutes because hydrocarbon gas yield was much lower while overall oil yields for the combined dissolution and upgrading stages were nearly the same. Use of a NiMo/$Al_2O_3$ catalyst in a trickle-bed second stage resulted in a higher oil yield and lower product heteroatom content than use of the same catalyst in the slurry phase. The total oil yield was lower with a pyrite slurry catalyst than with a NiMo/$Al_2O_3$ slurry catalyst.

With Belle Ayr coal and added pyrite, there was no change in total oil yield, conversion or product quality brought about by adding an 8-minute first stage at 450°C (842°F) to a 2-hour second stage operated at 420°C (788°F).

# 1.0 SUMMARY

Multiple-stage and short contact time coal liquefaction were studied during the third quarter of 1983.

## 1.1 Short Contact Time Coal Liquefaction

Thirteen runs were conducted with subbituminous Belle Ayr coal to study the effects of residence time, temperature, partial slurry recycle and catalysis in short contact time operation.

Increasing the residence time from 5 to 45 minutes with added pyrite increased the hydrocarbon gas yield from 1.1 to 4.6 wt % (based on MF coal) and lowered the IOM yield from 18.8 to 8.8 wt %. Total oil and SRC yields exhibited an unusually large amount of scatter and no trend was observed. Hydrogen consumption increased from 2.0 wt % at 5 minutes to 3.1 wt % at 45 minutes.

Increasing the temperature from 430 to 460°C (806 to 860°F) with added pyrite increased the hydrocarbon gas yield from 1.8 to 3.6 wt % and decreased the IOM yield from 18.7 to 8.7 wt %. Scatter was again present in the total oil and SRC yields. Hydrogen consumption increased only slightly from 2.6 to 2.9 wt %. Whereas nearly 40 minutes residence time was required to reduce IOM yield to 10 wt % without bottoms recycle, only 10 minutes was required with recycle.

Three different slurry catalysts were studied in the SCT dissolution. These catalysts were pyrite, cobalt molybdenum on alumina (HDS 1442) and ammonium molybdate emulsion.

PYRITE WAS THE MOST EFFECTIVE CATALYST FOR INCREASING CONVERSION FOLLOWED BY THE AMMONIUM MOLYBDATE EMULSION, THEN HDS 1442 CATALYST.

Corresponding IOM yields were 18.1, 22.6 and 24.6 wt %. Hydrocarbon gas yields were essentially the same with all of the slurry catalysts. Total oil yield was highest (19.5 wt %) with the HDS 1442 catalyst followed by pyrite (14.3 wt %) and the molybdenum emulsion (11.5 wt %).

## 1.2 Multiple-Stage Liquefaction

### 1.2.1 Short Contact Time versus SRC I Coal Dissolution Stages

Illinois No. 6 coal was dissolved at short (6 minutes) and conventional (30 minutes) contact times at 450°C (842°F) and 2250 psig. In both cases, the filtrate from the first stage was upgraded in a trickle-bed reactor at 410°C (770°F) and 0.25 LHSV.

THE SCT FIRST STAGE IS PREFERRED AS THE FIRST STAGE IN THE TWO-STAGE PROCESS.

The hydrocarbon gas yield was more than three times as great at 30 minutes in the coal dissolution stage than at 6 minutes (5.3 vs 1.5 wt %). Hydrogen consumption was 2.4 compared to 1.4 wt %, based on MF coal. Oil yield was 10.9 vs 5.2 wt % and IOM yield was slightly lower.

The yields in the catalytic upgrading step were quite similar with feed from either dissolution stage except for a slightly higher conversion of the short contact time SRC to oil. This was balanced by the higher oil yield in the 30-minute first stage so that the overall oil yields* were nearly the same (36.5 wt % with the 6-minute first stage vs 34.9 wt % with the 30-minute first stage).

There was no evidence for retrogressive reactions between 6 and 30 minutes in the first stage.

### 1.2.2 Comparison of Fixed-Bed and Slurry Catalysts

Illinois No. 6 coal was dissolved at short contact time conditions to prepare filtrate for use in upgrading studies with slurry catalysts. Both high quality (HDS 1443, $NiMo/Al_2O_3$) and disposable (pyrite) slurry catalysts were investigated in the second stage.

$NI/MO/AL_2O_3$ WAS LESS EFFECTIVE AS A SLURRY CATALYST THAN WHEN USED IN A FIXED BED.

The total oil yield was 30.2 compared to 41.0 wt %, based on SRC fed to the second stage. In addition, product quality was lower. The sulfur and nitrogen were 0.14 and 0.87 wt %, respectively, in the vacuum distillate, compared to 0.05 and 0.13 wt %.

The total oil yield was higher with the $NiMo/Al_2O_3$ slurry catalyst than with pyrite (30.2 vs 23.5 wt % at 415°C [779°F] and 40.2 vs 27.9 wt % at 430°C [806°F]). Increasing the reaction temperature to 430 from 415°C increased the hydrocarbon gas yield by 3.5 wt % with both catalysts. Use of the $NiMo/Al_2O_3$ catalyst resulted in a higher hydrogen consumption at both temperatures (5.9 vs 3.6 wt % at 415°C and 7.2 vs 4.5 wt % at 430°C).

### 1.2.3 Integrated SRC II Operation with Temperature Staging

Eight experiments were conducted to investigate temperature staging with subbituminous Belle Ayr coal. These runs were conducted with a high-temperature first stage and low-temperature second stage in an integrated mode without depressurization or solids separation between stages.

In a comparison with and without the first stage, the first stage (top three zones of the preheater) was operated at 450°C (842°F) while the dissolver (second stage) was at 420°C (788°F). The residence time was 8 minutes in the first stage and 2 hours in the second stage.

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* Sum of the oil yields from both stages based on MF coal fed to first stage.

THERE WAS NO APPARENT ADVANTAGE IN TEMPERATURE STAGING AS PRACTICED IN THIS STUDY.

Hydrocarbon gas yield was increased by 2 wt %, based on MF coal, with the high temperature first stage but there was little change in total oil yield, conversion or product quality.

Hydrocarbon gas yield increased to 10.2 from 8.7 wt %, based on MF coal, as residence time in the first stage was increased to 9.4 from 6.0 minutes. There was a corresponding increase in second stage residence time to 2.4 from 1.5 hours. There was little effect on oil yield, conversion or product quality, however.

Hydrocarbon gas yield was reduced to 6.8 from 10.2 wt %, based on MF coal, by decreasing the second stage (dissolver) temperature to 400°C (752°F) from 420°C (788°F). This was accompanied by slight reductions in oil yield and conversion. As a result, the ratio of distillate to hydrocarbon gas increased to 6.6 from 4.4. The distillate sulfur level was increased by a small amount.

There was no evidence that the addition of titanium tetraphenoxide, which has been reported to be a cracking catalyst, improved the yield structure at the conditions in this study.

# 2.0 INTRODUCTION

## 2.1 Contract Objectives

The work reported herein was conducted at the Merriam Laboratory under a contract* between Gulf Research & Development Company and the DOE which commenced August 1, 1982.

The Merriam Laboratory is conducting a bench scale research investigation on advanced coal liquefaction. The objectives of the project are to:

- investigate and optimize potential technology improvements of possible economic benefit,
- improve understanding of the chemistry and mechanisms,
- better define the role of coal characteristics upon performance,
- investigate short contact time coal liquefaction,
- investigate the effects of slurry phase and disposable catalysts,
- investigate the effects of solvent characteristics and components,
- investigate the product characteristics with respect to integrated process development and end use needs.

## 2.2 Currently Reported Experiments

Work was conducted on two experimental tasks this quarter. Studies on short contact time coal liquefaction are discussed in section 3. Work on multiple-stage liquefaction is described in section 4. Two experiments included in section 4, DOE 504RF and G, involve addition of titanium and could also be considered as catalyst studies (contract task 1c2).

Progress during the third quarter of 1983 on the epidemiology research program is summarized in section 5.

Information on characterization of distillate products (particularly by liquid chromatography) is given in Appendix A. Characterization of distillation residue products based on solubility in pyridine/hexane mixtures is presented in Appendix B.

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* Contract No. DE-AC22-82PC50001.

## 2.3 Future Work

Five additional runs with Belle Ayr coal, which complete the short contact time series begun this quarter, will be described in the fourth quarter 1983 report. These are: a baseline run without added catalyst, a repeat of run DOE 500A and experiments using elemental sulfur and carbon disulfide as hydrogen sulfide progenitors. Additional work on staged processing will also be discussed in the fourth quarter report. A comparison will be made between upflow and downflow reactors for filtrate upgrading with a fixed bed of spherical, nickel-tungsten catalyst.

# 3.0 SHORT CONTACT TIME COAL LIQUEFACTION

Runs DOE 499-503

## 3.1 Objectives

The effects of residence time, temperature, slurry catalyst, and partial slurry recycle on the short contact time (SCT) dissolution of Amax Belle Ayr coal were investigated. Of particular interest was the effect of these variables on conversion and solubility of the nondistillable part of the high temperature, high pressure separator bottoms. This work fell under contract tasks 1-C-1 and 1-C-2, "Short Contact Time Coal Liquefaction Research" - "Process Variables Study" and "Disposable Catalysts", respectively.

## 3.2 Background

Preliminary SCT work with Belle Ayr coal using pyrite, pyrrhotite (processed pyrite), and previously hydrotreated solvent was presented in the third quarter 1981 progress report*. The effect of solvent quality and pyrite addition were discussed in the first quarter 1983 report**. Significant findings are that:

1. Pyrite addition is beneficial with both SRC I and Lummus solvents, resulting in increased conversion (reduced insoluble organic matter [IOM] yield).
2. Oil yield is higher with SRC I solvent than with Lummus solvent. Oil yield is increased by pyrite addition with SRC I solvent, but there is no effect on oil yield with Lummus solvent.
3. Increasing pyrite addition level is beneficial over a certain range.
4. Total conversion to pyridine soluble material is quite similar with SRC II, filtered Lummus or SRC I solvents.
5. Yields are improved with SRC I solvent when the solvent has been previously hydrotreated.

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* "Research on Solvent Refined Coal," Quarterly Technical Progress Report for the Period July 1, 1981 through September 30, 1981; July 1982, PC40005-9.

** "Advanced Coal Liquefaction Research," Quarterly Technical Progress Report for the Period January 1, 1983 through March 31, 1983; December 1983, PC50001-15.

## 3.3 Experimental

### 3.3.1 Run Conditions

Residence times of 5, 10, 15, 30 and 45 minutes were investigated in runs DOE 499A, B, and C, and 500A and B. Temperatures of 430, 440, 450, and 460°C (806, 824, 842 and 860°F) were run in DOE 500A, C, D, and F. A short supply of solvent forced us to use reclaimed* solvent in runs DOE 500E, F, and G. The effect of reducing the pyrite level to 1 wt % from 2 wt % was determined when comparing run DOE 500G to DOE 500A. Other run conditions are shown in Table I.

### 3.3.2 Coal

The coal was from the Amax Belle Ayr Mine in Campbell County, Wyoming, (Wyodak-Anderson seam) and ranks as subbituminous. It is a run-of-mine sample, ground by Empire Coke and sieved through a 150 mesh screen at Merriam before use. Runs DOE 499 through DOE 500E used a lot received in 3/82, while DOE 500F through DOE 503 used a coal received in 2/83 (lot RM 1030). These lots are believed to be of similar reactivity.

The compositional analyses for both lots are shown in Table IIIa and the petrographic analysis of the second lot is shown in Table IIIc.

### 3.3.3 Additive

The pyrite used in runs DOE 499 through 501R was obtained from C-E Minerals (a division of Combustion Engineering) and was mined at Washington, Georgia, as a discrete mineral. The catalyst was finely ground in nitrogen by the Jet Pulverizer Co., Palmyra, New Jersey. A particle size distribution is shown in Figure 1. Other available analyses are shown in Table IV.

Cyanamid HDS 1442 (cobalt-molybdenum on alumina), developed for the H-Coal process, was used in run DOE 502. It was supplied as nominal 1/16" cylindrical extrudates and was ground by hand to pass 150 mesh before use. Measurements performed by Coors Spectro-Chemical Laboratory of Golden, Colorado, before and after grinding showed no appreciable loss of surface area. Available analyses are shown in Table IV.

An aqueous emulsion of ammonium molybdate was used in run DOE 503. This was prepared at Merriam by dissolving $(NH_4)_6Mo_7O_{24}.4H_2O$ (Mallinckrodt analytical reagent grade) in water. The solution was added to oil boiling >250°C (482°F) and blended in a Ross emulsifier for five (5) minutes. The emulsion was reasonably stable and was added to the mix pot as another component of the feed slurry.

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* Reclaimed from run DOE 499 and earlier parts of run DOE 500.

### 3.3.4 Solvent

The solvent used in runs DOE 499A through DOE 500D was from the Fort Lewis pilot plant. Due to the short supply, it was reclaimed by distillation for use in runs DOE 500E, F, G, 502, and 503. The solvent was recycled in run DOE 501R. Available analyses are presented in Table V.

## 3.4 Results

The yields and product analyses are shown in Table II and the solvent extraction data in Table VI. Detailed solubility analyses of the residue products are given in Appendix B.

### 3.4.1 Operability

Run DOE 499 was uneventful except for pyrite plugging at the end of part C. Apparently the low feed rate allowed the suspended pyrite to settle out.

Difficulty with calcium carbonate plugs was experienced during parts F and G of run DOE 500. This was probably a result of extended run time in the single pass mode - not variables being studied in those parts of the run. While no major operability problem was observed in runs DOE 500A or B, the reported water yields are unrealistically low. This is believed to be due to the short material balance period and fluctuations in the product stream containing the bulk of the water.

No problems with calcium carbonate plugs were encountered when in the recycle mode of operation during run DOE 501R.

Problems with calcium carbonate plugs were again experienced during runs DOE 502 and 503.

### 3.4.2 Effect of Residence Time on SCT Processing of Belle Ayr Coal

The effect that residence times from five (5) to forty-five (45) minutes had on yields is shown in Figure 2 and in Table VII.

#### 3.4.2.1 Yields

Increasing the residence time increased the hydrocarbon gas yield from 1.1 wt % (based on MF coal) at 5 minutes to 4.6 wt % at 45 minutes. Due to a large amount of scatter in the data, the effect of residence time on the total oil yield can not be determined. The scatter is probably due in part to the unrealistically low water yields in runs DOE 500A and B which affect the yields of the hydrocarbons. The variation in oil yield was over a fairly small range (19-24 wt %). With the exception of the run at 10 minutes residence time, the SRC yield was fairly constant (varying from 43 to 46 wt %) over the residence times studied. The IOM yield decreased with increasing residence time from 18.8 wt % at 5 minutes to 8.8 wt % at 45 minutes. Hydrogen consumption increased from 2.0 wt % at 5 minutes to 3.1 wt % at 45 minutes.

#### 3.4.2.2 Product Quality

The elemental analyses of the vacuum distillates generally showed only a slight decrease in sulfur level with increasing residence time. Analysis of the distillation residue indicates that the sulfur level decreased with increasing residence time while the nitrogen level increased.

Solubility data (Table XII) indicate that the maltene and preasphaltene levels have apparent minimums and maximums, respectively, near 15 minutes residence time.

### 3.4.3 Effect of Temperature and Solvent

The effects of temperature on SCT processing of Belle Ayr coal are shown in Figure 3 and Table VIII.

#### 3.4.3.1 Yields

The yield of hydrocarbon gases increased with increasing temperature from 1.7 wt % at 430°C to 3.6 wt % at 460°C. Total oil yield increased with increasing temperature: 15.7 wt % at 430°C to 20.3 wt % at 460°C. SRC yield increased from 46.9 wt % at 430°C to 49.2 wt % at 460°C. Scatter was observed in both the total oil and SRC yields which was due to a low water yield in run DOE 500A. The IOM yield showed a steady decrease with increasing temperature: from 16-19 wt % (depending on solvent) at 430°C to 8.7 wt % at 460°C.

The effect of using reclaimed rather than fresh solvent can be seen when comparing run DOE 500E to 500D. No effect is apparent on either the hydrocarbon gas yield or hydrogen consumed. Using reclaimed solvent lowered the total oil and SRC yields approximately 2 wt %. The IOM yield increased by 2.7 wt %.

#### 3.4.3.2 Product Quality

Analysis of the vacuum distillate and distillation residue indicates no noticeable pattern or effect due to the reaction temperature (Table II). The effect of temperature is confounded by the use of two different process solvents.

### 3.4.4 Effect of Partial Slurry Recycle

#### 3.4.4.1 Yields

Table IX shows the effect of partially recycling the high temperature separator bottoms (HTSB) and solvent. In run DOE 501R equal amounts of HTSB and distillate solvent were recycled as the liquid and solid components of feed slurry. This had the desired effect in that the IOM yield was reduced to 10.4 wt % with only a 10 minute residence time at 440°C (824°F).

#### 3.4.4.2 Product Quality

When partial slurry recycle was used, a decrease in the levels of carbon and nitrogen was observed in the vacuum distillate while the hydrogen and oxygen levels increased (Table II).

### 3.4.5 Effect of Slurry Catalysts

#### 3.4.5.1 Yields

The effects of slurry catalysts are compared in Table X. Run DOE 502 used cobalt molybdenum on alumina (HDS 1442), run DOE 503 used an ammonium molybdate emulsion, and pyrite was used in run DOE 500G.

Pyrite was significantly more effective in increasing conversion (decreasing IOM yield) than the other catalysts. This is in contrast to other comparisons in which the other catalysts are more effective than pyrite in effecting hydrogenation levels (or in increasing distillate yields in the SRC II process). This suggests that pyrite plays some role in promoting the dissolution of Belle Ayr coal other than that of a hydrogenation catalyst.

Hydrocarbon gas yield was lowest (2.1 wt %, based on MF coal) when using pyrite. When using HDS 1442 or ammonium molybdate emulsion, gas yield was about 0.5 wt % higher. No difference was apparent between the molybdenum catalysts.

When using HDS 1442, total oil yield was highest (19.5 wt %), followed by pyrite (14.3 wt %), with the emulsion giving the lowest yield (11.5 wt %).

HDS 1442 catalyst gave the lowest SRC yield (33.4 wt %). Pyrite and ammonium molybdate emulsion gave higher SRC yields, 47.6 and 46.5 wt % respectively.

The hydrogen consumption was highest when using HDS 1442, 3.2 wt % compared to 2.6 wt % when using ammonium molybdate and 2.2 wt % with pyrite.

#### 3.4.5.2 Product Quality

Using pyrite as the baseline case, ground HDS 1442 catalyst increased the levels of hydrogen in both the vacuum distillate and distillation residue (Table II). Sulfur level decreased in the vacuum distillate and distillation residue. Nitrogen levels in the vacuum distillate were about the same and decreased in the distillation residue. The fusion point decreased by about 25°C. The maltene and asphaltene levels increased while the preasphaltene level decreased.

Ammonium molybdate emulsion, compared to pyrite, decreased levels of hydrogen and sulfur in the vacuum distillate while the nitrogen level was unchanged. A slight decrease in the hydrogen, sulfur and nitrogen levels was noted in the distillation residue. The fusion point decreased slightly (about 10°C). The maltene level increased slightly while the asphaltene and preasphaltene levels were unchanged.

### 3.4.6 Effect of Pyrite Addition Level

#### 3.4.6.1 Yields

Table XI compares the effect of pyrite addition levels of 1 wt % (DOE 500G) and 2 wt % (DOE 500A), slurry basis. Although the comparison is confounded by a change in solvent, the trend is in the expected direction. When increasing the pyrite level, distillate yields increased while the IOM yield decreased.

#### 3.4.6.2 Product Quality

Analysis of the vacuum distillate showed that increasing the pyrite level decreased the hydrogen content while increasing the sulfur and nitrogen levels. However, the yield of heavy distillate (which is similar in boiling range to vacuum distillate) was 22.5 wt % in DOE 500A (2 wt % pyrite) and 1.2 wt % in DOE 500G (1 wt % pyrite). The levels of sulfur, nitrogen and carbon in the distillation residue increased when increasing the pyrite level. The hydrogen level and fusion point decreased with increasing pyrite level.

## 3.5 Conclusions

Increasing the residence time over the range of 5-45 minutes with Belle Ayr coal results in more conversion (lower IOM yield) but this also increases the hydrocarbon gas yield.

An increase in conversion can be obtained by increasing the reaction temperature. This increase will also produce more total oil and hydrocarbon gas.

Partial slurry recycle increases the conversion of Belle Ayr coal (decreased IOM yield) with a slight decrease in total oil yield. Light hydrocarbon gases appear to increase but the difference is within experimental error. Recycle also appears to eliminate calcium carbonate deposition.

Pyrite appears to be more effective in increasing conversion than either cobalt-molybdenum on alumina (HDS 1442) or an aqueous emulsion of ammonium molybdate. However, there was more than four (4) times as much pyrite added compared to molybdenum. Hydrocarbon gases were only slightly affected by the different catalysts. The HDS 1442 catalyst gave the largest total oil yield, followed by pyrite and then the emulsion.

Conversion can also be increased by increasing the amount of pyrite fed. An increase in pyrite level from 1 to 2 wt % increased the conversion and total oil yield. Light hydrocarbon gas yield was essentially the same (within experimental error). This increase in conversion was at the expense of a higher hydrogen consumption.

# 4.0 MULTIPLE-STAGE LIQUEFACTION

## 4.1 Objectives

Three series of experiments were conducted to explore the concept of enhancing coal liquefaction by optimizing conditions for each of several stages. The work this quarter involved two-stage processing.

The objective in the first series was to determine the effect of conditions in a first stage coal dissolution on upgradability in the second stage. In the second series, slurry catalysts were compared to those in a fixed bed for upgrading. In the final block of work, the staged temperature approach was utilized, but an integrated system was employed without depressurization and solids separation between stages.

These experiments are all part of contract task 1-B-6: "Coal Liquefaction Variable Research; Multiple Stage Reactors."

## 4.2 Background

Staged liquefaction was first studied in depth at Merriam during the second quarter of 1983. The possible advantages of such an approach were discussed in the report covering that time period*. The work during the second quarter consisted of two series of 3-stage liquefaction runs. In these two series, Illinois No. 6 coal was dissolved at 450°C (842°F), 2250 psig and 6 minutes residence time in the first stage of a 3-stage process.

Stripped filtrate from the first stage coal dissolution was hydrogenated in a trickle bed of $NiMo/Al_2O_3$ catalyst at 2250 psig and a liquid hourly space velocity of 0.25. Total oil yield increased to 41 from 16 wt % as temperature was increased from 356 (673) to 412°C (774°F). Hydrocarbon gas yield rose to 4.4 from 0.6 wt %, based on SRC fed. The hydrogen level in the products went through a maximum, however, peaking in the range of 380-400°C (716-752°F). This level varied from 8.0 to 9.3 wt % in the high temperature, high pressure separator bottoms compared to 6.5 wt % in the feed.

Hydrogenated filtrate from the second stage was thermally hydrocracked at 10 minutes residence time and 2250 psig. Increasing the hydrocracking temperature to 475°C (887°F) from 460°C (860°F) increased oil yield by only 2 wt %, to 13.5 wt %, based on SRC fed, while doubling hydrocarbon gas yield to 3.5 wt %. Adding pyrite at 460°C increased oil yield by 4 wt % while hydrocarbon gas was unaffected. The distillation residue was dehydrogenated during the hydrocracking step, dropping from 7.4 wt % hydrogen in the nondistillable part of the feed to 6.7-7.0 wt % depending on operating temperature and whether pyrite was added. The hexane solubility was also significantly decreased.

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* "Advanced Coal Liquefaction Research," Quarterly Technical Progress Report for the Period April 1, 1983 through June 30, 1983; December 1983, PC50001-18.

## 4.3 Short Contact Time versus SRC I Coal Dissolution Stages (Runs DOE 493 through 495D)

### 4.3.1 Experimental

#### 4.3.1.1 Run Conditions

Conditions for all runs are summarized in Table I.

#### 4.3.1.1.1 Coal Dissolution (Runs DOE 493 and 494)

Run DOE 493 was conducted at the same conditions used for the short contact time coal dissolution steps in the two previous staged liquefaction series. Run DOE 494 was also made at those nominal conditions except that the slurry residence time was increased to 30 from 6 minutes*. The latter residence time is typical of SRC I (solid product) operations. Both runs were single pass (no recycle of solvent).

In each case, about 60 kg of filtered high temperature, high pressure separator bottoms was prepared. The filtrates were stripped to 175°C (347°F) under vacuum to obtain about 50 wt % nondistillable (at 270°C [518°F] and 2 mmHg) material in the product.

#### 4.3.1.1.2 Filtrate Upgrading (Run DOE 495)

The stripped filtrates from the coal dissolution runs were hydrotreated at 415°C (779°F, nominal), 2250 psig and a liquid hourly space velocity of 0.5, based on total feed (0.25 based on fresh feed). This temperature was somewhat higher than used in the catalytic step (second stage) of the previous series because there were only two stages instead of three. The feed was comprised of 50 wt % fresh stripped filtrate and 50 wt % recycled high temperature separator bottoms (HTSB).

Due to relatively low oil yields in the hydrotreater, the HTSB products from the first two parts of run DOE 495 were passed through the reactor again at the same conditions to determine the amount of additional distillate that could be obtained. Again, the feed was 50 wt % fresh material with the balance made up of recycle HTSB.

#### 4.3.1.2 Coal

The coal used in runs DOE 493 and 494 was from the Consolidation Coal Company's Burning Star No. 2 Mine (Illinois No. 6 seam) in DuQuoin, Perry County, Illinois, and is ranked as high volatile-C bituminous. The coal was cleaned at the conventional mine-site preparation plant. Coal used in these runs was from a 33 drum lot received in March 1983. It was ground by Empire Coke Co. and sieved through a 150 mesh screen at Merriam before use.

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* The hydrogen feed rate was also increased to 2 from 1 wt %, based on slurry, because the conversion was expected to be higher.

The compositional analysis of the coal is shown in Table IIIa and the petrographic analysis in Table IIIb.

#### 4.3.1.3 Solvent

The solvent used in runs DOE 493 and 494 was from a 23 drum shipment received from the Fort Lewis Pilot Plant (Lot 2335). It was a fuel oil blend which contained 53.3 wt % oil boiling below 250°C (482°F) as received. It was stripped to 250°C at GR&DC, Harmarville, before use. Available analyses are shown in Table V.

#### 4.3.1.4 Catalyst System

The Shell 324 catalyst used in the trickle-bed hydrotreater was provided by C-E Lummus as modified* for their use. The catalyst contained 2.7 wt % Ni (as Ni) and 13.2 wt % Mo (as Mo) on alumina. The surface area of fresh catalyst was 150 $m^2$/g and the pore volume 0.48 $cm^3$/g.

The bed was comprised of three different materials since the catalyst was in short supply. About 75 vol % of the bed was catalyst from run DOE 490 which had been washed with toluene, then acetone, and air dried. About 18 vol % of the bed was catalyst from run DOE 486. This material had been washed with toluene, then acetone, and fired at 550°C (1022°F) to remove visible carbon. The remainder of the bed was filled with glass beads. The volume of the catalyst bed excluding glass beads was 1819 $cm^3$ (upon which the liquid hourly space velocity was based).

Since most of the catalyst was already in the sulfide form, it was felt that the sulfur in the startup oil would be sufficient to sulfide the rest. The temperature in the bed was brought up slowly to allow adequate time for sulfiding to occur.

### 4.3.2 Results

The yields and product analyses for all runs are shown in Table II and the solubilities of the distillation residues in hexane, toluene and pyridine in Table VI. Liquid chromatography analyses of the distillate products are presented in Appendix A and characterization of the residues by detailed solubility analysis in Appendix B.

#### 4.3.2.1 Operability

##### 4.3.2.1.1 Coal Dissolution (Runs DOE 493 and 494)

Although no difficulties were reported during run DOE 493, coal particles apparently settled out of the feed slurry in run DOE 494, blocking the charge pump check valves. Since the formulations and pump rates were the same for both runs, the difference in behavior is not understood. It may be that the slurry was inadvertently heated during run DOE 494.

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* The catalyst is treated to reduce the cracking function and is supplied as 1/32 inch extrudates rather than 1/16 inch as normally produced.

#### 4.3.2.1.2 Filtrate Upgrading (Run DOE 495)

Part A of the run was uneventful, but pumping problems developed when part B was started. This was apparently because of an increase in feed viscosity* which could not be immediately accommodated for by an increase in slurry temperature.

There were salt deposits in the product separation system during the last three parts of the run which were cleared by water injection. Plugging of the slurry letdown valves was also a problem throughout most of the experiment and led to a shutdown of the last part.

### 4.3.2.2 Comparison of Short Contact Time and SRC I Coal Dissolution Stages in Two-Stage Processing

#### 4.3.2.2.1 Yields

The yields are compared below for the coal dissolution stage, the filtrate upgrading stage and for the combined first and second stages:

| Conditions† | DOE 493/495A | DOE 494/495B |
|---|---|---|
| Residence Time in First Stage, min | 6.0 | 31.5 |
| Yields, wt % | | |
| 1st Stage (based on coal) | | |
| $C_1$-$C_4$ | 1.5 | 5.3 |
| Total Oil | 5.2 | 10.9 |
| SRC | 72.4 | 62.1 |
| IOM | 6.7 | 5.3 |
| $H_2$ Consumed | 1.4 | 2.4 |
| 2nd Stage (based on SRC) | | |
| $C_1$-$C_4$ | 4.1 | 4.1 |
| Total Oil | 41.0 | 36.4 |
| SRC | 52.5 | 57.4 |
| $H_2$ Consumed | 7.9 | 7.6 |
| Combined (based on coal) | | |
| $C_1$-$C_4$ | 4.6 | 8.0 |
| Total Oil | 36.5 | 34.9 |
| SRC | 36.2 | 34.0 |
| IOM | 6.7 | 5.3 |
| $H_2$ Consumed | 7.4 | 7.4 |

† Both first stages at 450°-451°C (842-844°F) and 2250 psig with 36 wt % Illinois No. 6 coal in the slurry and 1 or 2 wt % hydrogen, based on slurry. Both second stages at 410-411°C (770-772°F), 2250 psig and 0.5 LHSV with 50 wt % stripped filtrate from first stage and 50 wt % recycle HTSB in the feed.

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* Part A was started with a mixture of solvent and stripped filtrate. The solvent was replaced by recycled high temperature separator bottoms as the run progressed. Part B was unintentionally started with feed consisting entirely of stripped filtrate, which was much higher in viscosity.

The hydrocarbon gas yield in the first stage was more than three times as great at the longer residence time while hydrogen consumption was increased to 2.4 from 1.4 wt %, based on MF coal. Oil yield was increased to 10.9 from 5.2 wt % and IOM yield was slightly lower after 32 minutes.

The yields in the upgrading step were quite similar in both series. Although the conversion of SRC to oil was somewhat higher with the SCT filtrate, this does not necessarily mean that the SRC made at 6 minutes residence time was more reactive. The most reactive part of the SRC may have already been converted to oil in the first stage at 32 minutes residence time.

The overall oil yields from the combined stages were nearly the same, in fact. The difference in hydrocarbon gas yields in the first stages is still apparent in the overall yields as is the difference in conversion.

It must be kept in mind that the yields shown are for single-pass* runs and do not represent the results that would be obtained in a recycle operation. In particular, hydrogen consumption would be considerably lower if the well-hydrogenated solvent range material were recycled. It is felt that the trends determined in this work are valid, however.

#### 4.3.2.2.2 Product Quality

The distillate products from the SCT and SRC I coal dissolution stages were not much different (Table II). The products from the SRC I operation tended to be lighter (lower boiling) and slightly more hydrogenated. There were no clear trends in heteroatom content. The residue from the 30-minute dissolution was lower in molecular weight and/or functional group concentration, having a lower fusion point and lower preasphaltene** level (Table VI).

The distillate products from the filtrate upgrading stages were also quite similar. There appeared to be a trend towards lower nitrogen levels and higher sulfur levels in the SCT product, but the absolute values were small (generally less than 0.1 wt %)***.

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* Solvent was not recycled back to the first stage.

** Toluene insoluble/pyridine soluble.

*** See also Appendix A.

The residues from the second stage are compared below:

| | DOE 493/495A | DOE 494/495B |
|---|---|---|
| Residence Time in First Stage, min. | 6.0 | 31.5 |
| **Distillation Residue Analyses** | | |
| Composition, wt % | | |
| H | 7.12 | 6.93 |
| S | 0.20 | 0.05 |
| N | 1.05 | 1.11 |
| Maltene† | 64 | 54 |
| Asphaltene†† | 24 | 40 |
| Preasphaltene | 12 | 6 |
| Fusion Point, °C | 72 | 69 |

† Nondistillable/hexane soluble.
†† Hexane insoluble/toluene soluble.

The differences in elemental analyses are small. The residue from upgrading of SCT filtrate was higher in maltene and preasphaltene and lower in asphaltene.

### 4.3.2.3 Comparison of Two-Stage and Three-Stage Processing

The overall yields from processing with two or three stages are compared below:

| | DOE 493/495A | DOE 488/490E/491A** |
|---|---|---|
| **Conditions*** | | |
| Number of Processing Steps | 2 | 3 |
| **Yields, wt % MF Coal** | | |
| $C_1$-$C_4$ | 4.6 | 4.8 |
| Total Oil | 36.5 | 39.9 |
| SRC | 36.2 | 33.6 |
| IOM | 6.7 | 6.8 |
| $H_2$ Consumed | 7.4 | 8.5 |

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| * Run Conditions | DOE 488 & 493 | DOE 490E | DOE 491A | DOE 495A |
|---|---|---|---|---|
| Temperature, °C | 450 | 403 | 459 | 411 |
| °F | (842) | (757) | (858) | (772) |
| Pressure, psig | <------------------2250-----------------> | | | |
| Residence Time, min. | 6 | -- | 10 | -- |
| LHSV, $hr^{-1}$ | -- | 0.5 | -- | 0.5 |

** "Advanced Coal Liquefaction Research," Quarterly Technical Progress Report for the Period April 1, 1983 through June 30, 1983; December 1983, PC50001-18.

There was little difference in yields except for a slightly higher oil yield and hydrogen consumption and slightly lower SRC yield in the 3-stage sequence. Since the increase in oil yield was small and there was also an increase in hydrogen consumption, there seems to be little advantage in going to three stages.

#### 4.3.2.4 Reprocessing of Hydrotreated Filtrate

##### 4.3.2.4.1 Yields

The high temperature separator bottoms products from runs DOE 495A and B were passed through the reactor again at the same conditions in runs DOE 495D and C, respectively:

| | DOE 495D | DOE 495C |
|---|---|---|
| Residence Time in Coal Dissolution Stage, min. | 6.0 | 31.5 |
| Yields, wt % SRC Fed | | |
| $C_1$-$C_4$ | 4.7 | 4.9 |
| Total Oil | 26.5 | 20.4 |
| SRC | 70.9 | 74.2 |
| $H_2$ Consumed | 3.8 | 4.5 |

Somewhat more oil was produced from the short contact time SRC as was the case during the first pass through the hydrotreater. Hydrocarbon gas yields and hydrogen consumption were not very different. In both cases, the yield of oil was less than in the first pass through the hydrotreater (20-27 vs 36-41 wt %).

##### 4.3.2.4.2 Product Quality

The distillate products from the reprocessing were essentially the same as those from the first pass through the hydrotreater except for slightly lower hydrogen levels in the naphthas and middle distillates.

The nitrogen levels in the residues were further* reduced by the additional processing as were the fusion points and preasphaltene levels.

### 4.3.3 Conclusions

There was no evidence that retrogressive reactions (producing a more refractory SRC) took place between 6 and 32 minutes residence time in the coal dissolution stage.

Short contact time coal dissolution is preferred as the first stage of a two-stage process because of the much lower hydrocarbon gas yield and the small difference in other overall results.

There is little advantage to thermal hydrocracking in a separate stage subsequent to hydrogenation of filtrate for producing high distillate yields.

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* From what they were in the first hydrotreating step.

## 4.4 Comparison of Fixed Bed and Slurry Catalysts (DOE 496-498)

### 4.4.1 Experimental

Illinois No. 6 coal was dissolved at short contact time (SCT) conditions to prepare filtrate for upgrading studies (run DOE 496). Previously, a high grade, fixed bed, commercial catalyst was used in the second stage to establish what could be accomplished when using a high concentration of quality catalyst. In the current work, the fixed bed has been replaced with slurry phase catalysts, both commercial grade (run DOE 497) and disposable pyrite (run DOE 498).

### 4.4.1.1 Run Conditions

All run conditions are summarized in Table I.

### 4.4.1.1.1 Filtrate Preparation

Run DOE 496 (filtrate preparation) was conducted at 450°C (842°F) and 2250 psig at a nominal residence time of six (6) minutes. The run conditions were chosen to match those used in previous short contact time filtrate preparations. The feed solvent was a heavy oil supplied by the Fort Lewis pilot plant. The formulation for the filtrate preparation was 36 wt % Illinois No. 6 conventionally cleaned coal, 63.9 wt % solvent, and 0.1 wt % sodium carbonate (added to prevent possible ammonium chloride deposits in later upgrading).

The high temperature separator bottoms (HTSB) product was filtered, then stripped to 175°C at 2 mmHg. The residue from the stripping process was supposed to be a solution of 1:1 distillate to SRC. Actually, the residue was over stripped so solvent stripped to 250°C (atmospheric) was added back during the slurry formulation process.

### 4.4.1.1.2 Upgrading Filtrate with HDS 1443 Slurry Catalyst

Initial conditions for filtrate upgrading using HDS 1443 as a slurry catalyst (run DOE 497) were 400°C (752°F), 2250 psig, 2 hours residence time, 5 wt % catalyst, and 1 wt % hydrogen, based on slurry. The catalyst was reclaimed from the products and recycled. The decision to use the catalyst in this way was based on 1) our short supply, and 2) if it was ever to be used as a slurry catalyst in a large-scale plant, cost would dictate that it be recovered. Therefore, the catalyst being fed to the reactor was a mixture of reclaimed and fresh catalyst. Initially, the formulation was to contain 5 wt % added catalyst. This appeared to be too high to sustain, so the level was dropped to 2.5 wt %. Based on input and output rates, a considerable amount of the catalyst fed (approximately 290 grams) remained in the reactor.

Preliminary observations of gas yields and product composition during DOE 497A indicated a need for more conversion so the temperature was increased to 415°C (779°F) for run DOE 497B. No data are reported for DOE 497A due to a formulation error during the material balance period. The

The catalyst being fed in DOE 497B continued to be a mixture of reclaimed and fresh. Fresh catalyst was added only to make up for handling losses.

Once all of the fresh catalyst had been used, the run continued at the same conditions and the catalyst being used consisted of catalyst that had all been reclaimed from previous products and had an opportunity to age somewhat. The change between fresh/recycle catalyst and all recycle is denoted as runs DOE 497B-1 and DOE 497B-2, respectively.

The reactor temperature was increased to 430°C (806°F) for run DOE 497C, all other conditions being the same as in DOE 497B.

#### 4.4.1.1.3 Upgrading Filtrate with Pyrite Slurry Catalyst

Run conditions for DOE 498A and 498B were the same as in DOE 497B and DOE 497C, respectively, with the exception that pyrite was substituted for the HDS 1443 catalyst. The pyrite was not reclaimed and recycled since it is considered to be a disposable catalyst.

### 4.4.1.2 Coal

The coal used in run DOE 496 (filtrate preparation) was from the Consolidation Coal Company's Burning Star No. 2 mine (Illinois No. 6 seam) in DuQuoin County, Illinois, and is ranked as high volatile - C bituminous. The coal was conventionally cleaned at the mine site preparation plant. The coal was from a 33 drum lot received in March 1983. It was ground by Empire Coke Company and sieved through a 150 mesh screen at Merriam before use.

The compositional analysis of the coal is shown in Table IIIa and the petrographic analysis in Table IIIb.

### 4.4.1.3 Additives

Sodium carbonate ground to pass 150 mesh was added during run DOE 496 in the amount of 0.1 wt % based on slurry. Sodium carbonate was added to reduce the chance of forming ammonium chloride salt deposits which have been responsible for the unit plugging in the past when liquefying coals containing high levels of chlorine.

The slurry catalyst being investigated in run DOE 497 was Cyanamid HDS 1443 catalyst (nickel-molybdenum on alumina). It was supplied as nominal 1/16" cylindrical extrudates and was ground by hand at Merriam to pass 150 mesh. Analysis of this catalyst is presented in Table IV.

The slurry catalyst investigated in run DOE 498 was pyrite obtained from C-E Minerals (a division of Combustion Engineering) which was mined at Washington, Georgia, as a discrete mineral. The catalyst was finely ground under nitrogen by the Jet Pulverizer Company, Palmyra, New Jersey. Available analyses are shown in Table IV.

#### 4.4.1.4 Solvent/Feedstock

The solvent used in run DOE 496 was received from the Fort Lewis pilot plant, lot 2397. Available analyses are shown in Table V.

The feedstock that was prepared in DOE 496 was used in runs DOE 497B-1, 497B-2, 497C, 498A, and 498B. Due to initially over stripping the feedstock, it was necessary to add some distillate (solvent stripped to 250°C, 482°F) during the slurry preparation step so that the ratio of distillate to SRC would be 1:1.

### 4.4.2 Results

The yields and product analyses are shown in Table II and the solvent extraction data in Table VI. Liquid chromatography analyses of distillates and detailed solubility analyses of residues are given in Appendices A and B, respectively.

#### 4.4.2.1 Operability

No process related problems were encountered during runs DOE 496, 497 or 498.

#### 4.4.2.2 Filtrate Production

Yields for recent filtrate preparation runs are shown below. Reaction conditions were nominally the same for all runs.

Comparison of Filtrate Preparation Runs

| Yield, wt % MF Coal | DOE 485 | DOE 488 | DOE 493 | DOE 496 |
|---|---|---|---|---|
| $C_1$-$C_4$ | 1.6 | 1.5 | 1.5 | 1.9 |
| Total Oil (loss) | 2.8 | 5.8 | 5.2 | (0.3) |
| SRC | 74.9 | 72.1 | 72.4 | 76.5 |
| IOM | 5.9 | 6.7 | 6.7 | 7.3 |
| $H_2$ consumed, wt % MF coal | 1.4 | 1.4 | 1.4 | 1.3 |

Differences between the runs are:

1. DOE 485 used a different lot of Illinois No. 6 coal than the other runs.
2. DOE 496 used Fort Lewis solvent lot 2397, whereas the previous runs used lot 2335.
3. In DOE 496, 0.1 wt % sodium carbonate was added in the slurry recipe.

In run DOE 496 the feed appears to be less reactive (higher IOM yield) and it produced more hydrocarbon gas and less oil than the other runs. The only possible reason for the lower reactivity is that DOE 496 used a different lot of solvent. The solvent used in DOE 496 (2397) is significantly lighter and is also of lower hydrogen content. Table V shows available analysis for the 2335 and 2397 solvents.

#### 4.4.2.3 Filtrate Upgrading; Fixed Bed versus Slurry Catalyst

A trickle bed of high quality Shell 324 catalyst was used in run DOE 495A. This run was reported in section 4.3. That catalyst, supplied by C-E Lummus, contained 2.7 wt % Ni (as Ni) and 13.2 wt % Mo (as Mo) on alumina. The catalyst had been reclaimed from previous runs.

##### 4.4.2.3.1 Yield Structure

Run conditions and results compared to a run using HDS 1443 (3.0 wt % nickel and 10.3 wt % molybdenum on alumina) as a slurry catalyst are presented below:

| | DOE 495A | DOE 497B-2 |
|---|---|---|
| Run conditions: | | |
| Pressure, psig | 2250 | 2250 |
| Temperature, °C | 415 | 415 |
| (°F) | (779) | (779) |
| Liquid Hourly Space Velocity, $hr^{-1}$ | 0.5 | --- |
| Residence Time, hr | --- | 2.0 |
| Hydrogen feed rate, wt % based on slurry | 3.1 | 1.0 |
| Catalyst | Fixed Bed<br>$NiMo/Al_2O_3$ | Slurry<br>$NiMo/Al_2O_3$ |
| Yields, wt % based on SRC fed | | |
| $C_1$-$C_4$ | 4.1 | 5.1 |
| Total Oil | 41.0 | 30.2 |
| SRC | 52.5 | 62.6 |
| Hydrogen consumed | 7.9 | 5.9 |

The Shell 324 catalyst gave greater yields of total oil, as would be expected due to better mass transfer characteristics of the trickle bed compared to the slurry catalyst. A larger hydrogen consumption rate was also observed.

##### 4.4.2.3.2 Product Quality

The trickle bed processing produced a cleaner product than that produced with the slurry catalyst. Elemental analyses of the vacuum distillates and distillation residue for both runs are shown below:

ELEMENTAL ANALYSES OF

| Run | Vacuum Distillate |  |  |  |  | Distillation Residue |  |  |  |  |
|---|---|---|---|---|---|---|---|---|---|---|
|  | % C | % H | % S | % N | % O | % C | % H | % S | % N | % O |
| 495A | 89.49 | 10.15 | 0.05 | 0.13 | 0.18 | 89.44 | 7.12 | 0.20 | 1.05 | 2.19 |
| 497B-2 | 89.73 | 8.25 | 0.14 | 0.87 | 1.01 | 89.26 | 6.81 | 0.14 | 1.49 | 2.30 |

The vacuum distillate produced when processing filtrate in the trickle bed mode with Shell 324 catalyst was more highly hydrogenated and lower in sulfur, nitrogen and oxygen than that produced using ground HDS 1443 as a slurry catalyst.

The distillation residue from run DOE 495A was lower in nitrogen but higher in sulfur compared to that produced when using the slurry catalyst.

### 4.4.2.4 Effect of Temperature and Catalyst on Filtrate Upgrading

#### 4.4.2.4.1 Yield Structure

The effects of temperature and catalyst on hydrocarbon gas, total oil and SRC yields and hydrogen consumption during filtrate upgrading are shown in Figure 4.

Increasing the temperature from 415°C to 430°C (779 to 806°F) increased the hydrocarbon gas yield about 3.5 wt %, based on SRC fed, with both catalysts. The ground HDS 1443 slurry catalyst (reclaimed) produced essentially the same amount of hydrocarbon gas as pyrite at both temperatures.

The total oil yield increased by nearly 4.5 wt % (based on SRC fed) when increasing the temperature from 415 to 430°C with pyrite slurry catalyst. When using HDS 1443 a 10 wt % increase was observed. The HDS 1443 produced higher oil yields than pyrite at both temperatures studied.

SRC yields decreased by about 7 wt % when increasing temperature using pyrite catalyst. Decreasing the temperature when using HDS 1443 decreased SRC yields by nearly 13.5 wt %.

Increasing the temperature from 415°C to 430°C increased hydrogen consumption 1.2 wt % (from approximately 6 to 7.2 wt %) using HDS 1443 and 0.9 wt % (from 3.6 to 4.5 wt %) using pyrite as the catalyst.

Neither the pyrite nor the HDS 1443 catalysts gave yields comparable to those obtained when filtrate was processed in the trickle bed mode using Shell 324 catalyst. The difference is believed to be a result of:

1. better mass transfer characteristics in a trickle bed (only a thin film of liquid is present between the hydrogen gas and catalyst surface),
2. less favorable concentration of slurry catalyst relative to the charge of filtrate being processed.

### 4.4.2.4.2 Product Quality

When using slurry catalysts, the HDS 1443 produced a lower nitrogen level in the vacuum distillates than that obtained when using pyrite. In comparison, the trickle bed run (DOE 495A, section 4.3) was substantially better, as can be seen below.

| Run Number | Catalyst | Basic Nitrogen (%) in Vacuum Distillate |
|---|---|---|
| DOE 495A | Shell 324 (trickle bed) | 0.1 |
| DOE 497B-2 | HDS 1443 (slurry) | 0.5 |
| DOE 498A | C-E pyrite (slurry) | 0.6 |

Figures 5 and 6 show the effect of temperature and catalyst on the elemental analyses (oxygen, nitrogen, and sulfur) of the distillation residue and distillate oils, respectively. It should be noted that the product from run DOE 496 was the feed used for upgrading in runs DOE 497B, 497C, 498A, 498B.

It can be seen in Figure 5 that the HDS 1443 catalyst was effective in the removal of sulfur, nitrogen and oxygen. There was a decline in activity when recycling HDS 1443, but increasing the reaction temperature from 415 to 430°C (779 to 806°F) compensated. Pyrite, which was not recycled, was effective in removing sulfur and oxygen from the distillation residue; however, it was not as effective as the HDS 1443. Pyrite had little effect on the nitrogen removal in the distillation residue. Increasing the temperature when using pyrite had no apparent effect on nitrogen or sulfur levels, but did bring about a decrease in the oxygen level.

Elemental analysis of the distillate oils (Figure 6) shows similar trends for the HDS 1443 catalyst as those observed in the distillation residue. The HDS 1443 catalyst was effective in the removal of sulfur, nitrogen and oxygen. There was a decline in activity during catalyst recycling (except in sulfur removal) but increasing the reaction temperature from 415 to 430°C compensated. Sulfur removal was apparent when using pyrite, but no real effect was noticed in nitrogen or oxygen removal. Increasing the temperature when using pyrite had no noticeable effect on either nitrogen or sulfur levels. However, the oxygen level increased when increasing the temperature.

When increasing the temperature while using pyrite, oxygen-bearing compounds are apparently being transferred from the distillation residue to the distillate oil. This is indicated by the decrease in oxygen level in the distillation residue and a corresponding increase in the distillate oil. Care should be exercised when interpreting patterns concerning elemental oxygen since this component is determined by difference.

### 4.4.3 Conclusions

Processing filtrate with slurry catalysts does not yield as much of the desired products as when using Shell 324 catalyst in the trickle-bed mode of operation.

Increasing the filtrate processing temperature increases the hydrogen consumption and the yields of hydrocarbon gas and total oil.

HDS 1443 (nickel molybdenum on alumina) slurry catalyst yields more total oil and consumes more hydrogen than pyrite in the slurry phase mode.

## 4.5 Integrated SRC II Operation with Temperature Staging (DOE 504RA through H)

### 4.5.1 Experimental

Since the earlier work had demonstrated little advantage in a high-temperature hydrocracking stage for product upgrading, a high temperature was applied in a first stage in this series.

### 4.5.1.1 Run Conditions

Conditions for all runs are shown in Table I. The initial conditions in the dissolver (stage 2) matched those in an earlier run* which represented the lowest temperature and longest residence time used previously with this coal. All of the runs in this series, in fact, were conducted with a relatively low temperature (400-420°C) and long residence time (1-1/2 - 2-1/2 hours) in the second stage dissolver. This has been found to give a higher distillate:$C_1$-$C_4$ ratio (6 vs about 4) than conventional processing at higher temperatures and shorter residence times. The temperature in the top three zones of the preheater (stage 1) was raised to 450°C (842°F) in an attempt to effect hydrocracking.

In parts B through E of the run, an effort was made to optimize the yield structure by varying the temperatures and residence times in both stages. In parts A, B and C, this was accomplished by changing the pump rate. In part D, the residence time in the first stage was changed by running just the top two zones of the preheater at the higher temperature instead of three.

Titanium tetraphenoxide has been reported to exhibit hydrocracking activity in coal liquefaction and was added to the feed slurry in addition to pyrite at two different dissolver temperatures and pump rates (DOE 504RF and G).

The final part of the run was a control with the same temperature in the top part of the preheater and dissolver.

### 4.5.1.2 Coal

The coal used in all runs was from the Amax Belle Ayr Mine in Campbell County, Wyoming (Wyodak-Anderson seam) and ranks as subbituminous. The coal is a run-of-mine sample, ground by Empire Coke Company and sieved

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* Run DOE 457RD, "Research on Solvent Refined Coal," Technical Progress Report for the Period April 1, 1982 through July 31, 1982; October 1982, PC40005-23.

through a 150 mesh screen at Merriam before use. This coal was received at Merriam in February 1983 (lot RM1030).

The compositional analyses are shown in Table IIIa and the petrographic analysis in Table IIIc.

#### 4.5.1.3 Additives

##### 4.5.1.3.1 Pyrite

The pyrite used in all runs was obtained from C-E Minerals (a division of Combustion Engineering) and was mined at Washington, Georgia, as a discrete mineral. The catalyst was finely ground under nitrogen by the Jet Pulverizer Company, Palmyra, New Jersey. Lot RM1003 was used in parts A through G of run DOE 504 and lot RM1024C in part H. Available analyses for both lots are shown in Table IV. The catalytic activity of the two samples is believed to be similar.

##### 4.5.1.3.2 Titanium Tetraphenoxide

This chemical was purchased from Sharpe Chemicals Company, Burbank, California (lot OM-1106). It was 88 wt % pure based on ashing at Merriam. No other analyses were performed.

### 4.5.2 Results

#### 4.5.2.1 Operability

Operation was satisfactory in part A with 2 hours residence time in the dissolver (second stage) at 420°C (788°F). Conversion dropped off quickly in part B, however, when the residence time was decreased to 1-1/2 hours. The feed slurry became very thick, even after the level of oil was increased to 10 from 4 wt %. The conditions were changed (pump rate decreased) before part B was completely lined out to avoid a shutdown. Operation at the part B conditions does not appear to be feasible.

Operation was smooth in parts C and D with 2-1/2 hours residence time in the dissolver at 420°C. Operation again became difficult in part E when the dissolver temperature was dropped to 400°C (752°F), but steady stage was achieved. The final 3 parts of the run proceeded smoothly.

The ash balance in run DOE 504RG was low at 92%, but the reason could not be determined. The balances in the other parts of the run ranged from 103 to 116% (after correction for sulfate in the ash) and are reasonable for this low rank coal. These imbalances are believed to be due to volatile losses and are therefore forced.

### 4.5.2.2 Effect of Temperature Staging

#### 4.5.2.2.1 Yield Structure

The effect of temperature staging (running the top three zones of the preheater at 454°C, 849°F) is shown below:

| | DOE 504RA | DOE 504RH |
|---|---|---|
| **Conditions†** | | |
| Temperature in First Stage, °C (°F)<br>(top 3 zones of preheater) | 454<br>(849) | 417<br>(783) |
| **Yields, wt % MF Coal** | | |
| $C_1$-$C_4$ | 9.5 | 7.4 |
| Total Oil | 50.0 | 46.0 |
| SRC | 20.8 | 25.1 |
| IOM | 1.7 | 2.5 |
| **Hydrogen Consumption, wt % MF Coal** | | |
| (by gas balance) | 5.0 | 4.7 |

† For both, temperature in the second stage was 420°C (788°C), pressure was 2250 psig and residence time was 7.5-7.6 minutes in the first stage and 1.9 hours in the second stage.

Although this comparison indicates a small improvement in oil yield and conversion due to the first stage, this result was not borne out during the other parts of the run*. In the other runs with a first stage temperature of 450°C (842°F) and second stage temperature of 420°C (788°F), total oil yield ranged from 46.5 to 48.7 wt % and IOM yield from 2.5 to 2.8 wt %. It appears, therefore, that any increase in oil yield or conversion brought about by the high temperature in the first stage was very small. The hydrocarbon gas yield was increased to 9.5 from 7.4 wt % by the higher first stage temperature.

#### 4.5.2.2.2 Product Quality

There were no significant differences in product quality due to the higher temperature in the first stage (Tables II and VI).

### 4.5.2.3 Effect of Residence Time

#### 4.5.2.3.1 Yield Structure

Residence time was varied in both stages (dissolver and top of preheater):

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* The yields in run DOE 504RA were better than expected, as discussed in the next section.

| Conditions† | DOE 504RB | DOE 504RA | DOE 504RC | DOE 504RD |
|---|---|---|---|---|
| Residence Time | | | | |
| First Stage, min | 6.0 | 7.5 | 9.4 | 6.3 |
| Second Stage, hr | 1.5 | 1.9 | 2.4 | 2.4 |
| Yields, wt % MF Coal | | | | |
| $C_1$-$C_4$ | 8.7 | 9.5 | 10.2 | 10.1 |
| Total Oil | 48.5 | 50.0 | 46.5 | 48.7 |
| SRC | 22.9 | 20.8 | 21.8 | 21.5 |
| IOM | 2.5 | 1.7 | 2.5 | 2.5 |
| Hydrogen Consumed, Wt % MF Coal (by gas balance) | 4.8 | 5.0 | 5.7 | 5.6 |

† All at 2250 psig and 443-454°C (829°-849°F) in the first stage and 419-421°C (786-790°F) in the second stage.

The hydrocarbon gas yield increased as the residence time in both stages increased from DOE 504RB to A to C. There was an unexplained maximum in oil yield and minimums in SRC and IOM yields at the intermediate residence time (DOE 504RA). The higher apparent reactivity in part A may have been due to the fresh reactor*. Part B of the run was not completely lined out and total oil yield would be expected to go lower and SRC yield higher if a steady state could be reached. There was no significant difference in yields brought about by reducing the residence time in the first stage while keeping the second stage residence time constant (DOE 504RD vs 504RC).

### 4.5.2.3.2 Product Quality

There were no significant differences in distillate elemental analyses in the first four parts of run DOE 504R (Table II). The reason for the unusually low nitrogen level in the DOE 504RA heavy distillate is not known.

There was also little difference in distillation residue properties except for a slight decrease in preasphaltene level (Table VI) as residence time in the dissolver was increased.

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* I.e., from the clean metal surface or longer actual residence time prior to possible deposition of solids later in the run. An effect of this size is not expected, however.

### 4.5.2.4 Effect of Temperature

#### 4.5.2.4.1 Yield Structure

The dissolver temperature was lowered in part E of the run:

| Conditions† | DOE 504RC | DOE 504RE |
|---|---|---|
| Temperature, °C (°F) in Dissolver (2nd stage) | 420 (788) | 400 (752) |
| **Yields, wt % MF Coal** | | |
| $C_1$-$C_4$ | 10.2 | 6.8 |
| Total Oil | 46.5 | 45.1 |
| SRC | 21.8 | 29.0 |
| IOM | 2.5 | 2.9 |
| **Hydrogen Consumed, Wt % MF Coal** (by gas balance) | 5.7 | 5.0 |

† Temperature of 448-449°C (838-840°F) in first stage, 2250 psig and residence times of 9.4-9.7 minutes in the first stage and 2.4 hours in the second stage.

The hydrocarbon gas yield was significantly higher at the higher second stage temperature and SRC yield lower. Hydrogen consumption was increased. There was also a slight increase in total oil yield and slight decrease in IOM yield at 420°C (788°F). The distillate to gas ratio was much higher at the lower dissolver temperature (6.6 vs 4.6).

#### 4.5.2.4.2 Product Quality

The sulfur level in the distillate products was higher at the lower dissolver temperature in run DOE 504RE (Table II). There was not much change in other distillate analyses.

The two distillation residues also had similar properties except for a slightly lower preasphaltene level at the higher dissolver temperature.

### 4.5.2.5 Effect of Titanium Addition

#### 4.5.2.5.1 Yield Structure

Titanium was added at two sets of conditions:

| | DOE 504RA | DOE 504RG | DOE 504RE | DOE 504RF |
|---|---|---|---|---|
| **Conditions†** | | | | |
| Temperature in Stage 2 (Dissolver), °C (°F) | 420 (788) | 420 (788) | 400 (752) | 401 (754) |
| Residence Time in | | | | |
| Stage 1, min. | 7.5 | 7.8 | 9.5 | 9.7 |
| Stage 2, hrs. | 1.9 | 2.0 | 2.4 | 2.5 |
| Titanium Added | No | Yes | No | Yes |
| **Yields, wt % MF Coal** | | | | |
| $C_1$-$C_4$ | 9.5 | 9.2 | 6.8 | 7.1 |
| Total Oil | 50.0 | 47.9 | 45.1 | 41.6 |
| SRC | 20.8 | 21.5 | 29.0 | 30.4 |
| IOM | 1.7 | 2.8 | 2.9 | 3.6 |
| **Hydrogen Consumption, wt % MF Coal** | | | | |
| (by gas balance) | 5.0 | 5.1 | 5.0 | 5.1 |

† All with 448-454°C (838-849°F) in the first stage and 2250 psig.

There was no evidence that titanium, which has been reported to be a cracking catalyst, improved the yield structure. In fact, in the two comparisons above, the yields were better without titanium addition. The total oil yields were higher and SRC and IOM yields lower.

#### 4.5.2.5.2 Product Quality

In most cases, the hydrogen and sulfur contents of the distillate products were slightly less when titanium was added (Table II). There was not much difference in other distillate analyses.

The residue from part G had a higher preasphaltene level than that from part A (Table VI) although the fusion point was lower. The distillation residues from parts E and F of the run had nearly identical properties.

### 4.5.3 Conclusions

There is no apparent advantage in temperature staging as practiced in this work. Hydrocarbon gas yield is increased by adding a higher temperature first stage without a significant increase in total oil yield or conversion.

At a second stage (dissolver) temperature of 420°C, there is no improvement in yields brought about by increasing the residence time in the first stage to 9.4 from 6.0 minutes and in the second stage to 2.4 from 1.5 hours. The system does not appear to be operable at the shortest residence time, however.

At 400°C (752°F) dissolver temperature, the oil yield and conversion are slightly lower than at 420°C (788°F). The gas yield is much lower, however, resulting in a much higher ratio of distillate to gas.

The addition of titanium (as titanium tetraphenoxide) does not improve the yield structure or product quality.

## 5.0 EPIDEMIOLOGY RESEARCH

Efforts this quarter were concentrated on the location, collection and preparation for computerization of medical records for all workers involved with the SRC process. Extra efforts were required to locate the medical records for former employees not readily available from within the medical department. All in-house medical records have been processed, coded and computerized and have undergone preliminary edit checks. However, due to various physical examination forms the computerized data still need to be standardized for future statistical analysis.

Other work this quarter centered around coding of the detailed work history for the SRC employees. This required locating and obtaining copies of the personnel records for all employees. Difficulty was encountered in locating personnel records of the former Merriam Lab (Spencer Chemical) employees because of the early years in which they worked. Only records for 8 out of 39 Spencer Chemical employees have been found and efforts are being continued to locate the remaining records. The detailed work history coding for all Fort Lewis employees (N=389) was completed. Similar coding for the Harmarville P-99 unit employees was begun at which time an additional 39 service (maintenance) employees were identified and have now also been included in the cohort file.

The follow-up of Gulf employees with a survey questionnaire has been delayed due to the necessity of receiving approval from OMB to administer the questionnaire. A proposal for obtaining this approval was drafted and sent to DOE for their review. Several revisions were made to the proposal, per DOE's suggestions. The final draft will be forwarded to OMB by DOE. Despite this delay, other work for preparation of the follow-up survey was continued. Aid was enlisted from several former Gulf Fort Lewis employees in identifying addresses and furnishing other leads for locating the ex-Fort Lewis employees who still had an unknown address after checks of local telephone and Polk directories.

# 6.0 BENCH SCALE UNIT MODIFICATIONS

## 6.1 Trickle Bed Reactor

A trickle-bed hydroterater was installed in the reactor air furnace for run DOE 495R. The reactor vessel (DOE #2) was 1-1/2 inches ID by 59 inches long. It was packed with catalyst as described in section 4.3.1.4.

# TABLE I

## Conditions Summary

| | DOE 493 | DOE 494 | DOE 495A | DOE 495B | DOE 495C | DOE 495D |
|---|---|---|---|---|---|---|
| Operating Mode | SCT | SRC I | <---------Filtrate Upgrading-----------> | | | |
| Coal[a] | <-Illinois No. 6----> | | -- | -- | -- | -- |
| Dissolver | Short Contact Time | DOE 3 | <----------------DOE 2----------------><br>Downflow Trickle Bed | | | |
| Slurry Formulation,[b] | 36 wt % coal<br>64 wt % +250°C<br>SRC II Solvent | | 50 wt % stripped Filtrate from DOE:<br>493<br>50 wt % Recycle HTSB[h] | 494 | 50 wt % HTSB[h] from DOE:<br>495B<br>50 wt % Recycle HTSB | 495A |
| Slurry Composition, wt%[b] | | | | | | |
| Coal | <-------36.0-------> | | -- | -- | -- | -- |
| Middle Distillate (193-250°C, 380-482°F) | <-------11.1-------> | | 6.6 | 7.5 | 12.2 | 12.6 |
| Heavy Distillate (>250°C, 482°F) | <-------51.5-------> | | 50.5 | 51.0 | 57.2 | 58.0 |
| SRC | <------- 1.4-------> | | 42.9 | 41.5 | 30.6 | 29.4 |
| Slurry Feed Rate | | | | | | |
| g/hr | 2284 | 2393 | 1091 | 1100 | 1096 | 1107 |
| lb/hr/ft$^3$[c] | 713 | 137 | 31.4 | 31.6 | 31.5 | 31.8 |
| Reactor Nominal Slurry[c] Residence Time, hr (min) | 6.0 | 31.5 | -- | -- | -- | -- |
| Liquid Hourly Space Velocity, hr$^{-1}$ | -- | -- | 0.52 | 0.53 | 0.52 | 0.53 |
| Preheater Nominal Slurry[d] Residence Time, min | 9.8 | 9.4 | 20.6 | 20.4 | 20.5 | 20.3 |
| Coal Feed Rate[b] | | | | | | |
| g/hr | 808 | 847 | -- | -- | -- | -- |
| lb/hr/ft$^3$ | 252 | 48.4 | -- | -- | -- | -- |
| Hydrogen Feed Rate[e] | | | | | | |
| Mole/hr | 11.50 | 24.34 | <----------------16.84----------------> | | | |
| wt % based on slurry | 1.02 | 2.05 | 3.12 | 3.09 | 3.10 | 3.07 |
| MSCF[f] /ton of coal | 10.79 | 21.78 | -- | -- | -- | -- |
| Pressure, psig | <--------------------------2250--------------------------> | | | | | |
| Reactor Temperature, °C Average (°F) | 451<br>(844) | 450<br>(842) | 411<br>(772) | 410<br>(770) | 411<br>(772) | 412<br>(774) |
| Dissolver Zone[g] | | | | | | |
| 6 (top) | -- | 451±0 | 394±2 | 387±1 | 395±1 | 396±1 |
| 5 | -- | 452±0 | 413±1 | 415±1 | 413±1 | 415±0 |
| 4 | -- | 451±1 | 416±1 | 415±1 | 415±1 | 416±1 |
| 3 | 450±0 | 451±0 | 417±0 | 415±0 | 417±0 | 416±0 |
| 2 | 452±0 | 452±0 | 414±0 | 415±0 | 414±0 | 415±0 |
| 1 (bottom) | 451±0 | 441±1 | 414±1 | 415±0 | 414±0 | 415±0 |
| Preheater Temperature[g], °C | | | | | | |
| Top | 402±3 | 398±1 | 365±1 | 359±2 | 359±1 | 361±0 |
| Middle | 376±4 | 374±3 | 378±1 | 370±1 | 368±0 | 371±0 |
| Bottom | 314±0 | 323±8 | 374±2 | 370±0 | 368±1 | 372±2 |

## TABLE I (Continued)

| Conditions | DOE 496 | DOE 497B-1 | DOE 497B-2 | DOE 497C | DOE 498A | DOE 498B |
|---|---|---|---|---|---|---|
| Operating Mode | Coal Dissolution | <--------Hydrogenation (2nd Stage)-------> | | | | |
| Coal[a] | Illinois #6 Conventionally Cleaned | -- | -- | -- | -- | -- |
| Solvent | Ft. Lewis Heavy Oil | -- | -- | -- | -- | -- |
| Dissolver | SCT (200cc) | <---------DOE #2 Upflow (2170cc)--------> | | | | |
| Slurry Formulation, wt %[b] | | | | | | |
| Coal | 36.0 | -- | -- | -- | -- | -- |
| Solvent | 63.9 | -- | -- | -- | -- | -- |
| Filtrate | -- | 48.75 | 48.75 | 48.75 | 48.75 | 48.75 |
| HTHP[h] Bottoms (Recycled) | -- | 48.75 | 48.75 | 48.76 | 48.75 | 40.75 |
| Additive | 0.1 | 2.5 | 2.5 | 2.5 | 2.5 | 2.5 |
| | $Na_2CO_3$ | <--------HDS 1443--------> | | | <----Pyrite---> | |
| Slurry Composition, wt %[b] | | | | | | |
| Coal | 36.00 | -- | -- | -- | -- | -- |
| Middle Distillate (193-250°C, 380-482°F) | 8.66 | 2.56 | 2.62 | 2.80 | 2.92 | 2.64 |
| Heavy Distillate (>250°C, 482°F) | 52.97 | 54.06 | 53.40 | 55.58 | 51.83 | 52.96 |
| SRC | 2.27 | 40.88 | 41.48 | 39.12 | 42.75 | 41.90 |
| Additive | 0.10 | 2.50 | 2.50 | 2.50 | 2.50 | 2.50 |
| Feed Rate, g/hr | | | | | | |
| Slurry | 2236.4 | 1233.5 | 1240.8 | 1228.5 | 1250.2 | 1237.9 |
| Coal | 791.1 | -- | -- | -- | -- | -- |
| Feed Rate, lb/hr/$ft^3$ | | | | | | |
| Slurry | 698.1 | 35.5 | 35.7 | 35.3 | 36.0 | 35.6 |
| Coal | 246.9 | -- | -- | -- | -- | -- |
| Additive Addition Rate, wt % based on slurry | | | | | | |
| Ni | -- | 0.075 | 0.075 | 0.074 | -- | -- |
| Mo | -- | 0.26 | 0.26 | 0.26 | -- | -- |
| Fe | -- | -- | -- | -- | 1.06 | 1.06 |
| Nominal Slurry Residence Time, Hr (Min.) | | | | | | |
| Reactor[c] | (6.2) | 2.0 | 2.01 | 2.03 | 2.00 | 2.02 |
| Preheater[d] | (10.0) | (18.2) | (18.1) | (18.3) | (17.9) | (18.1) |
| Hydrogen Feed Rate,[e] | | | | | | |
| Mole/hr | 11.42 | 25.13 | 25.13 | 25.13 | 25.12 | 25.12 |
| wt %, based on slurry | 1.03 | 4.11 | 4.08 | 4.12 | 4.05 | 4.09 |
| MSCF[f]/ton of coal | 11.0 | -- | -- | -- | -- | -- |
| Pressure, psig | <-------------------2250-------------------> | | | | | |
| Dissolver Temperature, °C | | | | | | |
| Average | 451 | 415 | 415 | 431 | 415 | 430 |
| Dissolver Zone[g] | | | | | | |
| 6 (top) | | 415+0 | 415+0 | 430+0 | 415+0 | 432+0 |
| 5 | | 415±0 | 416±0 | 431±0 | 416±0 | 431±0 |
| 4 | | 415±0 | 415±0 | 431±0 | 415±1 | 431±0 |
| 3 | 450+0 | 415±0 | 415±0 | 431±0 | 414±0 | 427±0 |
| 2 | 451±0 | 415±0 | 416±0 | 431±0 | 416±0 | 431±0 |
| 1 (bottom) | 451±0 | 415±1 | 416±0 | 431±1 | 415±0 | 429±0 |
| Preheater Temperature[g], °C | | | | | | |
| Top | 402+2 | 401+0 | 401+1 | 404+0 | 403+1 | 403+0 |
| Middle | 395±7 | 399±0 | 401±0 | 402±2 | 399±0 | 400±0 |
| Bottom | 325±5 | 388±1 | 389±0 | 390±1 | 386±1 | 387±0 |

## TABLE I (Continued)

| Conditions | DOE 499A | DOE 499B | DOE 499C | DOE 500A | DOE 500B | DOE 500C | DOE 500D | DOE 500E | DOE 500F | DOE 500G |
|---|---|---|---|---|---|---|---|---|---|---|
| Operating Mode | Short Contact Time | | | | | | | | | |
| Coal[a] | Belle Ayr | | | | | | | | | |
| Solvent | IBT Single Pass | | | | | | | Reclaimed | | |
| Dissolver | 445cc | | | SCT (200cc) | | | | | | |
| Slurry Formulation[b], wt % | | | | | | | | | | |
| Coal | 36.0 | | | | | | | | | |
| Solvent | 62.0 | | | | | | | | | 63.0 |
| HTHP[h] Bottoms | -- | -- | -- | -- | -- | -- | -- | -- | -- | -- |
| Additive | 2.0 | | | | | | | | | 1.0 |
| | Pyrite | | | | | | | | | |
| Feed Rate, g/hr | | | | | | | | | | |
| Slurry | 1979.4 | 1032.8 | 657.1 | 1284.3 | 2716.9 | 1344.6 | 1365.0 | 1361.4 | 1354.4 | 1349.0 |
| Coal | 685.7 | 357.6 | 227.7 | 445.0 | 942.4 | 466.3 | 473.1 | 471.0 | 470.6 | 468.9 |
| Feed Rate, lb/hr/ft$^3$ | | | | | | | | | | |
| Slurry | 277.7 | 322.4 | 205.1 | 400.9 | 848.1 | 419.7 | 426.1 | 424.9 | 422.8 | 421.1 |
| Coal | 96.2 | 111.6 | 71.1 | 138.9 | 294.2 | 145.6 | 147.7 | 147.0 | 146.9 | 146.4 |
| Additive Addition Rate, wt % based on slurry | | | | | | | | | | |
| Fe | 0.85 | 0.85 | 0.85 | 0.85 | 0.85 | 0.85 | 0.85 | 0.85 | 0.85 | 0.42 |
| Co | -- | -- | -- | -- | -- | -- | -- | -- | -- | -- |
| Mo | -- | -- | -- | -- | -- | -- | -- | -- | -- | -- |
| Nominal Slurry Residence Time, Hr. (Min.) | | | | | | | | | | |
| Reactor[c] | (15.5) | (29.7) | (46.7) | (10.7) | (5.1) | (10.3) | (10.1) | (10.1) | (10.2) | (10.2) |
| Preheater[d] | (11.3) | (21.7) | (34.1) | (17.5) | (8.3) | (16.7) | (16.4) | (16.5) | (16.6) | (16.6) |
| Hydrogen Feed Rate[e] | | | | | | | | | | |
| Mole/hr | 20.3 | 10.55 | 6.92 | 13.68 | 27.15 | 13.68 | 13.68 | 13.68 | 13.68 | 13.68 |
| wt % based on slurry | 2.07 | 2.06 | 2.12 | 2.15 | 2.02 | 2.05 | 2.02 | 2.03 | 2.04 | 2.04 |
| MSCF[f]/ton of coal | 22.5 | 22.4 | 23.1 | 23.3 | 21.9 | 22.3 | 21.9 | 22.0 | 22.1 | 22.1 |
| Pressure, psig | 2250 | | | | | | | | | |
| Dissolver Temperature, °C | | | | | | | | | | |
| Average | 439 | 439 | 438 | 438 | 439 | 450 | 431 | 430 | 457 | 439 |
| Dissolver Zone[g] | | | | | | | | | | |
| 6 (top) | 440±1 | 440±0 | 440±0 | | 439±1 | | | | | |
| 5 | 440±0 | 440±0 | 440±0 | 434±0 | 434±0 | | | | | |
| 4 | 439±1 | 439±0 | 439±0 | 439±0 | 444±0 | | | | | |
| 3 | 439±0 | 438±1 | 438±0 | 440±0 | 439±0 | 449±0 | 431±0 | 430±0 | 459±0 | 439±1 |
| 2 | 439±1 | 438±1 | 437±0 | 441±0 | 440±0 | 450±0 | 431±0 | 431±0 | 460±0 | 441±0 |
| 1 (bottom) | 438±0 | 436±1 | 434±0 | 440±0 | 439±0 | 450±1 | 430±0 | 429±0 | 451±1 | 437±2 |
| Preheater Temperature[g], °C | | | | | | | | | | |
| Top | 364±0 | 400±1 | 400±0 | 394±1 | 365±3 | 397±0 | 397±0 | 399±1 | 400±1 | 397±1 |
| Middle | 365±1 | 407±1 | 411±0 | 397±0 | 368±2 | 401±0 | 401±0 | 402±0 | 405±0 | 403±0 |
| Bottom | 358±1 | 390±1 | 398±0 | 382±0 | 357±2 | 385±1 | 384±1 | 385±1 | 387±0 | 386±2 |

## TABLE I (Continued)

| Conditions | DOE 501R | DOE 502 | DOE 503 |
|---|---|---|---|
| Operating Mode | <------Short Contact Time--------> | | |
| Coal[a] | <----------Belle Ayr----------> | | |
| Solvent | Recycled | <-----Reclaimed-----> | |
| Dissolver | <----------SCT (200cc)----------> | | |
| Slurry Formulation[b], wt % | | | |
| Coal | <----------36.0----------> | | |
| Solvent | 31.0 | 62.0 | 54.0 |
| HTHP[h] | 31.0 | -- | -- |
| Additive | <----------2.0----------> | | |
| | Pyrite | HDS1442 | Ammonium Molybdate |
| Slurry Composition, wt %[b] | | | |
| Coal | 36.0 | -- | -- |
| Middle Distillate (193-250°C, 380-482°F) | 4.2 | -- | -- |
| Heavy Distillate (>250°C, 482°F) | 43.7 | -- | -- |
| SRC | 10.0 | -- | -- |
| IOM | 2.0 | -- | -- |
| Ash | 2.1 | -- | -- |
| Pyrite | 2.0 | -- | -- |
| Feed Rate, g/hr | | | |
| Slurry | 1359.3 | 1372.2 | 1344.4 |
| Coal | 470.7 | 474.6 | 466.2 |
| Feed Rate, lb/hr/ft$^3$ | | | |
| Slurry | 424.3 | 428.3 | 419.6 |
| Coal | 146.9 | 148.1 | 145.5 |
| Additive Addition Rate, wt % based on slurry based on coal | | | |
| Fe | 0.85 | -- | -- |
| Co | -- | 0.047 | -- |
| Mo | -- | 0.21 | 0.26 |
| Nominal Slurry Residence Time, Hr. (Min.) | | | |
| Reactor[c] | (10.2) | (10.1) | (10.3) |
| Preheater[d] | (16.5) | (16.3) | (16.7) |
| Hydrogen Feed Rate[e], | | | |
| Mole/hr | 13.79 | 13.70 | 13.77 |
| wt % based on slurry | 2.04 | 2.01 | 2.06 |
| MSCF[f]/ton of coal | 22.2 | 21.9 | 22.4 |
| Pressure, psig | <----------2250----------> | | |
| Dissolver Temperature, °C | | | |
| Average | 441 | 439 | 442 |
| Dissolver Zone[g] | | | |
| 6 (top) | | | |
| 5 | | | |
| 4 | | | |
| 3 | 440±0 | 439±0 | 441±1 |
| 2 | 441±0 | 442±0 | 443±1 |
| 1 (bottom) | 441±1 | 437±1 | 443±0 |
| Preheater Temperature[g], °C | | | |
| Top | 389±1 | 380±0 | 390±1 |
| Middle | 402±1 | 387±1 | 397±0 |
| Bottom | 397±1 | 377±0 | 386±1 |

## TABLE I (Continued)

| | DOE 504RA | DOE 504RB | DOE 504RC | DOE 504RD | DOE 504RE | DOE 504RF | DOE 504RG | DOE 504RH |
|---|---|---|---|---|---|---|---|---|
| Operating Mode | <-------SRC II with Temperature Staging-------> | | | | | | | -- |
| Coal[a] | <-------Belle Ayr-------> | | | | | | | |
| Dissolver | <-------DOE 2-------> | | | | | | | |
| Slurry Formulation, wt%[b] | | | | | | | | |
| Coal | 30.0 | 30.0 | 30.0 | 30.0 | 30.0 | 30.0 | 30.0 | 30.0 |
| Recycled HTSB[h] | 64.4 | 64.4 | 64.4 | 64.4 | 61.4 | 60.8 | 63.8 | 61.4 |
| Recycle Solvent | 4.0 | 4.0 | 4.0 | 4.0 | 7.0 | 7.0 | 4.0 | 7.0 |
| Additive | 1.6 | 1.6 | 1.6 | 1.6 | 1.6 | 2.2 | 2.2 | 1.6 |
| Slurry Composition, wt%[b] | | | | | | | | |
| Coal | 30.0 | 30.0 | 30.0 | 30.0 | 30.0 | 30.0 | 30.0 | 30.0 |
| Middle Distillate (193-288°C, 380-550°F) | 4.0 | 3.3 | 6.2 | 4.6 | 4.1 | 4.4 | 3.2 | 3.6 |
| Heavy Distillate (>288°C, 550°F) | 21.5 | 20.2 | 18.7 | 19.2 | 24.7 | 25.0 | 23.7 | 25.2 |
| SRC | 26.8 | 28.2 | 26.8 | 27.4 | 26.9 | 25.2 | 23.9 | 26.0 |
| IOM | 2.2 | 3.1 | 3.1 | 3.2 | 2.7 | 3.0 | 3.1 | 2.6 |
| Ash (from recycled HTSB) | 13.9 | 13.6 | 13.6 | 14.0 | 10.0 | 10.2 | 13.9 | 11.0 |
| Pyrite | 1.6 | 1.6 | 1.6 | 1.6 | 1.6 | 1.6 | 1.6 | 1.6 |
| Titanium Tetraphenoxide | -- | -- | -- | -- | -- | 0.6 | 0.6 | -- |
| Total Solids | 47.7 | 48.3 | 48.3 | 48.8 | 44.3 | 45.4 | 49.2 | 45.2 |
| Slurry Feed Rate | | | | | | | | |
| g/hr | 1333 | 1645 | 1055 | 1045 | 1042 | 1020 | 1273 | 1315 |
| lb/hr/ft$^3$ | 38.3 | 47.3 | 30.3 | 30.0 | 30.0 | 29.3 | 36.6 | 37.8 |
| Dissolver Nominal Slurry Residence Time, hr (min)[c] | 1.87 | 1.52 | 2.37 | 2.39 | 2.39 | 2.45 | 1.96 | 1.90 |
| Preheater Nominal Slurry Residence Time, min[d] | | | | | | | | |
| High Temperature Zone | 7.5 | 6.0 | 9.4 | 6.3 | 9.5 | 9.7 | 7.8 | 7.6 |
| Low Temperature Zone | 5.0 | 4.0 | 6.3 | 9.5 | 6.4 | 6.5 | 5.2 | 5.0 |
| Coal Feed Rate[b] | | | | | | | | |
| g/hr | 388 | 479 | 307 | 303 | 303 | 296 | 369 | 382 |
| lb/hr/ft$^3$ | 11.2 | 13.8 | 8.8 | 8.7 | 8.7 | 8.5 | 10.6 | 11.0 |
| Hydrogen Feed Rate[e] | | | | | | | | |
| Mole/hr | 24.91 | 34.27 | <-------19.64-------> | | | | <-----24.91-----> | |
| wt %, based on slurry | 3.77 | 4.21 | 3.76 | 3.80 | 3.81 | 3.89 | 3.95 | 3.83 |
| MSCF[f]/ton of coal | 48.7 | 54.2 | 48.5 | 49.1 | 49.1 | 50.3 | 51.2 | 49.4 |
| Pressure, psig | <-------2250-------> | | | | | | | |
| Dissolver Temperature, °C | | | | | | | | |
| Average °C | 420 | 419 | 420 | 421 | 400 | 401 | 420 | 420 |
| (°F) | (788) | (786) | (788) | (790) | (752) | (754) | (788) | (788) |
| Dissolver Zone[g] | | | | | | | | |
| 6 (top) | 420±0 | 419±0 | 420±0 | 421±0 | 399±1 | 400±1 | 421±0 | 420±0 |
| 5 | 421±0 | 419±0 | 420±0 | 421±0 | 400±1 | 401±0 | 420±0 | 420±0 |
| 4 | 420±0 | 419±0 | 420±0 | 420±0 | 399±2 | 399±1 | 419±0 | 418±0 |
| 3 | 420±0 | 419±0 | 420±0 | 420±1 | 400±0 | 401±0 | 421±0 | 421±0 |
| 2 | 420±0 | 419±0 | 420±1 | 421±1 | 401±1 | 401±0 | 421±0 | 421±0 |
| 1 (bottom) | 419±6 | 419±0 | 420±0 | 420±0 | 400±1 | 401±0 | 420±0 | 420±0 |
| Preheater Temperature, °C | | | | | | | | |
| Average in High Temp. Zone (First Stage) | 454 | 443 | 449 | 451 | 448 | 448 | 449 | 417 |
| Preheater Zone | | | | | | | | |
| High Temperature Zone | | | | | | | | |
| 5 (top) | 456±5 | 442±3 | 448±0 | 450±2 | 451±1 | 451±1 | 452±1 | 421±1 |
| 4 | 455±6 | 446±1 | 450±1 | 452±1 | 451±1 | 451±1 | 451±1 | 420±1 |
| 3 | 451±4 | 442±2 | 448±1 | | 441±1 | 443±1 | 443±1 | 411±1 |
| Preheater Zone | | | | | | | | |
| 3 | | | | 426±3 | | | | |
| 2 | 430±2 | 430±2 | 435±1 | 357±1 | 407±1 | 414±2 | 411±2 | 376±1 |
| 1 (bottom) | 335±10 | 375±3 | 317±8 | 272±3 | 368±5 | 334±16 | 314±16 | 347±2 |

a) See Table III for coal analyses. b) Dry coal basis. c) Reactor volume 200 cm$^3$ (0.00706 ft$^3$) for runs DOE 494, 496, 499B & C, 500A-G, 501, 502 and 503; 1091 cm$^3$ (0.03853 ft$^3$) in run DOE 494; 2170 cm$^3$ (0.07663 ft$^3$) in runs DOE 495, 4975-1 & 2, 497C, 498A & B and 504 A-H; 445 cm$^3$ (0.01571 ft$^3$) in DOE 499A; assumed slurry density 1.15 gm/cm$^3$. d) Preheater volume - 240 cm in runs DOE 504A-H, 325 cm$^3$ in others. Top two zones of preheater used as first stage reactor in run DOE 504RD. Top 3 zones used as such in other parts of run DOE 504R. e) Hydrogen feed rates do not include that added as DP cell purge. f) One thousand cubic feet at 60°F and one atmosphere. g) Average and standard deviation. h) High temperature, high pressure separator bottoms.

# TABLE II

## Results Summary

| | DOE 493 | DOE 494 | DOE 495A | DOE 495B | DOE 495C | DOE 495D |
|---|---|---|---|---|---|---|
| **Yields, wt %**[a] | | | | | | |
| $H_2O$ | 2.4 | 4.3 | 7.2 | 6.4 | 3.6 | 1.4 |
| $CO$ | 0.2 | 0.3 | 0.0 | 0.0 | 0.0 | 0.0 |
| $CO_2$ | 1.0 | 1.3 | 0.0 | 0.0 | 0.0 | 0.0 |
| $H_2S$ | 0.9 | 1.3 | 1.3 | 1.3 | 0.5 | 0.1 |
| $NH_3$ | 0.1 | 0.1 | 1.8 | 2.0 | 0.9 | 0.2 |
| $C_1$ | 0.7 | 2.3 | 1.5 | 1.4 | 1.4 | 1.4 |
| $C_2$ | 0.4 | 1.4 | 1.1 | 1.1 | 1.1 | 1.0 |
| $C_3$ | 0.3 | 1.1 | 0.9 | 1.0 | 1.2 | 1.2 |
| $C_4$ | 0.1 | 0.5 | 0.6 | 0.6 | 1.2 | 1.1 |
| Total $C_1$-$C_4$ | 1.5 | 5.3 | 4.1 | 4.1 | 4.9 | 4.7 |
| $C_5$+ (gas) | 0.8 | 1.5 | 1.7 | 1.6 | 3.6 | 2.7 |
| Naphtha, <193°C (380°F) | 5.8 | 10.2 | 13.9 | 10.1 | 9.2 | 9.7 |
| Middle Distillate 193-250°C (380-482°F) | (13.4) | (0.3) | 15.6 | 13.8 | 12.8 | 12.7 |
| Heavy Distillate >250°C (482°F) | 12.0 | (0.5) | 9.8 | 10.9 | (5.2) | 1.4 |
| Total Oil ($C_5$-Heavy Distillate) | 5.2 | 10.9 | 41.0 | 36.4 | 20.4 | 26.5 |
| SRC | 72.4 | 62.1 | 52.5 | 57.4 | 74.2 | 70.9 |
| Insoluble Organic Matter | 6.7 | 5.3 | -- | -- | -- | -- |
| Ash | 11.0 | 11.5 | -- | -- | -- | -- |
| Total | 101.4 | 102.4 | 107.9 | 107.6 | 104.5 | 103.8 |
| Hydrogen Consumed (by gas balance) | 1.4 | 2.4 | 7.9 | 7.6 | 4.5 | 3.8 |
| **Product Analyses** | | | | | | |
| Naphtha | | | | | | |
| % C | 83.93 | 84.16 | 86.31 | 86.23 | 86.55 | 86.62 |
| % H | 12.33 | 12.47 | 13.60 | 13.65 | 13.15 | 13.25 |
| % S | 1.44 | 1.16 | 0.18 | 0.02 | 0.05 | 0.16 |
| % N | 0.15 | 0.20 | 0.02 | 0.02 | 0.01 | 0.00 |
| % O (by difference) | 2.15 | 2.01 | -- | 0.03 | 0.24 | 0.00 |
| Middle Distillate | | | | | | |
| % C | 85.10 | 84.99 | 87.81 | 87.83 | 87.82 | 87.80 |
| % H | 8.92 | 9.10 | 11.93 | 11.77 | 11.61 | 11.84 |
| % S | 0.40 | 0.41 | 0.03 | 0.01 | 0.03 | 0.03 |
| % N | 0.74 | 0.74 | 0.05 | 0.08 | 0.04 | 0.00 |
| % O (by difference) | 4.84 | 4.76 | 0.18 | 0.31 | 0.50 | 0.33 |
| Heavy Distillate | | | | | | |
| % C | 87.15 | 87.56 | 88.73 | 89.27 | 89.32 | 88.97 |
| % H | 8.81 | 8.66 | 11.08 | 10.18 | 10.30 | 10.82 |
| % S | 0.26 | 0.37 | 0.04 | 0.03 | 0.02 | 0.02 |
| % N | 0.97 | 0.99 | 0.05 | 0.12 | 0.10 | 0.02 |
| % O (by difference) | 2.81 | 2.42 | 0.10 | 0.40 | 0.26 | 0.17 |
| Distillation Residue | | | | | | |
| % C | 85.41 | 87.00 | 89.44 | 90.22 | 90.79 | 90.59 |
| % H | 5.66 | 5.72 | 7.12 | 6.93 | 7.17 | 7.46 |
| % S | 1.33 | 0.83 | 0.20 | 0.05 | 0.04 | 0.03 |
| % N | 1.94 | 2.10 | 1.05 | 1.11 | 0.69 | 0.62 |
| % Ash | 0.08 | 0.02 | -- | -- | -- | -- |
| % O (by difference) | 5.58 | 4.33 | 2.19 | 1.69 | 1.31 | 1.30 |
| Fusion Point, °C | 155 | 125 | 72 | 69 | 51 | <40 |

## TABLE II (Continued)

| Yields, wt %[a] | DOE 496 | DOE 497B-1 | DOE 497B-2 | DOE 497C | DOE 498A | DOE 498B |
|---|---|---|---|---|---|---|
| $H_2O$ | 1.9 | 6.2 | 5.8 | 6.9 | 3.4 | 4.1 |
| CO | 0.2 | 0.0 | 0.0 | 0.1 | 0.1 | 0.2 |
| $CO_2$ | 1.2 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| $H_2S$[b] | 1.1 | 1.2 | 1.2 | 1.2 | 2.8 | 3.3 |
| $NH_3$ | 0.1 | 1.1 | 1.0 | 1.3 | 0.4 | 0.4 |
| $C_1$ | 0.8 | 1.8 | 1.8 | 3.0 | 1.9 | 3.3 |
| $C_2$ | 0.5 | 1.3 | 1.3 | 2.2 | 1.2 | 1.9 |
| $C_3$ | 0.4 | 1.3 | 1.2 | 2.1 | 1.0 | 1.8 |
| $C_4$ | 0.2 | 0.8 | 0.8 | 1.3 | 0.7 | 1.2 |
| Total $C_1$-$C_4$ | 1.9 | 5.2 | 5.1 | 8.6 | 4.8 | 8.2 |
| Naphtha, $C_5$ -193°C (380°F) | 1.0 | 8.9 | 8.1 | 11.7 | 6.8 | 9.0 |
| Middle Distillate 193-250°C (380-482°F) (loss) | (10.9) | 7.0 | 6.2 | 10.0 | 5.0 | 5.4 |
| Heavy Distillate >250°C (482°F) | 9.6 | 17.3 | 15.9 | 18.5 | 12.7 | 13.5 |
| Total Oil ($C_5$-Heavy Distillate) | (0.3) | 33.2 | 30.2 | 40.2 | 23.5 | 27.9 |
| SRC | 76.5 | 59.2 | 62.6 | 48.9 | 71.1 | 63.8 |
| Insoluble Organic Matter | 7.3 | -- | -- | -- | -- | -- |
| Ash | 11.6 | 0.0 | 0.0 | -- | -- | -- |
| Total | 101.3 | 106.2 | 105.9 | 107.2 | 107.0 | 107.9 |
| Hydrogen Consumed | 1.3 | 6.2 | 5.9 | 7.2 | 3.6 | 4.5 |
| Catalyst Conversion Byproducts | -- | -- | -- | -- | 3.4 | 3.4 |
| **Product Analyses, wt %** | | | | | | |
| Naphtha | | | | | | |
| % C | 83.57 | -- | -- | -- | -- | -- |
| % H | 12.60 | -- | -- | -- | -- | -- |
| % S | 2.05 | -- | -- | -- | -- | -- |
| % N | 0.18 | -- | -- | -- | -- | -- |
| % O (by difference) | 1.60 | -- | -- | -- | -- | -- |
| Middle Distillate | | | | | | |
| % C | 83.00 | -- | -- | -- | -- | -- |
| % H | 9.63 | -- | -- | -- | -- | -- |
| % S | 1.19 | -- | -- | -- | -- | -- |
| % N | 0.55 | -- | -- | -- | -- | -- |
| % O (by difference) | 5.63 | -- | -- | -- | -- | -- |
| Heavy Distillate[c] | | | | | | |
| % C | 89.36 | 89.91 | 89.73 | 90.18 | 89.20 | 89.22 |
| % H | 7.26 | 8.22 | 8.25 | 8.29 | 7.51 | 7.73 |
| % S | 0.76 | 0.20 | 0.14 | 0.10 | 0.42 | 0.46 |
| % N | 1.85 | 0.81 | 0.87 | 0.79 | 1.09 | 1.11 |
| % O (by difference) | 0.77 | 0.86 | 1.01 | 0.64 | 1.78 | 1.48 |
| Distillation Residue | | | | | | |
| % C | 85.89 | 90.36 | 89.26 | 90.18 | 88.20 | 88.50 |
| % H | 5.71 | 6.88 | 6.81 | 8.29 | 6.49 | 6.66 |
| % S | 1.18 | 0.07 | 0.14 | 0.10 | 0.49 | 0.54 |
| % N | 1.91 | 1.40 | 1.49 | 1.36 | 1.84 | 1.85 |
| % Ash | -- | -- | -- | -- | -- | -- |
| Fusion Point, °C | 140 | 74 | 77 | 78 | -- | -- |

## TABLE II (Continued)

| | DOE 499A | DOE 499B | DOE 499C | DOE 500A | DOE 500B | DOE 500C | DOE 500D | DOE 500E | DOE 500F | DOE 500G |
|---|---|---|---|---|---|---|---|---|---|---|
| Yields, wt %[a] | | | | | | | | | | |
| $H_2O$ | 7.1 | 6.8 | 7.6 | 0.2 | 3.7 | 7.9 | 6.5 | 7.2 | 7.7 | 6.3 |
| CO | 0.6 | 0.5 | 0.6 | 0.5 | 0.4 | 0.5 | 0.4 | 0.4 | 0.6 | 0.5 |
| $CO_2$ | 6.5 | 6.5 | 6.9 | 5.9 | 5.3 | 6.5 | 6.4 | 6.3 | 6.1 | 6.2 |
| $H_2S$[b] | 1.1 | 1.1 | 1.4 | 1.4 | 1.1 | 1.2 | 1.1 | 1.2 | 1.2 | 0.8 |
| $NH_3$ | 0.2 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 |
| $C_1$ | 1.1 | 1.6 | 1.9 | 1.0 | 0.5 | 1.3 | 0.8 | 0.7 | 1.6 | 0.9 |
| $C_2$ | 0.7 | 0.9 | 1.2 | 0.6 | 0.3 | 0.8 | 0.5 | 0.5 | 1.0 | 0.6 |
| $C_3$ | 0.5 | 0.8 | 1.0 | 0.5 | 0.2 | 0.6 | 0.4 | 0.3 | 0.7 | 0.4 |
| $C_4$ | 0.2 | 0.3 | 0.5 | 0.2 | 0.1 | 0.3 | 0.1 | 0.2 | 0.3 | 0.2 |
| Total $C_1$-$C_4$ | 2.5 | 3.6 | 4.6 | 2.3 | 1.1 | 3.0 | 1.8 | 1.7 | 3.6 | 2.1 |
| Naphtha, $C_5$-193°C (380°F) | 3.4 | 5.4 | 7.0 | 2.4 | 0.5 | 1.3 | 2.9 | 5.8 | 6.9 | 7.4 |
| Middle Distillate 193-250°C (380-482°F) (loss) | (4.3) | 3.4 | 5.5 | (3.2) | 2.4 | 3.0 | 4.3 | 2.5 | 2.9 | 5.7 |
| Heavy Distillate >250°C (482°F) (loss) | 20.1 | 15.1 | 10.8 | 22.5 | 21.0 | 15.2 | 10.6 | 7.4 | 10.5 | 1.2 |
| Total Oil ($C_5$-Heavy Distillate) | 19.2 | 23.9 | 23.3 | 21.7 | 23.9 | 19.5 | 17.8 | 15.7 | 20.3 | 14.3 |
| SRC | 46.0 | 43.2 | 44.9 | 52.3 | 43.1 | 47.8 | 48.3 | 46.9 | 49.2 | 47.6 |
| Insoluble Organic Matter | 14.5 | 12.3 | 8.8 | 13.6 | 18.8 | 11.9 | 16.0 | 18.7 | 8.7 | 18.1 |
| Ash | 6.6 | 6.5 | 6.5 | 6.7 | 6.4 | 6.2 | 6.2 | 6.2 | 7.1 | 7.2 |
| Total | 104.4 | 104.5 | 104.9 | 104.7 | 103.8 | 104.6 | 104.4 | 104.4 | 104.7 | 103.1 |
| Hydrogen Consumed | 2.6 | 2.7 | 3.1 | 2.9 | 2.0 | 2.8 | 2.6 | 2.6 | 2.9 | 2.2 |
| Catalyst Conversion Byproducts | 1.8 | 1.8 | 1.8 | 1.8 | 1.8 | 1.8 | 1.8 | 1.8 | 1.8 | 0.9 |
| Product Analyses, wt % | | | | | | | | | | |
| Vacuum Distillate[c] | | | | | | | | | | |
| % C | 87.83 | 87.80 | 87.97 | 87.83 | 87.95 | 87.76 | 87.89 | 87.80 | 87.79 | 87.85 |
| % H | 7.58 | 7.79 | 7.74 | 7.78 | 7.47 | 7.60 | 7.68 | 7.82 | 7.77 | 7.98 |
| % S | 0.39 | 0.34 | 0.33 | 0.37 | 0.40 | 0.36 | 0.41 | 0.36 | 0.38 | 0.34 |
| % N | 0.81 | 0.76 | 0.78 | 0.75 | 0.69 | 0.75 | 0.76 | 0.71 | 0.73 | 0.70 |
| % O (by difference) | 3.39 | 3.31 | 3.18 | 3.27 | 3.49 | 3.54 | 3.26 | 3.31 | 3.33 | 3.13 |
| Distillation Residue | | | | | | | | | | |
| % C | 85.55 | 85.73 | 86.45 | 85.13 | 83.99 | 85.48 | 84.76 | 84.02 | 86.31 | 84.66 |
| % H | 6.49 | 6.19 | 6.18 | 6.22 | 6.22 | 6.05 | 6.01 | 6.25 | 6.13 | 6.36 |
| % S | 0.34 | 0.32 | 0.31 | 0.51 | 0.53 | 0.38 | 0.36 | 0.34 | 0.38 | 0.29 |
| % N | 1.65 | 1.73 | 1.81 | 1.72 | 1.54 | 1.73 | 1.64 | 1.54 | 1.63 | 1.50 |
| % Ash | 0.44 | 0.22 | 0.26 | -- | -- | -- | -- | -- | -- | -- |
| Fusion Point, °C | -- | -- | -- | 116 | 132 | 132 | 131 | 142 | 130 | 135 |

TABLE II (Continued)

| | DOE 501R | DOE 502 | DOE 503 |
|---|---|---|---|
| **Yields, wt %**[a] | | | |
| $H_2O$ | 4.5 | 9.3 | 6.2 |
| CO | 0.4 | 0.4 | 0.7 |
| $CO_2$ | 6.4 | 5.8 | 4.8 |
| $H_2S$[b] | 1.3 | 0.3 | 0.3 |
| $NH_3$ | 0.1 | 0.0 | 0.1 |
| $C_1$ | 1.0 | 1.1 | 1.2 |
| $C_2$ | 0.8 | 0.7 | 0.7 |
| $C_3$ | 0.6 | 0.6 | 0.6 |
| $C_4$ | 0.3 | 0.2 | 0.3 |
| Total $C_1$-$C_4$ | 2.7 | 2.6 | 2.8 |
| Naphtha,[c] $C_5$-193°C (380°F) | 4.8 | (1.6) | 5.6 |
| Middle Distillate 193-250°C (380-482°F) (loss) | 5.6 | 6.1 | 8.7 |
| Heavy Distillate >250°C (482°F) (loss) | 9.6 | 15.0 | (2.8) |
| Total Oil ($C_5$-Heavy Distillate) | 20.0 | 19.5 | 11.5 |
| SRC | 51.6 | 33.4 | 46.5 |
| Insoluble Organic Matter | 10.4 | 24.6 | 22.6 |
| Ash | 7.2 | 7.3 | 7.2 |
| Total | 104.6 | 103.2 | 102.8 |
| Hydrogen Consumed | 2.8 | 3.2 | 2.6 |
| Catalyst Conversion Byproducts | 1.8 | -- | 0.2 |
| **Product Analyses, wt %** | | | |
| Naphtha | | | |
| % C | 83.19 | -- | -- |
| % H | 11.97 | -- | -- |
| % S | 1.06 | -- | -- |
| % N | 0.11 | -- | -- |
| % O (by difference) | 3.67 | -- | -- |
| Middle Distillate | | | |
| % C | 82.88 | -- | -- |
| % H | 9.00 | -- | -- |
| % S | 0.28 | -- | -- |
| % N | 0.39 | -- | -- |
| % O (by difference) | 7.45 | -- | -- |
| Heavy Distillate[c] | | | |
| % C | 86.72 | 87.84 | 87.89 |
| % H | 7.99 | 8.23 | 7.90 |
| % S | 0.39 | 0.25 | 0.29 |
| % N | 0.68 | 0.73 | 0.70 |
| % O (by difference) | 4.22 | 2.95 | 3.22 |
| Distillation Residue | | | |
| % C | 72.49 | 84.45 | 85.48 |
| % H | 4.78 | 6.69 | 6.31 |
| % S | 1.95 | 0.16 | 0.25 |
| % N | 1.28 | 1.41 | 1.38 |
| % Ash | 17.22 | 0.68 | -- |
| Fusion Point, °C | 186 | 118 | 124 |

# TABLE II (Continued)

| | DOE 504RA | DOE 504RB | DOE 504RC | DOE 504RD | DOE 504RE | DOE 504RF | DOE 504RG | DOE 504RH |
|---|---|---|---|---|---|---|---|---|
| Yields, wt %[a] | | | | | | | | |
| $H_2O$ | 9.3 | 7.5 | 10.0 | 8.3 | 7.4 | 8.6 | 9.5 | 9.4 |
| CO | 1.3 | 1.2 | 1.3 | 1.2 | 1.0 | 1.1 | 1.5 | 1.2 |
| $CO_2$ | 5.0 | 5.8 | 5.5 | 5.7 | 5.3 | 5.5 | 5.3 | 5.6 |
| $H_2S$[b] | 1.6 | 1.5 | 1.7 | 1.7 | 1.7 | 1.9 | 1.8 | 1.8 |
| $NH_3$ | 0.4 | 0.4 | 0.5 | 0.4 | 0.3 | 0.3 | 0.4 | 0.3 |
| $C_1$ | 3.5 | 3.3 | 3.8 | 3.9 | 2.6 | 2.6 | 3.3 | 2.7 |
| $C_2$ | 2.2 | 2.1 | 2.4 | 2.4 | 1.7 | 1.7 | 2.3 | 1.8 |
| $C_3$ | 2.4 | 2.0 | 2.5 | 2.4 | 1.6 | 1.8 | 2.3 | 1.8 |
| $C_4$ | 1.4 | 1.3 | 1.5 | 1.4 | 0.9 | 1.0 | 1.3 | 1.1 |
| Total $C_1$-$C_4$ | 9.5 | 8.7 | 10.2 | 10.1 | 6.8 | 7.1 | 9.2 | 7.4 |
| $C_5$+ (gas) | 3.0 | 4.0 | 2.9 | 2.7 | 1.5 | 1.6 | 2.6 | 1.8 |
| Naphtha, <193°C (380°F) | 11.0 | 8.9 | 10.6 | 10.6 | 9.0 | 9.4 | 9.8 | 8.6 |
| Middle Distillate[b] 193-288°C (380-550°F) | 20.8 | 20.3 | 18.7 | 20.7 | 22.8 | 15.7 | 15.5 | 19.8 |
| Heavy Distillate[c] >288°C (550°F) | 15.2 | 15.3 | 14.3 | 14.7 | 11.8 | 14.9 | 20.0 | 15.8 |
| Total Oil ($C_5$-Heavy Distillate) | 50.0 | 48.5 | 46.5 | 48.7 | 45.1 | 41.6 | 47.9 | 46.0 |
| SRC | 20.8 | 22.9 | 21.8 | 21.5 | 29.0 | 30.4 | 21.5 | 25.1 |
| Insoluble Organic Matter | 1.7 | 2.5 | 2.5 | 2.5 | 2.9 | 3.6 | 2.8 | 2.5 |
| Ash | 7.1 | 7.5 | 7.4 | 7.3 | 7.2 | 7.0 | 7.2 | 7.1 |
| Total | 106.7 | 106.5 | 107.4 | 107.4 | 106.7 | 107.1 | 107.1 | 106.4 |
| Hydrogen Consumed (by gas balance) | 5.0 | 4.8 | 5.7 | 5.6 | 5.0 | 5.1 | 5.1 | 4.7 |
| Catalyst Conversion Byproducts | 1.7 | 1.7 | 1.7 | 1.8 | 1.7 | 2.0 | 2.0 | 1.7 |
| Product Analyses | | | | | | | | |
| Naphtha | | | | | | | | |
| % C | 83.82 | 85.07 | 84.22 | 83.97 | 83.75 | 83.90 | 83.18 | 83.07 |
| % H | 12.17 | 12.61 | 12.45 | 12.60 | 12.28 | 12.27 | 11.56 | 12.35 |
| % S | 0.31 | 0.33 | 0.27 | 0.24 | 0.60 | 0.46 | 0.24 | 0.42 |
| % N | 0.19 | 0.16 | 0.17 | 0.15 | 0.15 | 0.15 | 0.17 | 0.15 |
| % O (by difference) | 3.51 | 1.83 | 2.89 | 3.14 | 3.22 | 3.22 | 4.85 | 3.21 |
| Middle Distillate[d] | | | | | | | | |
| % C | 83.86 | 83.50 | 83.95 | 83.94 | 83.45 | 83.09 | 83.17 | 83.60 |
| % H | 9.39 | 9.25 | 9.48 | 9.38 | 9.33 | 9.20 | 9.14 | 9.34 |
| % S | 0.12 | 0.06 | 0.03 | 0.08 | 0.17 | 0.15 | 0.04 | 0.11 |
| % N | 0.79 | 0.79 | 0.83 | 0.82 | 0.75 | 0.75 | 0.77 | 0.73 |
| % O (by difference) | 5.84 | 6.40 | 5.71 | 5.78 | 6.30 | 6.81 | 6.88 | 6.22 |
| Heavy Distillate[e] | | | | | | | | |
| % C | 87.29 | 87.57 | 87.62 | 87.47 | 87.06 | 87.63 | 87.61 | 87.46 |
| % H | 9.25 | 8.84 | 8.72 | 8.81 | 8.84 | 8.73 | 8.95 | 8.77 |
| % S | 0.18 | 0.07 | 0.04 | 0.07 | 0.13 | 0.08 | 0.06 | 0.06 |
| % N | 0.77 | 1.00 | 0.98 | 0.95 | 0.91 | 0.91 | 0.95 | 0.96 |
| % O (by difference) | 2.51 | 2.52 | 2.64 | 2.70 | 3.06 | 2.65 | 2.43 | 2.75 |
| Distillation Residue | | | | | | | | |
| % C | 62.55 | 63.70 | 62.63 | 62.46 | 67.06 | 66.50 | 63.51 | 64.94 |
| % H | 3.99 | 4.22 | 4.03 | 3.91 | 4.66 | 4.71 | 4.23 | 4.53 |
| % S | 3.72 | 3.93 | 3.87 | 4.46 | 3.65 | 3.66 | 4.37 | 3.96 |
| % N | 1.08 | 1.12 | 1.10 | 1.08 | 1.19 | 1.15 | 1.12 | 1.15 |
| % Ash | 34.23 | 32.20 | 33.03 | 33.30 | 26.83 | 27.99 | 32.68 | 29.52 |
| Fusion Point, °C | 143 | 142 | 138 | 135 | 141 | 135 | 133 | 135 |

a) Based on SRC fed in runs DOE 495, 497B-1 & 2, 497C, 498A & B; based on dry feed coal in others.

b) Includes $H_2S$ from added pyrite.

c) Vacuum distillate from high temperature, high pressure separator bottoms in runs DOE 497B & C, 498A & B, 500 A-G, 502 and 503.

# TABLE III
## Coal Analyses[a]

### a. Compositional Analyses

| Coal Identification | | | |
|---|---|---|---|
| Company | Consol | Amax | Amax |
| Mine | Burning Star | Belle Ayr | Belle Ayr |
| Seam | Illinois No. 6 | Wyodak-Anderson | Wyodak-Anderson |
| | Composite 33 Drums | Composite | |
| | (RM 1032) | (RM 1030) | (Received 3/82) |
| | 71-115880 | 71-115879 | 71-93666 |
| Proximate Analysis | | | |
| % Ash | 10.77 | 7.16 | 7.52 |
| % Volatile | 36.59 | 43.50 | 48.03 |
| % Fixed Carbon | 52.64 | 49.34 | 44.45 |
| | 100.00 | 100.00 | 100.00 |
| % Moisture | 3.22 | 6.74 | 4.96 |
| Heating Value, Btu/lb | 12513 | 11877 | 11898 |
| Free Swelling Index | 2 1/2 | 0 | 0 |
| Sulfur Forms | | | |
| % Pyritic Sulfur | 1.28 | 0.01 | 0.35 |
| % Sulfate Sulfur | 0.05 | 0.01 | 0.01 |
| % Organic Sulfur | 1.60 | 0.57 | 0.30 |
| Ultimate Analysis, wt % | | | |
| Carbon | 70.00 | 68.98 | 68.90 |
| Hydrogen | 4.96 | 5.07 | 4.99 |
| Nitrogen | 1.22 | 0.91 | 0.83 |
| Chlorine | 0.10 | 0.04 | 0.01 |
| Sulfur | 2.93 | 0.57 | 0.66 |
| Ash | 10.77 | 7.16 | 7.52 |
| Oxygen (difference) | 10.02 | 17.27 | 17.09 |
| | 100.00 | 100.00 | 100.00 |
| Mineral Analyses of Ash, wt % | | | |
| Ignited Basis | | | |
| Silica, $SiO_2$ | 45.37 | 32.02 | 29.26 |
| Alumina, $Al_2O_3$ | 18.62 | 15.61 | 15.48 |
| Titania, $TiO_2$ | 0.84 | 1.15 | 1.19 |
| Ferric Oxide, $Fe_2O_3$ | 16.68 | 5.40 | 4.97 |
| Lime, CaO | 7.40 | 21.38 | 21.29 |
| Magnesia, MgO | 0.95 | 3.70 | 3.72 |
| Potassium Oxide, $K_2O$ | 1.98 | 0.45 | 0.43 |
| Sodium Oxide, $Na_2O$ | 0.90 | 1.60 | 1.24 |
| Sulfur Trioxide, $SO_3$ | 6.43 | 16.87 | 19.76 |
| Phos. Pentoxide, $P_2O_5$ | 0.12 | 0.90 | 1.14 |
| Strontium Peroxide, SrO | 0.00 | 0.37 | 0.44 |
| Barium Oxide, BaO | 0.06 | 0.46 | 0.47 |
| Manganese Oxide, $Mn_3O_4$ | 0.12 | 0.09 | 0.02 |
| Undetermined | 0.53 | 0.00 | 0.59 |
| | 100.00 | 100.00 | 100.00 |
| Iron in Coal | 1.26 | -- | 0.26 |
| Fusion Temperature of Ash, °F (Reducing) | | | |
| Initial Deformation | 2125 | 2110 | 2060 |
| Softening (H=W)[b] | 2175 | 2140 | 2090 |
| Softening (H=1/2W) | 2220 | 2160 | 2110 |
| Fluid | 2260 | 2185 | 2145 |
| % Equilibrium Moisture | 10.34 | 19.74 | 27.66 |

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

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

## TABLE III (Continued)

## b. Petrographic Analysis of Illinois No. 6 Coal

MACERAL ANALYSIS
(VOLUME PERCENT)
(MINERAL-MATTER CONTAINING BASIS)

| MACERAL | | MACERAL GROUP | |
|---|---|---|---|
| VITRINITE | 83.4 | VITRINITE | 83.4 |
| PSEUDOVITRINITE | 0.0 | | |
| EXINITE | 1.4 | EXINITE (LIPTINITE) | 1.5 |
| RESINITE | 0.1 | | |
| SEMI-FUSINITE* | 5.3 | | |
| SEMI-MACRINITE* | 0.0 | | |
| FUSINITE | 2.3 | INERTINITE | 8.3 |
| MACRINITE | 0.1 | | |
| MICRINITE | 0.6 | | |
| MINERAL MATTER** | 6.8 | | 6.8 |
| TOTAL | 100% | | 100% |

TOTAL REACTIVES- 86.7
TOTAL INERTS- 13.3

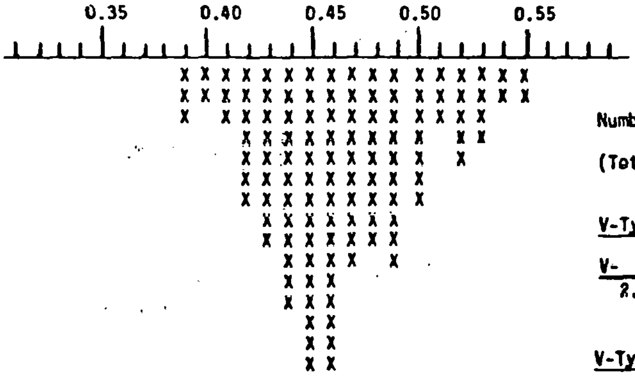
++++++++++++

* CONSIDERED 1/3 REACTIVE, 2/3 INERT FOR PURPOSES OF COKE STABILITY PREDICTIONS.

** CALCULATED FROM10.84 % DRYASH, 3.14 % DRY SULFUR

Distribution of Vitrinite Reflectance Readings:
%Ro

Mean-Maximum Vitrinite Ro: 0.46



Number of Counts

(Total = 118 )

V-Type Table for Vitrinites (=100%)

| V- 3 | V- 4 | V- 5 | V- |
|---|---|---|---|
| 2.6 | 78.0 | 19.5 | |

V-Type Table for Vitrinites (= 83.4 %)
(Adjusted to =Maceral % of Reactive Vitrinit

| V- 3 | V- 4 | V- 5 | V- |
|---|---|---|---|
| 2.0 | 65.1 | 16.3 | |

## TABLE III (Continued)

### c. Petrographic Analysis of Belle Ayr Coal (RM 1030)

MACERAL ANALYSIS
(VOLUME PERCENT)
(MINERAL-MATTER CONTAINING BASIS)

| MACERAL | | MACERAL GROUP | |
|---|---|---|---|
| VITRINITE | 83.7 | VITRINITE | 83.9 |
| PSEUDOVITRINITE | 0.2 | | |
| EXINITE | 1.4 | EXINITE (LIPTINITE) | 1.8 |
| RESINITE | 0.4 | | |
| SEMI-FUSINITE* | 9.1 | | |
| SEMI-MACRINITE* | 0.0 | | |
| FUSINITE | 1.3 | INERTINITE | 10.4 |
| MACRINITE | 0.0 | | |
| MICRINITE | 0.0 | | |
| MINERAL MATTER** | 3.9 | | 3.9 |
| TOTAL | 100% | | 100% |

TOTAL REACTIVES- 88.8
TOTAL INERTS- 11.3

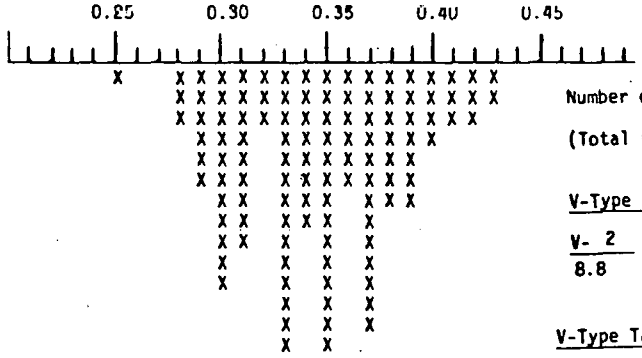
++++++++++++

* CONSIDERED 1/3 REACTIVE, 2/3 INERT FOR PURPOSES OF COKE STABILITY PREDICTIONS.

** CALCULATED FROM 7.07 % DRYASH, 0.57 % DRY SULFUR

Distribution of Vitrinite Reflectance Readings:
%Ro

Mean-Maximum Vitrinite Ro: 0.35



Number of Counts

(Total = 114)

V-Type Table for Vitrinites (=100%)

| V- 2 | V- 3 | V- 4 | V- |
|---|---|---|---|
| 8.8 | 80.7 | 10.5 | |

V-Type Table for Vitrinites (= 83.9 %)

(Adjusted to =Maceral % of Reactive Vitrini

| V- 2 | V- 3 | V- 4 | V- |
|---|---|---|---|
| 7.5 | 67.6 | 8.8 | |

# TABLE IV

## Additive Analyses

| Composition, wt %[a] | C-E Pyrite (RM 1003) | C-E Pyrite (RM 1024C) | CoMo on Alumina (HDS 1442) | NiMo on Alumina (HDS 1443) |
|---|---|---|---|---|
| Fe | 42.5 | 42.35 | | |
| S | 52.3 | 52.71 | | |
| $CoO$ | | | 3.0 | |
| $NiO$ | | | | 3.8 |
| $MoO_3$ | | | 16.1 | 15.5 |
| $Na_2O$ | | | 0.01 | 0.02 |
| $SO_4$ | | | 0.3 | 0.6 |
| Ash[b] | 67.45 | 67.37 | 94.0 | 94.0 |
| **Physical Properties[c]** | | | <----Through 150 Mesh-----> | |
| Surface Area, $m^2/g$[d] | 5.2 | | 287 | 312 |
| Average Particle Size*, m (by Coulter Counter) | 1.9 | 2.4 | | |

* Conducted by Jet Pulverizer Company; particle size distributions shown in Figure 1.

a) Dry basis.
b) Wet basis.
c) As fed.
d) B.E.T. measurement by Coors Spectro-Chemical Laboratory.

# TABLE V

## Analysis of Feed Solvents

### a. Elemental Analyses

| Solvent | % C | % H | % S | % N[a] | % O[b] |
|---|---|---|---|---|---|
| 2335 Solvent[a] | 87.97 | 7.76 | 0.33 | 1.06 | |
| | 87.99 | 7.81 | 0.31 | 1.07 | |
| Average | 87.98 | 7.79 | 0.32 | 1.07 | 2.84 |
| 2397 Solvent | 89.70 | 7.29 | 0.53 | 0.53 | |
| | 89.55 | 7.29 | 0.56 | | |
| Average | 89.63 | 7.29 | 0.54 | | |
| IBT Solvent | 87.68 | 7.80 | 0.46 | | |
| | 87.61 | 7.77 | 0.42 | | |
| Average | 87.64 | 7.78 | 0.44 | | |

### b. Vacuum Distillation

| | | SRC II Solvent to Still | Recycle Solvent | Distillation Residue | Cold Trap | Loss | Endpoint °C Vapor | Endpoint °C Pot | Pressure @ Endpoint mm Hg |
|---|---|---|---|---|---|---|---|---|---|
| 2335 | Weight, gm | 1705.2 | 1652.77 | 36.5 | 19.2 | 1.8 | 270 | 315 | 2.0 |
| | Weight % | | 96.92 | 2.14 | 0.83 | 0.11 | | | |
| IBT | Weight, gm | 2039.1 | 1892.3 | 137.2 | 7.9 | 1.8 | 270 | 301 | 2.0 |
| | | 1961.2 | 1791.4 | 152.9 | 13.5 | 3.4 | 270 | 334 | 2.0 |
| Total | | 4000.3 | 3683.6 | 290.1 | 21.4 | 5.2 | | | |
| | Weight % | | 92.08 | 7.25 | 0.54 | 0.13 | | | |

a) Bottoms from atmospheric distillation to 250°C.

TABLE V (Continued)

## c. Simulated Distillation (by Gas Chromatography)[c]

| Fraction Boiling Below, % | 2335 Solvent<br>Temp (°C) | 2397 Solvent<br>Temp (°C) | IBT Solvent<br>Temp (°C) |
|---|---|---|---|
| IBP | 200.5 | 104.7 | 82.8 |
| 5 | 229.8 | 186.9 | 208.9 |
| 10 | 237.8 | 195.0 | 223.7 |
| 15 | 245.7 | 208.8 | 238.5 |
| 20 | 253.6 | 215.6 | 246.4 |
| 25 | 253.9 | 223.4 | 254.4 |
| 30 | 262.2 | 231.3 | 262.7 |
| 35 | 270.5 | 238.9 | 271.4 |
| 40 | 270.9 | 239.3 | 279.0 |
| 45 | 278.1 | 247.0 | 286.4 |
| 50 | 285.4 | 254.8 | 294.6 |
| 55 | 293.2 | 255.1 | 310.4 |
| 60 | 293.6 | 263.6 | 318.6 |
| 65 | 309.6 | 271.9 | 319.3 |
| 70 | 317.9 | 286.3 | 334.4 |
| 75 | 325.9 | 294.4 | 342.6 |
| 80 | 341.4 | 310.9 | 357.8 |
| 85 | 357.1 | 326.9 | 373.2 |
| 90 | 372.8 | 350.5 | 389.3 |
| 95 | 404.2 | 381.5 | 428.3 |
| FBP | 479.5 | 468.9 | 499.6 |
| | Sim.Dist.% | Sim.Dist.% | Sim.Dist.% |
| Oil, IBP-193°C | 0.00 | 8.77 | 4.43 |
| Oil, 193-250°C | 17.72 | 38.16 | 17.82 |
| Oil, >250°C | 82.28 | 53.08 | 77.75 |
| Total | 100.00 | 100.00 | 100.00 |

a) The highest value from the Kjeldahl analysis is believed to be the most accurate and is therefore the only number used in the average.
b) Oxygen by difference.
c) Bottoms from atmospheric distillation to 250°C.

# TABLE VI

## Solvent Extraction of Distillation Residue

| | DOE 493 | DOE 494 | DOE 495A | DOE 495B | DOE 495C | DOE 495D |
|---|---|---|---|---|---|---|
| **Liquefaction Conditions** | | | | | | |
| Operating Mode | SCT | SRC I | <----------Filtrate Upgrading----------> | | | |
| Tmperature, °C | 451 | 450 | 411 | 410 | 411 | 412 |
| °F | (844) | (842) | (772) | (770) | (772) | (774) |
| Pressure, psig | <------------------------2250------------------------> | | | | | |
| Residence Time, min. | 6.0 | 31.5 | -- | -- | -- | -- |
| Liquid Hourly Space Velocity, $hr^{-1}$ | -- | -- | 0.52 | 0.53 | 0.52 | 0.53 |
| Slurry Formulation | | | | | | |
| | 36 wt % coal | | 50 wt % stripped | | 50 wt % HTSB from | |
| | 64 wt % +250°C | | Filtrate from DOE: | | DOE: | |
| | SRC II Solvent | | 493 | 494 | 495B | 495A |
| | | | 50 wt % Recycle HTSB | | 50 wt % Recycle HTSB | |
| **Solubility of Distillation Residue, wt % in** | | | | | | |
| Hexane | 16.8 | 28.0 | 64.0 | 55.4 | 70.6 | 74.3 |
| | 17.6 | 27.3 | 64.1 | 52.3 | 69.4 | 75.0 |
| Toluene | 62.7 | | 87.8 | 93.3 | 96.6 | 96.4 |
| | 61.1 | 77.1 | 87.3 | 93.5 | 96.4 | 96.0 |
| Pyridine | 99.8 | 99.9 | 99.9 | 99.9 | 99.9 | 100.0 |
| | 99.8 | 99.9 | 99.9 | 99.9 | 99.9 | 100.0 |
| **Ratio of Average Solubilities** | | | | | | |
| Hexane/Pyridine | 0.172 | 0.277 | 0.641 | 0.539 | 0.701 | 0.747 |
| Toluene/Pyridine | 0.620 | 0.772 | 0.876 | 0.935 | 0.966 | 0.962 |
| **Residue Composition, wt %** | | | | | | |
| Maltene[a] | 17.2 | 27.7 | 64.1 | 53.9 | 70.0 | 74.7 |
| Asphaltene[b] | 44.7 | 49.5 | 23.5 | 39.6 | 26.5 | 21.5 |
| Preasphaltene[c] | 37.9 | 22.8 | 12.4 | 6.5 | 3.4 | 3.8 |

## TABLE VI (Continued)

| | DOE 496 | DOE 497B-1 | DOE 497B-2 | DOE 497C | DOE 498A | DOE 498B |
|---|---|---|---|---|---|---|
| **Liquefaction Conditions** | | | | | | |
| Operating Mode | Coal Dissolution | <--------------Hydrogenation------------> | | | | |
| Coal | Illinois #6 | -- | -- | -- | -- | -- |
| Solvent | Fort Lewis Heavy Oil | -- | -- | -- | -- | -- |
| Catalyst | $Na_2CO_3$ | <----------HDS 1443---------> | | | <----Pyrite---> | |
| | | Fresh/ Reclaimed | Reclaimed | | | |
| Average Dissolver Temperature, °C | 450 | 415 | 415 | 430 | 415 | 430 |
| (°F) | (842) | (779) | (779) | (806) | (779) | (806) |
| Dissolver Pressure, psig | <----------------------------2250----------------------------> | | | | | |
| Residence Time, hr (min) | (6.2) | 2.02 | 2.01 | 2.03 | 2.00 | 2.02 |
| **Solubility of Distillation Residue, wt % in** | | | | | | |
| Hexane | 22.5 | 23.1 | 25.0 | 25.9 | 30.4 | 35.0 |
| | 21.3 | 22.1 | 20.7 | 26.5 | 29.7 | 34.2 |
| Toluene | 64.1 | 99.4 | 97.1 | 99.5 | 97.6 | 97.2 |
| | 65.9 | 99.5 | 97.5 | 99.5 | 96.7 | 97.2 |
| Pyridine | 99.9 | 100.0 | 99.9 | 99.9 | 99.8 | 99.6 |
| | 99.9 | 100.0 | 99.9 | 99.9 | 99.8 | 99.5 |
| **Ratio of Average Solubilities** | | | | | | |
| Hexane/Pyridine | 0.219 | 0.226 | 0.229 | 0.262 | 0.301 | 0.348 |
| Toluene/Pyridine | 0.651 | 0.995 | 0.974 | 0.996 | 0.973 | 0.977 |
| **Residue Composition, wt %** | | | | | | |
| Maltene[a] | 21.9 | 22.6 | 22.9 | 26.2 | 30.1 | 34.6 |
| Asphaltene[b] | 43.1 | 76.9 | 74.5 | 73.3 | 67.1 | 62.6 |
| Preasphaltene[c] | 34.9 | 0.4 | 2.6 | 0.4 | 2.7 | 2.3 |

TABLE VI (Continued)

| | DOE 499A | DOE 499B | DOE 499C | DOE 500A | DOE 500B | DOE 500C | DOE 500D | DOE 500E | DOE 500F | DOE 500G |
|---|---|---|---|---|---|---|---|---|---|---|
| **Liquefaction Conditions** | | | | | | | | | | |
| Operating Mode | SRC I | | | | | | | | | |
| Coal | Amax Belle Ayr | | | | | | | | | |
| Solvent | IBT Single Pass | | | | | | | Reclaimed | | |
| Average Dissolver Temperature, °C | 439 | 439 | 438 | 438 | 439 | 450 | 431 | 430 | 457 | 439 |
| (°F) | (822) | (822) | (820) | (820) | (822) | (842) | (808) | (806) | (855) | (822) |
| Dissolver Pressure, psig | 2250 | | | | | | | | | |
| Residence Time, hr (min) | (15.5) | (29.7) | (46.7) | (10.7) | (5.1) | (10.3) | (10.1) | (10.1) | (10.2) | (10.2) |
| **Solubility of Distillation Residue, wt % in** | | | | | | | | | | |
| Hexane | 27.8 | 32.0 | 43.0 | 36.1 | 34.2 | 29.6 | 36.9 | 27.1 | 37.0 | 37.3 |
| | 29.0 | 34.2 | 42.4 | 38.4 | 34.2 | 32.0 | 38.7 | 29.0 | 36.4 | 36.7 |
| Toluene | 72.5 | 71.1 | 80.3 | 68.0 | 75.2 | 73.4 | 76.4 | 72.3 | 73.1 | 73.1 |
| | 69.3 | 74.2 | 85.2 | 70.0 | 75.6 | 71.5 | 77.9 | 71.4 | 76.9 | 74.9 |
| Pyridine | 99.9 | 99.9 | 99.9 | 99.9 | 99.4 | 99.9 | 99.9 | 99.9 | 99.8 | 99.8 |
| | 99.9 | 99.1 | 99.9 | 99.9 | 99.4 | 99.9 | 99.9 | 99.9 | 99.8 | 99.8 |
| **Ratio of Average Solubilities** | | | | | | | | | | |
| Hexane/Pyridine | 0.284 | 0.333 | 0.427 | 0.373 | 0.344 | 0.308 | 0.378 | 0.281 | 0.368 | 0.371 |
| Toluene/Pyridine | 0.710 | 0.730 | 0.828 | 0.691 | 0.759 | 0.725 | 0.772 | 0.719 | 0.752 | 0.741 |
| **Residue Composition, wt %** | | | | | | | | | | |
| Maltene[a] | 28.4 | 33.1 | 42.7 | 37.3 | 34.2 | 30.8 | 37.8 | 28.1 | 36.7 | 37.0 |
| Asphaltene[b] | 42.5 | 39.5 | 40.1 | 31.8 | 41.2 | 41.7 | 39.4 | 43.8 | 38.3 | 37.0 |
| Preasphaltene[c] | 29.0 | 26.9 | 17.2 | 30.9 | 24.0 | 27.5 | 22.8 | 28.1 | 24.8 | 25.8 |

TABLE VI (Continued)

| | DOE 501R | DOE 502 | DOE 503 |
|---|---|---|---|
| **Liquefaction Conditions** | | | |
| Operating Mode | SRC II | SRC I | SRC I |
| Coal | <-----------Amax Belle Ayr-----------> | | |
| Solvent | Recycled | <------Reclaimed------> | |
| Catalyst | Pyrite | HDS1442 | Ammonium Molybdate |
| Average Dissolver Temperature, °C | 441 | 439 | 442 |
| (°F) | (826) | (822) | (828) |
| Dissolver Pressure, psig | <----------------2250----------------> | | |
| Residence Time, hr (min) | (10.2) | (10.1) | (10.3) |
| **Solubility of Distillation Residue, wt % in** | | | |
| Hexane | 23.7 | 47.3 | 37.8 |
| | 23.5 | 46.1 | 38.4 |
| Toluene | 48.0 | 87.7 | 75.0 |
| | 48.5 | 87.1 | 74.7 |
| Pyridine | 70.8 | 99.6 | 99.2 |
| | 70.8 | 99.6 | 99.2 |
| **Ratio of Average Solubilities** | | | |
| Hexane/Pyridine | 0.333 | 0.469 | 0.384 |
| Toluene/Pyridine | 0.681 | 0.878 | 0.755 |
| **Residue Composition, wt %** | | | |
| Maltene[a] | 23.6 | 46.7 | 38.1 |
| Asphaltene[b] | 24.7 | 40.7 | 36.8 |
| Preasphaltene[c] | 22.6 | 12.2 | 24.4 |

TABLE VI (Continued)

| Liquefaction Conditions | DOE 504RA | DOE 504RB | DOE 504RC | DOE 504RD | DOE 504RE | DOE 504RF | DOE 504RG | DOE 504RH |
|---|---|---|---|---|---|---|---|---|
| Average Temperature, °C (°F) | | | | | | | | |
| First Stage | 454 | 443 | 449 | 451 | 448 | 448 | 449 | 417 |
| (top zone of preheater) | (849) | (829) | (840) | (844) | (838) | (838) | (840) | (783) |
| Second Stage | 420 | 419 | 420 | 421 | 400 | 401 | 420 | 420 |
| (dissolver) | (788) | (786) | (788) | (790) | (752) | (754) | (788) | (788) |
| Pressure | <----------2250----------> | | | | | | | |
| Residence Time, hr (min) | | | | | | | | |
| First Stage | (7.5) | (6.0) | (9.4) | (6.3) | (9.5) | (9.7) | (7.8) | (7.6) |
| Second Stage | 1.87 | 1.52 | 2.37 | 2.39 | 2.39 | 2.45 | 1.96 | 1.90 |
| Titanium Tetraphenoxide Addition Rate, wt % slurry | -- | -- | -- | -- | -- | 0.6 | 0.6 | -- |
| **Solubility of Distillation Residue, wt % in** | | | | | | | | |
| Hexane | 36.6 | 35.1 | 35.0 | 36.1 | 38.2 | 39.6 | 37.1 | 36.7 |
| | 37.3 | 35.6 | 36.2 | 36.7 | 39.1 | 39.8 | 37.1 | 37.0 |
| Toluene | 54.7 | 52.0 | 52.9 | 53.2 | 57.5 | 58.4 | 54.0 | 58.2 |
| | 54.5 | 52.1 | 53.3 | 54.0 | 56.8 | 58.7 | 54.2 | 58.6 |
| Pyridine | 61.4 | 61.0 | 59.5 | 59.3 | 66.5 | 68.1 | 65.0 | 68.1 |
| | 61.7 | 61.0 | 59.5 | 59.4 | 66.4 | 67.4 | 64.6 | 67.9 |
| **Ratio of Average Solubilities** | | | | | | | | |
| Hexane/Pyridine | 0.600 | 0.580 | 0.598 | 0.613 | 0.582 | 0.586 | 0.573 | 0.542 |
| Toluene/Pyridine | 0.887 | 0.853 | 0.892 | 0.903 | 0.860 | 0.864 | 0.835 | 0.860 |
| **Residue Composition, wt %** | | | | | | | | |
| Maltene[a] | 37.0 | 35.4 | 35.6 | 36.4 | 38.7 | 39.7 | 37.1 | 36.9 |
| Asphaltene[b] | 17.7 | 16.7 | 17.5 | 17.2 | 18.5 | 18.9 | 17.0 | 21.7 |
| Preasphaltene[c] | 7.0 | 9.0 | 6.4 | 5.8 | 9.3 | 9.2 | 10.7 | 9.5 |

a) Non-distillable--hexane soluble.
b) Hexane insoluble--toluene soluble.
c) Toluene insoluble--pyridine soluble.

## TABLE VII

### Effect of Residence Time on Processing Belle Ayr Coal

| Run | DOE 500B | DOE 500A | DOE 499A | DOE 499B | DOE 499C |
|---|---|---|---|---|---|
| Residence Time, min. | 5 | 10 | 15 | 30 | 45 |
| Yields, wt % MF Coal | | | | | |
| $C_1$-$C_4$ | 1.1 | 2.3 | 2.5 | 3.6 | 4.6 |
| Total Oil | 23.9 | 21.7 | 19.2 | 23.9 | 23.3 |
| SRC | 43.1 | 52.3 | 46.0 | 43.2 | 44.9 |
| IOM | 18.8 | 13.6 | 14.5 | 12.3 | 8.8 |
| Hydrogen Consumed | 2.0 | 2.9 | 2.6 | 2.7 | 3.1 |

Run Conditions: 440°C, 2250 psig, 36% Belle Ayr coal, 62% solvent, 2% CE pyrite, 2% hydrogen (slurry basis).

## TABLE VIII

### Effect of Temperature on Processing Belle Ayr Coal

| Run | DOE 500D | DOE 500E | DOE 500A | DOE 500C | DOE 500F |
|---|---|---|---|---|---|
| Temperature, °C | 430 | 430 | 440 | 450 | 460 |
| Solvent* | A | B | A | A | B |
| Yields, wt % MF Coal | | | | | |
| $C_1$-$C_4$ | 1.8 | 1.7 | 2.3 | 3.0 | 3.6 |
| Total Oil | 17.8 | 15.7 | 21.7 | 19.5 | 20.3 |
| SRC | 48.3 | 46.9 | 52.3 | 47.8 | 49.2 |
| IOM | 16.0 | 18.7 | 13.6 | 11.9 | 8.7 |
| Hydrogen Consumed | 2.6 | 2.6 | 2.9 | 2.8 | 2.9 |

* Solvent A is SRC I process solvent containing 8% nondistillable material. Solvent B is distillate reclaimed from DOE 499 and DOE 500A-C.

Run Conditions: 10 minutes residence time, 2250 psig, 36% Belle Ayr coal, 62% solvent, 2% CE pyrite, 2% hydrogen (slurry basis).

## TABLE IX

### Effect of Partial Slurry Recycle on Processing Belle Ayr Coal

| Conditions* | DOE 500A | DOE 501R |
|---|---|---|
| Slurry Formulation, wt % | | |
| Belle Ayr Coal | 36 | 36 |
| Recycle Coal Solution | | 31 |
| Solvent | 62 | 31 |
| CE Pyrite | 2 | 2 |
| **Yields, wt % MF Coal** | | |
| $C_1$-$C_4$ | 2.3 | 2.7 |
| Total Oil | 21.7 | 20.0 |
| SRC | 52.3 | 51.6 |
| IOM | 13.6 | 10.4 |
| $H_2$ Consumed (gas balance) | 2.9 | 2.8 |

* Both at 440°C, 10 minutes residence time, 2250 psig.

## TABLE X

### Comparison of Slurry Catalysts on Processing Belle Ayr Coal

| Conditions* | DOE 500G | DOE 502 | DOE 503 |
|---|---|---|---|
| Catalyst | Pyrite | $CoMo/Al_2O_3$ (HDS 1442) | Ammonium Molybdate Emulsion |
| Addition Rate, wt % $FeS_2$ or Mo based on MF coal | 2.5 | 0.60 | 0.60 |
| **Yields, wt % MF Coal** | | | |
| $C_1$-$C_4$ | 2.1 | 2.6 | 2.8 |
| Total Oil | 14.3 | 19.5 | 11.5 |
| SRC | 47.6 | 33.4 | 46.5 |
| IOM | 18.1 | 24.6 | 22.6 |
| Hydrogen Consumed | 2.2 | 3.2 | 2.6 |

* All at 440°C (824°F), 2250 psig and 10 minutes residence time with 36% Belle Ayr coal.

## TABLE XI

## Effect of Pyrite Level on Processing Belle Ayr Coal

| | DOE 500G | DOE 500A |
|---|---|---|
| Pyrite Level | 1% | 2% |
| Solvent* | B | A |
| **Yields, wt % MF Coal** | | |
| $C_1$-$C_4$ | 2.1 | 2.3 |
| Total Oil | 14.3 | 21.7 |
| SRC | 47.6 | 52.3 |
| IOM | 18.1 | 13.6 |
| Hydrogen Consumed | 2.2 | 2.9 |

* Solvent A is SRC I process solvent containing 8% nondistillable material.
Solvent B is distillate reclaimed from DOE 499 and DOE 500A-C.

Run Conditions: 440°C, 10 minutes residence time, 2250 psig, 36% coal.

## TABLE XII

## Effect of Residence Time on the Elemental Analyses and Solubility Data When Processing Belle Ayr Coal

### a. Elemental Analyses

| Run No. | Residence Time, min | Vacuum Distillate % C | Vacuum Distillate % H | Vacuum Distillate % S | Vacuum Distillate % N | Distillation Residue % C | Distillation Residue % H | Distillation Residue % S | Distillation Residue % N |
|---|---|---|---|---|---|---|---|---|---|
| 500B | 5 | 87.95 | 7.47 | 0.40 | 0.69 | 83.99 | 6.22 | 0.53 | 1.54 |
| 500A | 10 | 87.83 | 7.78 | 0.37 | 0.75 | 85.13 | 6.22 | 0.51 | 1.72 |
| 499A | 15 | 87.83 | 7.58 | 0.39 | 0.81 | 85.55 | 6.49 | 0.34 | 1.65 |
| 499B | 30 | 87.80 | 7.79 | 0.34 | 0.76 | 85.73 | 6.19 | 0.32 | 1.73 |
| 499C | 45 | 87.97 | 7.74 | 0.33 | 0.78 | 86.45 | 6.18 | 0.31 | 1.81 |

### b. Solubility of Distillation Residue

| Run No. | Residence Time, min | Wt % Soluble in Hexane | Wt % Soluble in Toluene | Wt % Soluble in Pyridine | Ratio of Solubilities Hexane/Pyridine | Ratio of Solubilities Toluene/Pyridine |
|---|---|---|---|---|---|---|
| 500B | 5 | 34.2 | 75.4 | 99.4 | 0.344 | 0.759 |
| 500A | 10 | 37.3 | 69.0 | 99.9 | 0.373 | 0.691 |
| 499A | 15 | 28.4 | 70.9 | 99.9 | 0.284 | 0.710 |
| 499B | 30 | 33.1 | 72.7 | 99.5 | 0.333 | 0.730 |
| 499C | 45 | 42.7 | 82.8 | 99.9 | 0.427 | 0.828 |

| | | Residue Composition | | |
|---|---|---|---|---|
| | | Maltene[a] | Asphaltene[b] | Preasphaltene[c] |
| 500B | 5 | 34.2 | 41.2 | 24.0 |
| 500A | 10 | 37.3 | 31.8 | 30.9 |
| 499A | 15 | 28.4 | 42.5 | 29.0 |
| 499B | 30 | 33.1 | 39.5 | 26.9 |
| 499C | 45 | 42.7 | 40.1 | 17.2 |

a) Non-distillable--hexane soluble
b) Hexane insoluble--toluene soluble
c) Toluene insoluble--pyridine soluble

## Figure 1

### Particle Size Distribution of C-E Pyrite

a. RM 1003

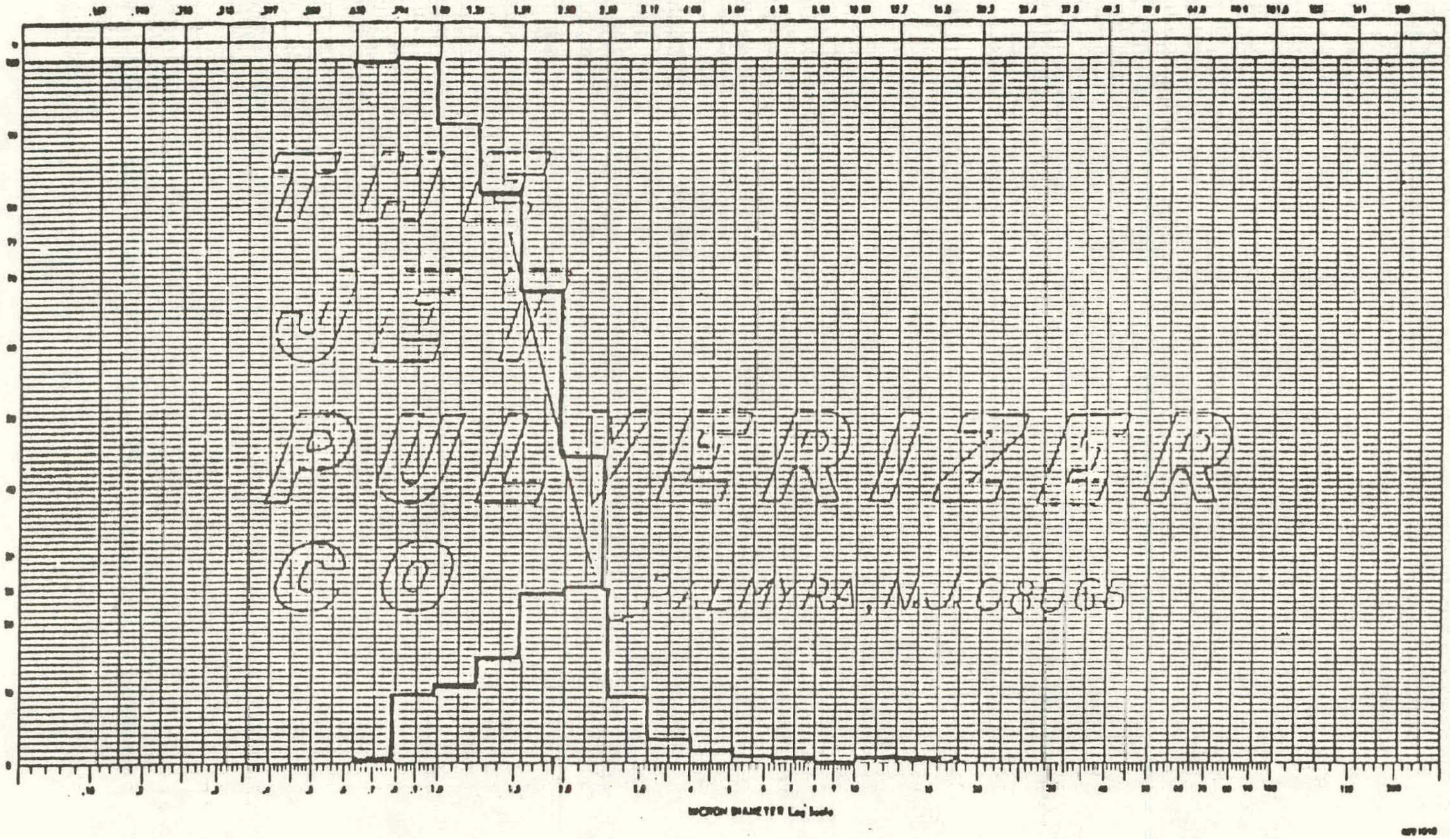


Figure 1 (Continued)

b. RM 1024C

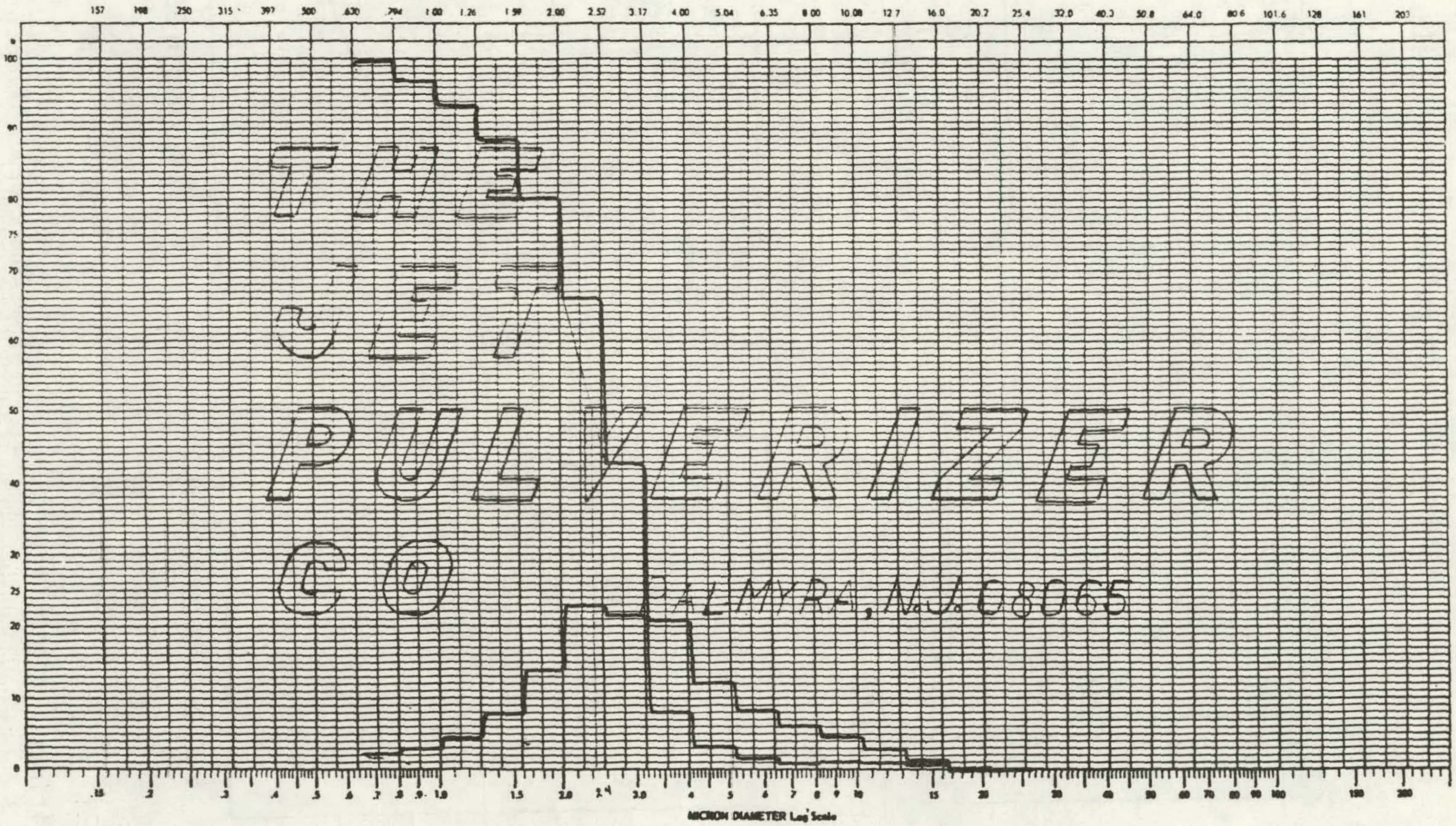
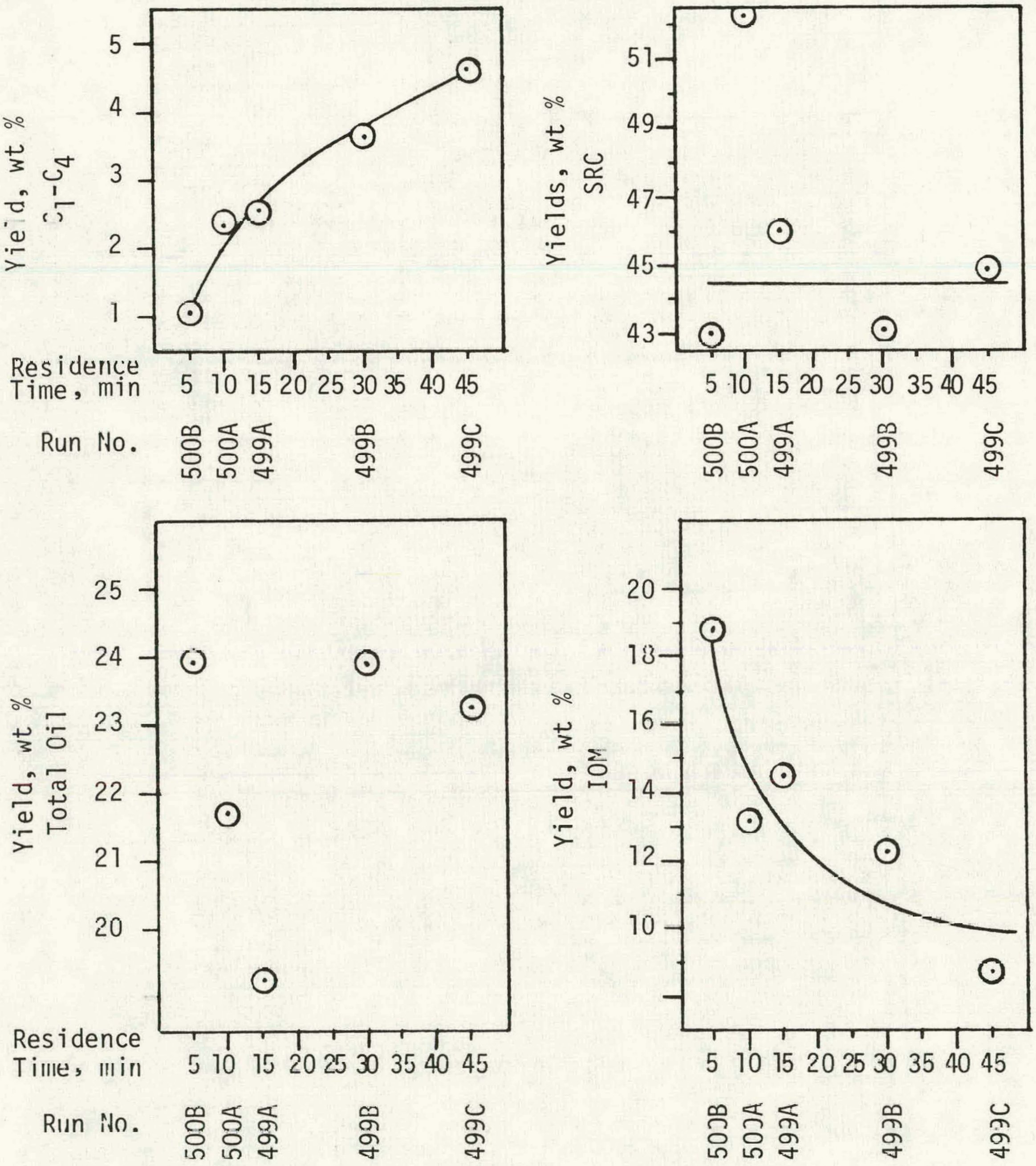


Figure 2

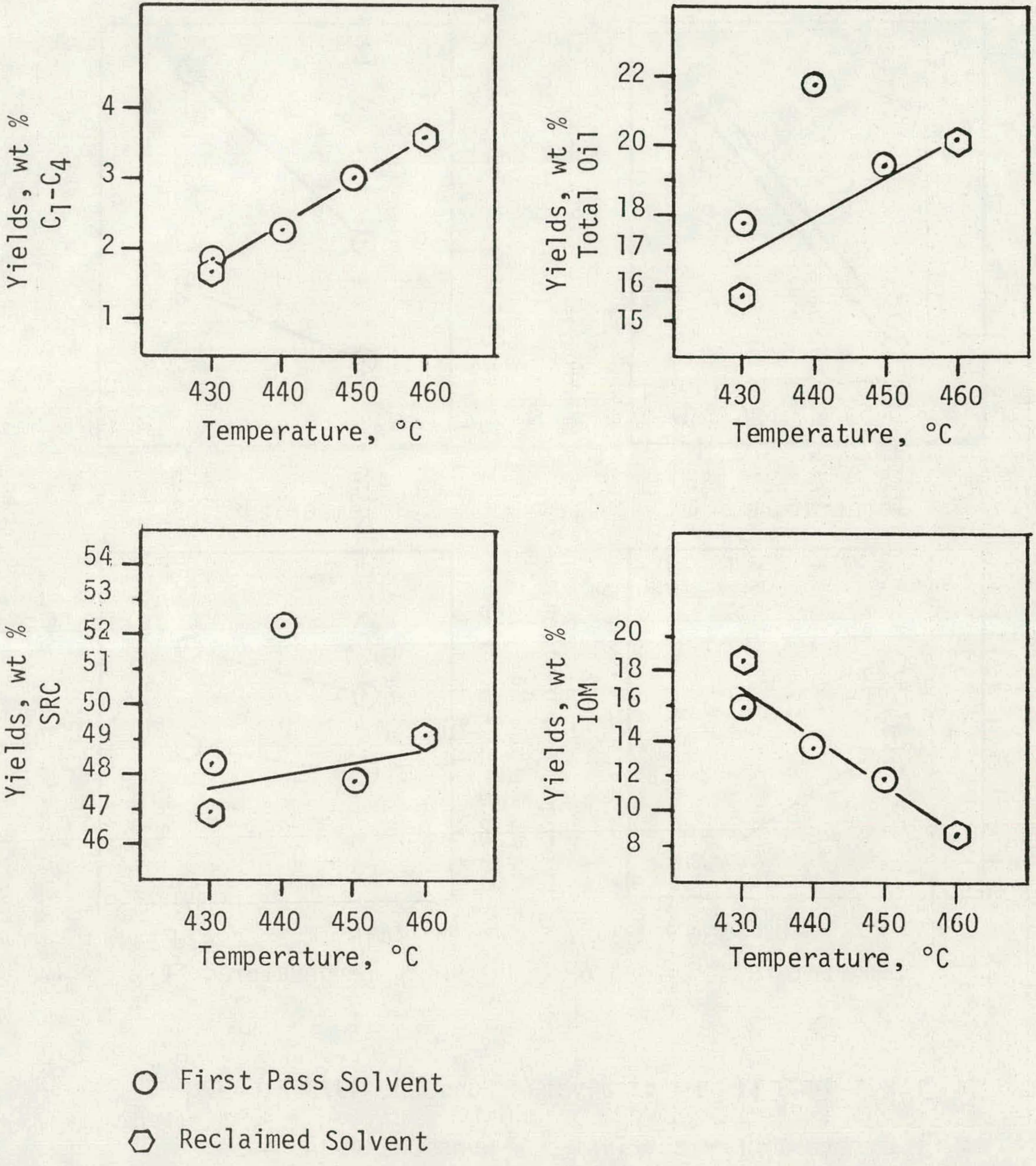
Effect of Residence Time on Belle Ayr Coal Yields*



* Run Conditions: 440°C, 2250 psig, 36 wt % coal, 62% solvent, 2% C-E Pyrite

Figure 3

Effect of Temperature on Yields with Belle Ayr Coal*



* Run Conditions: 10 minutes residence time, 2250 psig, 36 wt % coal, 62% solvent, 2% C-E Pyrite, 2 wt % $H_2$.

Figure 4

Effect of Temperature and Catalyst on Yields using SRC Derived from Illinois #6 Coal

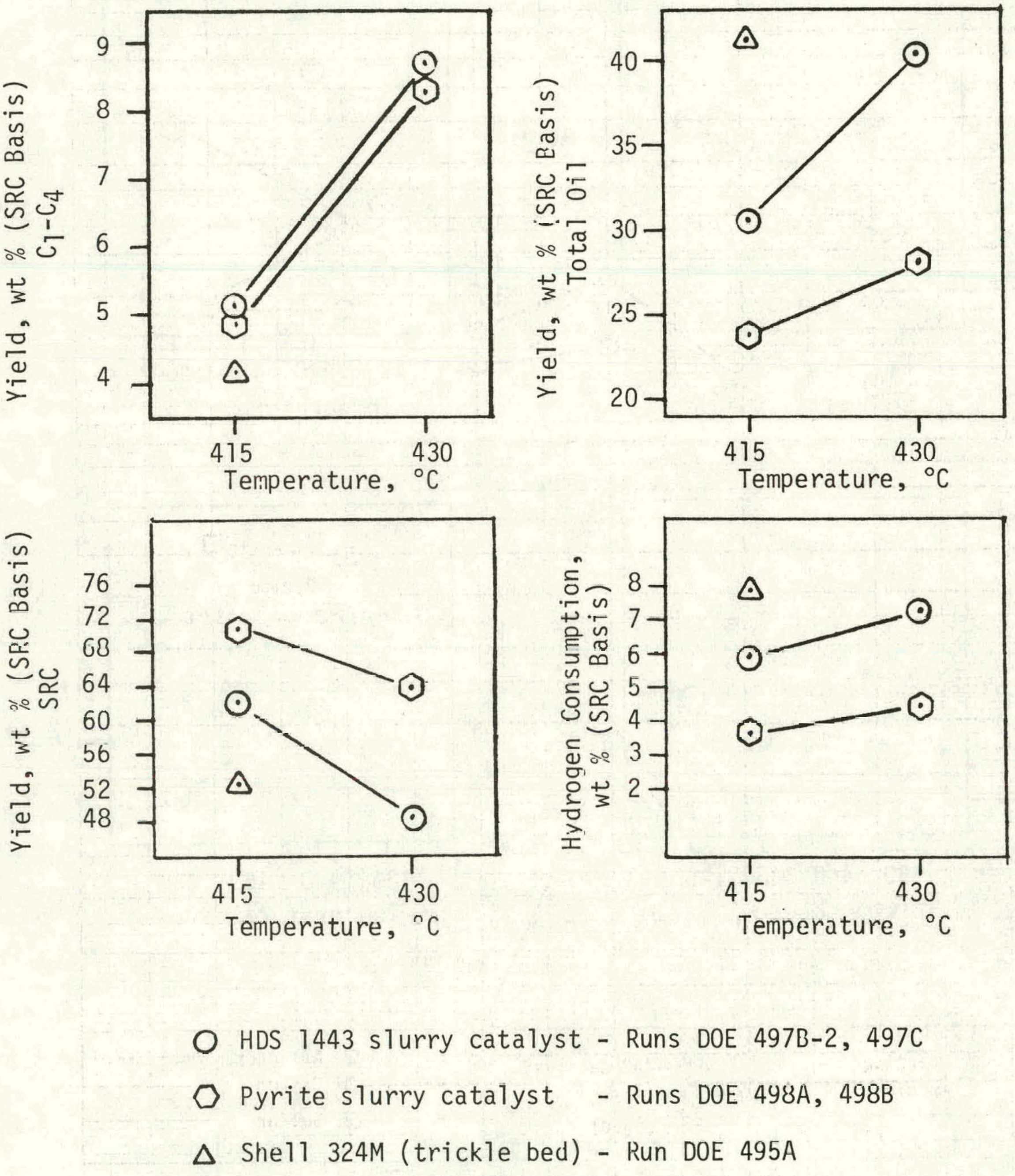


Figure 5

Effect of Catalyst and Temperature on the Elemental Analysis of the Distillation Residue

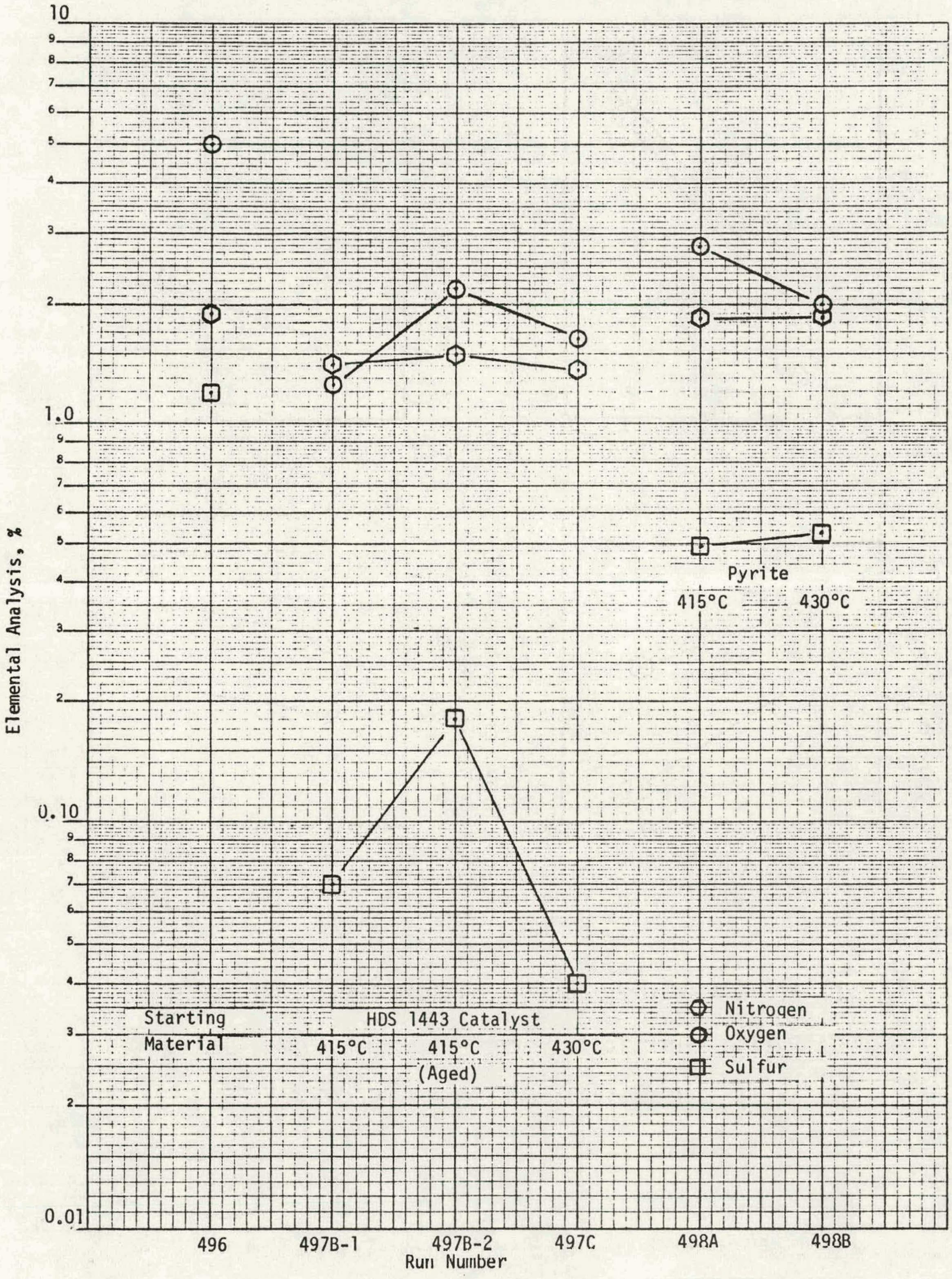
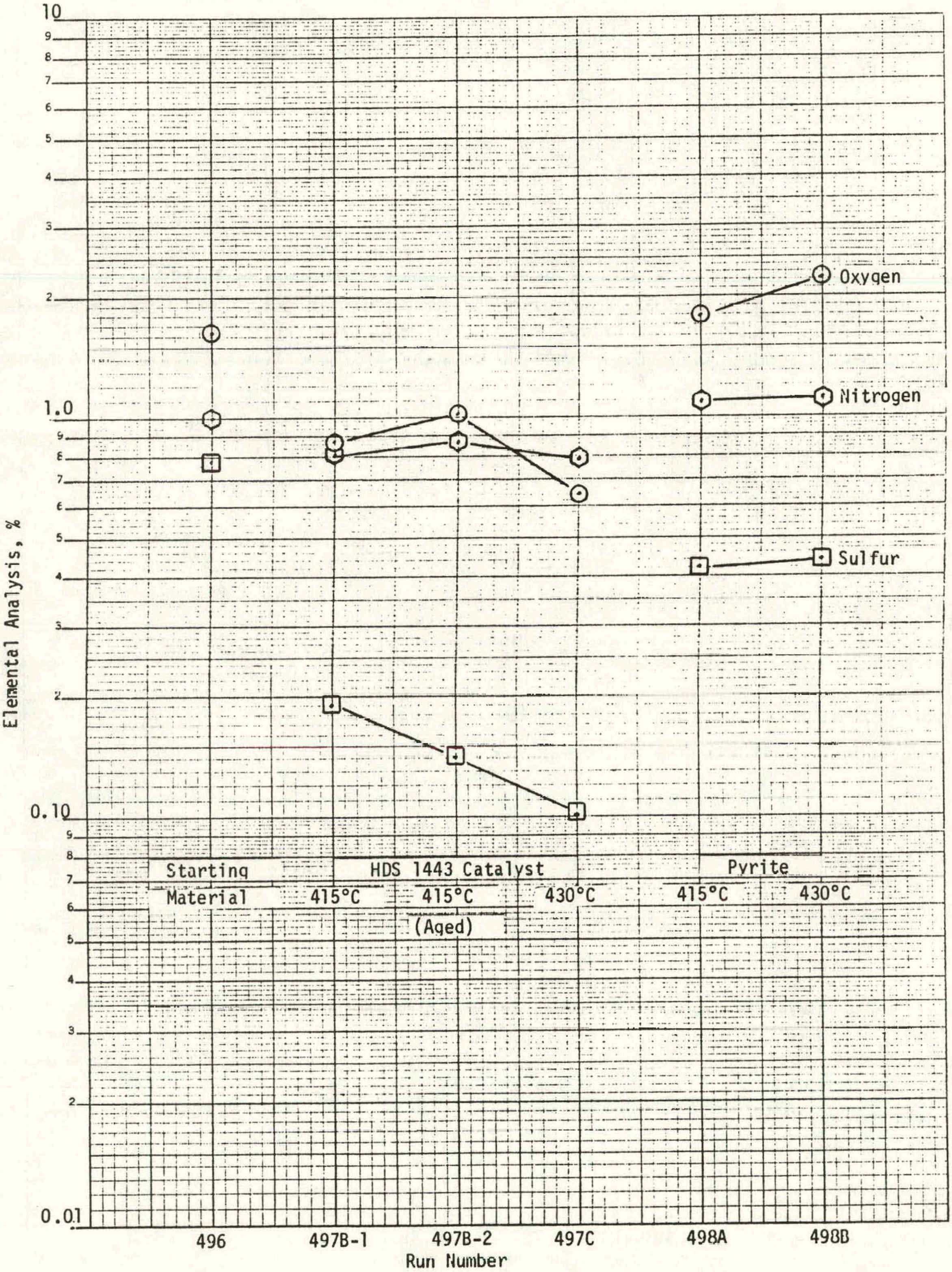


Figure 6

Effect of Catalyst and Temperature on the Elemental Analysis of Distillate Oils



# APPENDIX A

# CHARACTERIZATION OF DISTILLATE PRODUCTS

## A.1 Short Contact Time versus SRC I Coal Dissolution Stages (Runs DOE 493-495D)

### A1.1 Introduction

This series of experiments was done to study the catalytic hydrogenation of stripped filtrate made in the short contact time operating mode and to compare its reactivity to filtrate made in the normal SRC I operating mode. Burning Star coal was used with stripped SRC II solvent made at Fort Lewis (lot 2335). The short contact time run (DOE 493) was done with 6.0 minutes nominal retention time at 450°C and with 2250 psig pressure. The conventional SRC I process was run with the same coal and solvent but with 30 minutes retention time at 2250 psig and with 450°C reactor temperature. In each case, the high temperature, high pressure separator bottoms product was filtered and stripped to a nominal 1:1 proportion of distillation residue to residual solvent.

The short contact time stripped filtrate was hydrogenated in experiment DOE 495A and the conventional SRC I stripped filtrate was hydrogenated in experiment DOE 495B. In order to study the effect of more conversion, the product from DOE 495B was reprocessed in run DOE 495C and the product from part A was reprocessed in DOE 495D.

Light oil blends (high temperature, high pressure separator overheads) were prepared to represent each of these experimental segments. In addition, the oil recovered by distillation of the hydrogenated filtrate samples (high temperature separator bottoms) was also analyzed. The basic nitrogen analysis was used to follow the course of the experiment by titration of a number of distillates during the runs. This allowed some information to be developed regarding the catalyst activity and the repeatability of the hydrogenation. Selected samples were analyzed for elemental composition as well.

### A1.2 Process Control

In order to control temperature in the catalyst bed, it was necessary to blend 1 part of recycle hydrogenated product with 1 part of fresh stripped filtrate. This return of material consumed some of the hydrogenated product. The remainder was split into two parts, one being distilled to reclaim the oil and determine the ratio of distillate to residue being obtained, and the other stored for some future application. The distillate oil was titrated for basic nitrogen content as it was obtained, and these values were used to determine if the catalyst remained stable and to obtain a preliminary indication of the effect of the variables in the experiment.

### Basic Nitrogen Content of Run DOE 495 Vacuum Distillates

| | Product Number | % Basic Nitrogen | | Product Number | % Basic Nitrogen |
|---|---|---|---|---|---|
| Part A | | | Part D | | |
| SCT Product | 11 | 0.0605 | Rework A | 93 | 0.0176 |
| | 15 | 0.0654 | | 97 | 0.0175 |
| | 20 | 0.0605 | | | |
| | 25 | 0.0586 | | | |
| | 30 | 0.0629 | | | |
| | 34 | 0.0688 | | | |
| | 38 | 0.0628 | | | |
| | 39 | 0.1268 | | | |
| Part B | | | Part C | | |
| SRC I Product | 46 | 0.0863 | Rework B | 81 | 0.0429 |
| | 50 | 0.0886 | | 85 | 0.0244 |
| | 60 | 0.0935 | | 88 | 0.0212 |
| | 64 | 0.1092 | | | |
| | 68 | 0.1111 | | | |
| | 71 | 0.1162 | | | |
| | 76 | 0.1073 | | | |

## A1.3 Results of Elemental Analyses

The elemental analyses of the light oil blends from the filtrate preparations are presented below. It can be seen that the compositions of the light products is not greatly influenced by the choice of short contact time or normal SRC I operating mode. The results are presented for oils which have been redistilled and washed in our usual procedure to eliminate the effect of dissolved ammonia and hydrogen sulfide.

| | DOE 493 | DOE 494 |
|---|---|---|
| Residence Time, min. | 6 | 30 |
| Composition, wt % | | |
| Carbon | 86.07 | 85.76 |
| Hydrogen | 9.26 | 9.77 |
| Nitrogen | 0.78 | 0.70 |
| Sulfur | 0.45 | 0.58 |
| Oxygen | 3.44 | 3.19 |
| Basic Nitrogen | 0.616 | 0.531 |
| Saturates by ASTM D 1019 (volume %) | 12 | 20 |

The elemental analyses of light oil blends from hydrogenation of the stripped filtrates are presented below. Conditions used allowed for extensive hydrogenation of the filtrate and the light oils produced were comparatively low in heteroatom content. The Kjeldahl method for determining total nitrogen is near its lower limit for these samples, while the basic nitrogen titration can still be done with good precision. Probably the results from the titration should be given more weight in comparison of these results.

| Composition, wt % | DOE 495A | DOE 495B | DOE 495C | DOE 495D |
|---|---|---|---|---|
| Carbon | 87.26 | 86.99 | 88.20 | 88.00 |
| Hydrogen | 12.57 | 11.87 | 11.43 | 11.76 |
| Nitrogen | 0.035 | 0.07 | 0.06 | 0.01 |
| Sulfur | 0.11 | 0.02 | 0.03 | 0.06 |
| Oxygen | 0.025 | 1.05 | 0.28 | 0.17 |
| Basic Nitrogen | 0.0277 | 0.0620 | 0.0448 | 0.0078 |
| Saturates by ASTM D 1019 (volume %) | 68 | 53 | 50 | 54 |

The elemental analyses of the oils reclaimed by vacuum distillation of the hydrogenated filtrates are presented below for one sample chosen from representative portions of each run.

| Composition, wt % | DOE 495A(34) | DOE 495B(76) | DOE 495C(88) | DOE 495D(97) |
|---|---|---|---|---|
| Carbon | 89.49 | 89.41 | 89.41 | 89.05 |
| Hydrogen | 10.15 | 9.60 | 10.39 | 10.54 |
| Nitrogen | 0.13 | 0.19 | 0.05 | 0.04 |
| Sulfur | 0.05 | 0.06 | 0.01 | 0.02 |
| Oxygen | 0.18 | 0.74 | 0.14 | 0.35 |
| Basic Nitrogen | 0.0688 | 0.1073 | 0.0212 | 0.0175 |
| Saturates by ASTM D 1019 (volume %) | 23 | 13 | 23 | 23 |

## A1.4 Discussion of Elemental Analysis Results

The light oils derived from either of the SRC processes are rich in functional groups containing sulfur, nitrogen or oxygen. There is little difference whether this is made in short contact time or normal reaction time mode. It is not possible to assign quantities to the amounts made from the solvent or made from the coal. From experience with well hydrogenated solvent reported previously, it is evident that some of the material is made from each. The appearance of this much function in the light oil is evidence that the volatile products escape from the reactor quickly in the vapor phase. It is evident that reduction of these compounds is prevented by rapid removal of the substances in the vapor phase. The normal contact time product contains more hydrogen and saturates.

The filtrate was stripped to 175°C at 2mm pressure, removing the most volatile half of the residual solvent. When the residue was hydrogenated with the Shell catalyst at 415°C, the yield of light oil was moderate due to the small cracking tendency of this modified catalyst. The feedstock was heavy enough to remain in contact with the catalyst and to allow effective hydrogenation of the residual solvent as well as the nondistillable components derived from the coal. The modest amount of light oil made was extensively converted, being rich in saturates and low in residual heteroatoms. The short contact time material was processed first and produced a light oil with only 0.028 percent of basic nitrogen, and a distillate oil averaging between 0.06 and 0.07 percent basic nitrogen. The normal contact time stripped filtrate was processed second. Both the light oil and the reclaimed distillate contained increased amounts of basic nitrogen. Some decline in catalyst activity may be involved, but the step increase in nitrogen content suggests that the normal contact time material is more refractory, resisting denitrogenation by comparison to the behavior of the short contact time material. This is also confirmed by the reprocessing experiments in which the order of feed was reversed, the normal contact time product being fed before the short contact time product. In this case, the nitrogen content of the material made from the short contact time product is again lowest even though it is made last (with the most aged catalyst). This pattern is also seen in the distillate oils.

### A1.5 Liquid Chromatographic Results*

The light oils were chromatographed using four amine columns in series and the elution program developed to maximize resolution. The oils from the filtrate preparations were injected as 10% solutions in hexane while the more hydrogenated materials made in the filtrate hydrogenation procedures were run at higher concentrations to allow inspection of traces of nitrogen and oxygen containing materials left in the products.

Figure A-1 is the display for DOE 493 light oils. Because of the low concentration of saturates present, it was possible to run the refractive index detector (right hand side of chart) at 16X throughout the whole useful range. This chart has been offset to make room for the rather large third peak area on the UV detector chart (left hand side of chart). These peaks have been numbered to allow easy correlation of the two detectors. The first RI detector peak is due to saturates and shows three well resolved shoulders. Peak 2 is a composite of compounds probably limited to one residual aromatic ring and peak 3, which is a composite of more aromatic materials, is the most abundant group in the hydrocarbon array. Volatility of higher materials is too low for much of this kind of material to appear in the light oil blend. A rich array of peaks is observed in the basic nitrogen region ( 80-140 min.) and again in the phenols region (140-250 min.). It is clear from this chart that an abundance of polar material is contained in the light oil blend.

Figure A-2 is the display for DOE 494 light oils. It was run at conditions matching the first chart. The first RI peak due to saturates is observed to be about half again larger than was observed for the short contact time product. The second peak is a little smaller, while the third is slightly larger. The same array of materials is present throughout the hydrocarbon array in each case and only the relative amounts have been shifted as noted. A considerable difference appears in the normal contact time product (Figure A-2) in the area just following

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* The liquid chromatography method was discussed in "Research on Solvent Refined Coal," Technical Progress Report for the Period April 1, 1982 through July 31, 1982; October 1982, PC40005-23; Appendix B.

the methylene chloride solvent front. (This is at 80 to 84 minutes retention time). The peaks in this area are considerably stronger for the normal contact time product. Throughout the basic nitrogen and the phenols region, the same array of peaks appears on both charts. The relative intensity of several peaks changes in response to the increase in reaction time in the normal SRC I mode.

The light oil blend originates by distillation of materials from the solvent and by thermal decomposition of the coal and the solvent as well. It is not possible to assign the origin of a component to solvent, or to coal in these cases, since the solvent has considerable heteroatom content which could appear in the volatile products. The differences from one case to the other appear to be differences in amounts and not in a tendency for different substances to be made.

The filtrate was vacuum stripped to 175°C at 2mm. When hydrogenated over a catalyst, the coal derived material reacts but a major consumption of reagent must be by the residual solvent boiling over the 175°C cut point. This makes up half of the feedstock. Again the light oils obtained originate in the hydrogenation products of both the coal and the solvent, but the probability is that the solvent is the major contributor. The liquid chromatographic studies were, therefore, extended to analysis of both the light blend and the oil reclaimed by distillation of the hydrogenated filtrate. The light oil blends will be discussed first.

The light oil from run DOE 495A is shown in Figure A-3. The elemental analysis indicated high conversion to hydrogenated material and this is confirmed by the large size of the peak for saturates (which is the first peak on the refractive index detector). The low concentration of heteroatoms shown in the elemental analysis is also a factor, these charts being run with samples at 25% concentration rather than at 10% as has usually been done in the past. This allows enough polar material to be injected to show the location of the traces of residual material present. The saturates peak is run at 128X and the second peak and the remainder of the RI chart at 16X. The saturates and the 3-double-bond region account for most of the hydrocarbons present. After 64 minutes, the UV detector was set to 0.05 absorbance units full scale (AUFS). The solvent front due to methylene chloride is at 80 minutes and is followed by several peaks in the 80 to 88 minutes region. These substances have not been identified, though peaks for hydrocarbons in this region usually correspond to fully aromatic hydrocarbons with several rings. Identification by trapping and subsequent analysis may be difficult at this low concentration but has not been done in any case. Peaks in the basic nitrogen region, corresponding to hydrogenated quinolines and related compounds, are of very low intensity. This is also true for the peaks in the region associated with phenols.

The light oil blend from run DOE 495B is shown in Figure A-4. This sample was run at 25% concentration in hexane with all conditions matching the DOE 495A sample. At 128X the first peak on the refractive Index chart is a little smaller and the second peak is a little larger than the corresponding peaks in the DOE 495A case. Thus, the instrumental method agrees with the results shown by the ASTM method for saturates and adds the information that the difference is mostly due to more 3-double-bond material in the hydrocarbon array. The whole array tends to contain slightly more of each of the aromatic species observed in the case of the DOE 495A sample. The area just following the methylene chloride front contains several peaks strong enough to run off scale or nearly full chart width on the 0.05 AUFS sensitivity. The basic nitrogen region also shows a number of well-defined peaks which are substantially stronger than those in the DOE 495A sample. Peaks in the phenols region are not enhanced, however.

The light oil blend from run DOE 495C is shown in Figure A-5. This sample was made by reprocessing the product from DOE 495B. The chromatograms for DOE 495B and C are similar. The peaks just following the solvent front were left at 0.5 AUFS to avoid the risk that they would run off scale. It appears that this would have been the case. It appears that the peaks in the phenols region are smaller while only minor differences can be seen in the basic nitrogen region.

The light oil blend from run DOE 495D is shown in Figure A-6. This sample results from reprocessing the filtrate hydrogenated in DOE 495A. Again, the chromatograms from A and D resemble each other and differ from the set obtained in DOE 495B and C. The reprocessing procedure made a light oil which looks a little less saturated and which has more of the 3-double-bond group of compounds in it. The group of compounds emerging just after the methylene chloride front is also a little stronger. The basic nitrogen region and the phenols region contain only weak peaks near the limit of observation at this concentration and wavelength.

Based on the light oil blends, the short contact time material seems to be more readily reduced (in heteroatoms) in both the first and second pass hydrotreating runs than was the case for the normal contact time material. This is supported by the results of the basic nitrogen titration and by the liquid chromatography analysis of the light oils distilled as the hydrogenated product is flashed from the reactor. The elemental analysis and basic nitrogen results available suggest that the same pattern is present in the oils distilled under vacuum from the hydrogenated product. It was, therefore, considered necessary to analyze these materials as well.

The vacuum distillate from run DOE 495A is shown in Figure A-7. This oil contains less saturated material than the corresponding light oil blend and produces a similar size peak at 64X on the RI detector as the peak at 128X for the light oil blend. Some difficulty was experienced in attempting to run the ASTM D 1019 method for saturates, as the sample tended to overheat. The method was modified to moderate the reaction by adding the oil to some sulfuric acid to partly react the sample, then adding the sulfuric acid-$P_2O_5$ reagent to the partly reacted sample. The value obtained may be a reasonable result based on the size of the first RI peak. The second RI peak is larger than the corresponding peak for the light oil blend also. The UV trace shows that the more aromatic components are present at higher concentrations also. The peak which emerges with the methylene chloride solvent front was run at 0.5 AUFS and is comparatively large. A series of moderate size peaks is found in the basic nitrogen region and little indication of phenolic material is evident. The correspondance in peak location on the chart for the distillate oil and the light oil blend chart is not close, suggesting that not much transfer of compounds from one boiling range to the other is involved here. In this catalytic reaction, the light oil is well reduced and the heavy oil remaining in contact with the SRC* is also being reduced with good effect. The amount of material observed by the basic nitrogen titration correlates with the amount of material observed in the basic nitrogen region of the liquid chromatogram.

The vacuum distillate from run DOE 495B is shown in Figure A-8. The liquid chromatographic analysis of this oil agrees with the results from elemental analysis and titration for basic nitrogen, that the normal contact time material was not as effectively hydrotreated as the short contact time product. The saturates peak is smaller and the hydrocarbon array is more aromatic in character. This is observed by comparison of the amount of material eluting in the last part of the array (between 60 and 80 minutes, for example). The peaks following the methylene chloride front are larger as well. The peaks in the basic nitrogen region are stronger with three peaks (retention times of 110, 116 and 122 minutes) tending to emerge stronger than the rest. These are observed in the light oil blend suggesting that the vapor pressure of these materials is sufficient to cause some distillation to the light oil flash. Peaks in the phenols region are quite weak.

The vacuum distillate from run DOE 495C is shown in Figure A-9. This material was made by reprocessing the product from DOE 495B in which the normal retention time filtrate was hydrogenated. When this material was reprocessed, the hydrogenation of the heavy oil increased and the basic nitrogen content decreased. The first peak on the RI chart increased in height, and the second peak is also larger. The UV trace shows that the areas due to the more aromatic substances in the hydrocarbon array decrease as would be expected if the product were more completely hydrotreated. The substantial decrease in the basic nitrogen content shown by the titration is confirmed by the marked reduction of the peaks in the 100 minute to 130 minute retention time region. These peaks are quite a bit smaller than those in the corresponding light oil blend. Possibly this is an indiction of inadequate flushing of the sample receivers for the flash components, particularly since the pattern of the basic compounds resembles the pattern in the part B light oil blend. An alternative cause could be the retention of quite a bit of this kind of material in the feed (see the distillate oil for DOE 495B and compare to the DOE 495C light oil blend). If contact is inadequate, this material may vaporize and be observed in the flashed oil. A longer run would be required to determine the mechanism involved.

The vacuum distillate from run DOE 495D is shown in Figure A-10. As would be expected from the increase in hydrogen content, the first peak in the RI detector chart is the strongest response for saturates in this set of samples. The second peak is reduced in intensity and the remainder of the hydrocarbon array is reduced in response compared to the DOE

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* Product which is nondistillable but soluble in product oil.

495A vacuum distillate or to the DOE 495C vacuum distillate. It is evident that reprocessing this material has removed most of the basic nitrogen function which can be observed at this sensitivity. Only trace peaks can be observed in the phenols region.

### A1.6 Discussion

It is evident that a difference in reactivity exists when the short contact time filtrate is compared to the normal contact time filtrate. More conversion is obtained in the longer reaction time of the conventional SRC I process and a more hydrogenated product with a higher oil yield is obtained in the first step. This does not help in the second stage where the filtrate is catalytically hydrogenated, however. Here the reactivity of the short contact time filtrate appears higher and nitrogen removal is more complete. When the materials are reprocessed (to effectively double the reaction time), the advantage of the short contact time appears to be retained though the longer time tends to bring both feedstocks to more nearly the same end composition.

The cause for this difficulty with the normal retention time product is obscure. When the composition of the vacuum bottoms (VB) is considered, the short contact time material contains more sulfur and less nitrogen per unit weight. The short contact time VB has 1.33% sulfur and 1.94% nitrogen in it (with 5.58% oxygen by difference). The normal contact time VB has 0.83% of sulfur and 2.10% nitrogen in it (with 4.33% oxygen by difference). It seems probable that similar behavior will be associated with the solvent range oils. Thus, the thermal chemistry of the poorly catalyzed step results in the preferential elimination of sulfur and oxygen and in the concentration of nitrogen as the reaction time is increased. The nitrogen remaining may also be the more thermally stable material or even rearrangement to more stable molecules may be a factor.

## A.2 Comparison of Fixed Bed and Slurry Catalyst (Runs DOE 496-498B)

### A2.1 Introduction

This sequence of runs was started with a short contact time conversion of Burning Star coal using the lot 2397 solvent made at Fort Lewis. The coal concentration was 36% and the nominal retention time was 6.0 minutes using 450°C reactor temperature and a pressure of 2250 psig. These conditions match previous preparations, the only difference in the operation being the substitution of a different lot of SRC II derived oil as solvent. The solution obtained was filtered and then stripped to make a feedstock with about 50% of distillation residue and 50% of distillate oil. All of the stripped products were blended to make a uniform feedstock which was then used in runs DOE 497 and DOE 498.

About half of the feedstock was used for DOE 497. The objective in this run was to use powdered HDS 1443 nickel molybdenum on alumina catalyst in an upflow reactor. A limited supply of this material was available;

therefore, it was necessary to reclaim and reuse the catalyst. This was also done to study aging effects (with any effect of the reclaim procedure added in). It was found that a feed rate of 2.5% catalyst and a reactor temperature of 415°C appeared to develop a system with operating characteristics which could be sustained with the amount of catalyst at hand. A considerable amount of the catalyst fed initially remained in the reactor based on input rates and output rates observed. A steady condition could be sustained at the 2.5% rate while the 5% rate initially used seemed to be too high to sustain. The feed slurry consisted of 1:1 fresh filtrate to recycle and retention time was 2.0 hours which matches the pump rate used in the trickle-bed catalyst runs.

DOE 497B-1: During this part of the experiment the catalyst consisted of some fresh material and some reclaim catalyst as required. The reactor was run at 415°C.

DOE 497B-2: During this part of the experiment, the catalyst consisted of only recycle catalyst. This was reclaimed by toluene washing the catalyst recovered by filtration and rinsing the toluene away with acetone then air drying. The reactor was run at 415°C.

DOE 497C: The reactor temperature was increased to 430°C while the catalyst return procedure developed and used in part A-2 was continued.

All of the components of the reactor were taken apart and thoroughly cleaned to remove catalyst residues before going to the pyrite catalyzed experiment, DOE 498. The remaining half of the feedstock made in DOE 496 was consumed in this work.

The first part of DOE 498 was lined out with 2.5% pyrite in the feed slurry. The reactor temperature was set at 415°C to match the condition in 497A-2. The pyrite was not reclaimed and reused since plenty was available to work in a single-pass mode.

The second experiment used pyrite at the same concentration and the temperature of the reactor was raised to 430°C. This then compares pyrite with the HDS 1443 catalyst at the higher temperature using the same feedstock and operating conditions.

In both runs with either the HDS 1443 catalyst or with pyrite, the operation was managed to allow an accounting of the amount of catalyst fed and the amount of catalyst recovered from products. Any product removed from the system was filtered and the used catalyst was reclaimed, washed and dried. These data allowed a preliminary estimate of the amount of catalyst settled in the reactor, which appeared to be about 30% by weight of total material in the reactor in either case.

## A2.2 On Line Observations of Product Oil

During these experiments the oil reclaimed by distillation of the high temperature separator bottoms (HTSB) product to 270°C at 2.0 mm was titrated with perchloric acid to determine the basic nitrogen content. The behavior of the catalyst could thus be followed during the course of the run. The HDS 1443 catalyst in the upflow system was not as effective as the Shell catalyst in the trickle-bed mode*. This is thought to be largely due to the effect of mixing and the less favorable concentration of catalyst relative to the charge being reacted. Differences in catalyst activity may be present but are not considered to be the controlling factor. Pyrite in the same configuration is considerably less effective in nitrogen and sulfur removal. The basic nitrogen results (in weight %) for the distillate oil follow:

| Product Interval | DOE 497B-1 | Product Interval | DOE 498A |
|---|---|---|---|
| 11 | 0.476 | 5 | 0.476 |
| 10 | 0.414 | 8 | 0.507 |
| 19 | 0.419 | 14 | 0.571 |
| 25 | 0.425 | 18 | 0.574 |
| 29 | 0.428 | 23 | 0.590 |
| 33 | 0.438 | 27 | 0.596 |
| 38 | 0.449 | 31 | 0.599 |
| | | 33 | 0.602 |
| | DOE 497B-2 | 37 | 0.613 |
| 42 | 0.457 | | |
| 46 | 0.463 | | DOE 498B |
| 50 | 0.475 | 41 | 0.598 |
| 55 | 0.472 | 46 | 0.603 |
| | | 50 | 0.611 |
| | DOE 497C | 54 | 0.625 |
| 65 | 0.428 | 57 | 0.599 |
| 70 | 0.427 | 58 | 0.606 |
| 73 | 0.441 | | |

The oil left in contact with the distillation residue in the stripped filtrate feed was reported to have the following analysis: carbon 89.32%, hydrogen 7.27%, sulfur 0.78%, nitrogen 1.00% and oxygen by difference 1.63%. The distillation residue had an analysis of: carbon 85.89%, hydrogen 5.70%, nitrogen 1.91%, sulfur 1.19%, ash 0.34% and oxygen by difference 4.97%. Since the filtrate contained an average of 51.45% of distillable oil, the computed composition of the feed is as follows: carbon 87.66%, hydrogen 6.51%, nitrogen 1.64%, sulfur 0.98% and oxygen by difference 3.21%.

## A2.3 Elemental Analysis of Light Oil Composites

The high temperature separator overheads from the short contact time filtrate preparation step were redistilled and the light fractions were washed with water as usual to eliminate the dissolved ammonia and hydrogen sulfide. The fractions were then analyzed and the composition of the

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* Run DOE 495A, see previous section.

clean sample was calculated. The combined sample was used for determination of the basic nitrogen and for the liquid chromatographic analysis. To save labor the recombined sample was used for elemental analysis as well as for the basic nitrogen and saturates determination for all of the flash condensates from the catalytic runs. These results follow:

| Composition, wt % | DOE 496 | DOE 497B-1 | DOE 497B-2 | DOE 497C | DOE 498A | DOE 498B |
|---|---|---|---|---|---|---|
| Carbon | 86.42 | 87.98 | 87.48 | 87.88 | 86.15 | 86.14 |
| Hydrogen | 9.62 | 10.04 | 10.20 | 10.33 | 9.17 | 9.13 |
| Nitrogen | 0.54 | 0.53 | 0.60 | 0.55 | 0.77 | 0.90 |
| Sulfur | 1.07 | 0.06 | 0.08 | 0.05 | 0.12 | 0.21 |
| Oxygen | 2.35 | 1.39 | 2.24 | 1.19 | 3.79 | 3.62 |
| Basic Nitrogen | 0.365 | 0.394 | 0.456 | 0.406 | 0.582 | 0.668 |
| Saturates ASTM, (volume %) | 16 | 26 | 26 | 29 | 16 | 16 |

### A2.4 Elemental Analysis of Vacuum Distillate Oils and Distillation Residues

The elemental analyses for the distillate oils and distillation residues recovered from vacuum distillation of the filtrate feed or hydrogenated product are presented in the following tables:

| Vacuum Distillate Composition, wt % | DOE 496 | DOE 497B-1 | DOE 497B-2 | DOE 497C | DOE 498A | DOE 498B |
|---|---|---|---|---|---|---|
| Carbon | 89.32 | 89.91 | 89.73 | 90.18 | 89.20 | 88.50 |
| Hydrogen | 7.27 | 8.22 | 8.25 | 8.29 | 7.51 | 7.74 |
| Nitrogen | 1.00 | 0.81 | 0.87 | 0.79 | 1.09 | 1.11 |
| Sulfur | 0.78 | 0.19 | 0.14 | 0.10 | 0.42 | 0.44 |
| Oxygen | 1.63 | 0.87 | 1.01 | 0.64 | 1.78 | 2.21 |
| Basic Nitrogen | 0.52 | 0.45 | 0.47 | 0.44 | 0.60 | 0.61 |
| Saturates ASTM (volume %) | 1-2 | 3-4 | 4 | 4-5 | 2 | 2 |

| Distillation Residue Composition, wt % | DOE 496 | DOE 497B-1 | DOE 497B-2 | DOE 497C | DOE 498A | DOE 498B |
|---|---|---|---|---|---|---|
| Carbon | 85.89 | 90.36 | 89.26 | 90.28 | 88.20 | 88.50 |
| Hydrogen | 5.70 | 6.88 | 6.81 | 6.47 | 6.49 | 6.66 |
| Nitrogen | 1.91 | 1.40 | 1.49 | 1.36 | 1.84 | 1.85 |
| Sulfur | 1.19 | 0.07 | 0.18 | 0.04 | 0.49 | 0.53 |
| Ash | 0.34 | 0.04 | 0.09 | 0.13 | 0.18 | 0.49 |
| Oxygen | 4.97 | 1.25 | 2.17 | 1.62 | 2.80 | 1.97 |

It can be seen that the HDS 1443 catalyst in this operating mode was effective in removing sulfur from both the oil phase and the distillation residue. A decline in activity is observed with use, and this loss is compensated for by the temperature increase. Pyrite in the same operating mode is not effective in nitrogen removal but has considerable effect on sulfur and oxygen removal. At the higher temperature it appears that pyrite may cause formation of oil which moves to the distillate category with functionality intact.

## A2.5 Inspections by Liquid Chromatography

For the past few months we have concentrated on the composition and the chromatographic analysis of the light oil composite representing the materials flashed at reactor pressure and near the operating temperature of the reactor. It was hoped that this kind of sample would give some advantage in considering the reactions which result in the formation of cracking products or certain substances which appear to form at low molecular weight and which carry a functional group out of the reactor promptly after the event which forms the material. This investigation has been extended this month to include the vacuum distillates from the high temperature separator bottoms since it has become apparent that material in this boiling range is also produced in significant amounts. Charts have been obtained which will allow the light oil blends and the distillate oil in the process to be compared.

Figure A-11 is a liquid chromatogram of the distillate oil recovered by vacuum distilling the DOE 496 stripped filtrate to determine the proportions of distillation residue and distillate in the feedstock. The samples were made at 10% weight/volume concentration throughout this series. The differential refractometer (right hand side of chart) was operated at 16X while the UV spectrophotometer was operated at 0.5 absorbance units full scale (AUFS) for about the first 88 minutes using 274.5 nm. The remainder of the chart was run at the same wavelength but at 0.10 AUFS. The first peak on the differential refractometer trace is quite small confirming the ASTM test for saturates which also gave a small value near the limit of detection in this case. The second peak (3-double-bond compounds) is quite weak on both the UV and the RI traces. See the 15 minute retention time region. The RI trace indicates more of the higher aromaticity compounds and peaks at a retention time of about 48 minutes. This pattern is also observed in the UV trace with the higher sensitivity of the heavy components tending to skew this to emphasize these materials. The hydrocarbon array is not fully eluted at the point where methylene chloride breaks through, and a few large area peaks are seen just following this front (see the region from 80 to 88 minutes rention time). Attention is directed to a complex of peaks at 96 to 100 minutes retention time. Another chracteristic group appears from 115 to 121 minutes retention time. Both of these are believed to be basic nitrogen compounds in partly reduced form. Another characteristic group appears at 160 to about 172 minutes retention time which may be due to a quinoline-like material or to a phenolic material. The strongest peak due to basic nitrogen compounds falls near the 120 to 121 minute retention time and a relatively large peak falls at about 115 to 116 minutes retention time. This peak in particular is due to a reactive material that can be observed to disappear in the course of the catalytic reductions.

Three liquid chromatograms are presented for vacuum distillates from the reduction of the filtrate at either 415°C or at 430°C using the HDS 1443 catalyst (Figures A-12, A-13 and A-14). In each case the first peak on the RI detector is stronger than in the feedstock and a shift in the hydrocarbon distribution is observed which increases the amount of 3-double-bond material (peak 2) and which decreases the amounts of the higher aromaticity substances. All of the charts are similar throughout the hydrocarbon region, and it is doubtful that the resolution obtained is enough to justify confidence in minor shifts from one chart to another. Generally, about the same amounts of the same kinds of materials are observed. The size of the area following the methylene chloride front is reduced in all cases by comparison to the area on the feed material chart. The more interesting observations are concerned with the basic nitrogen region. Here the complex of peaks at 96 to 100 minutes retention time is reduced to a fraction of the original area in the oil from the feed. The peak at 115 minutes is substantially reduced also. At the same time, a peak has developed at about 109 minutes retention time which was not present in the feedstock. A strong peak is observed at about 134 minutes retention time which seems resistant to reduction while the complex of peaks at 160 to 172 minutes retention time appears at reduced intensity.

Two charts are presented showing the chromatographic analysis of the vacuum distillate oil obtained using pyrite catalysis at either 415°C or at 430°C (Figures A-15 and A-16). These show the kind of response which ought to be observed in the case of a less effective catalyst. The saturated peak is small in both cases, and the hydrocarbon array is of intermediate aromaticity between the feedstock case and the HDS 1443 catalysed case. The complex of basic nitrogen peaks at 96 to 100 minutes is still present at moderate intensity though much reduced from the feedstock values. The peak at 121 minutes retention time is the major component in the basic nitrogen region and is actually larger than in the feedstock case. This suggests that this material is coming from the non-distillable component of the system. The peak at about 135 minutes remains prominent, but the peak at 109 minutes, which developed over the HDS catalyst, is not present in any appreciable amount. Only minor alterations in the group at 160 to 172 minutes retention time are evident, the tendency for the first peak to diminish and the second to retain its peak height is noted.

The light oil composite representing the short contact time dissolution of the coal to make the solution which was filtered and stripped to prepare the feedstock was made with condensates collected in the product interval from 101 through 140. The first run of this sample with the liquid chromatograph produced an unsatisfactory baseline on the RI detector but produced a satisfactory UV chart (Figure A-17). A repeat run was done later and this gave a satisfactory baseline for the RI detector, but the pump rate was somewhat higher or the activity of the column had declined enough to shorten the retention time of a number of peaks (Figure A-18). Figure A-18 is now considered because the base line is better in the RI chart, but the retention time skew should be remembered when comparing it to other charts in this set. The first peak on the RI chart, due to saturates, is fairly strong on the 16X attenuation, an observation in line with the result from the ASTM measurement. Use of the lot 2397 solvent resulted in the appearance of a small peak area for the 3-double-bond region seen as the second RI peak or the first UV peak. A number of more aromatic substances appear in the third region and probably are due to distillation of the more volatile part of the solvent. These must contain four or more double bonds. Finally, the low volatility of the solvent results in a low concentration of the heavy solvent derived materials and little response is observed in the retention time area from about 50 to 80 minutes. A number of the peaks observed in the basic nitrogen region are present in the vacuum distillate and in the light oil composite. This suggests that they are present in the light oil by partial distillation in the high pressure flash. A number of peaks in the phenols region appear in the light oil composite but do not appear to any significant amount in the vacuum distillate. Presumably, these materials must come from the short contact time dissolution of the coal. Both of the runs with the DOE 496 light oil composite are shown to illustrate how the effect of variation in temperature or column activity or the occasionally eccentric pumping may combine to alter the chromatogram. The cause of the drift is not well established, but a small change in the pump rate seems the most likely. This change seems to be associated with the inability of the computer controlling the pump to hold an absolute reference to produce the same flow rate at all times.

The chromatograms for the light oil composites for DOE 497B-1, 497B-2 and 497C are all similar (Figures A-19, A-20 and A-21). The first peak on the RI detector has the same height in all three charts. The second peak accounts for much of the remaining hydrocarbon material and also matches well on all three charts. The higher boiling and less hydrogenated hydrocarbons are generally present in minor to trace amounts. The basic nitrogen region from about 90 to 125 minutes contains two main peaks and a number of minor peaks which match reasonably well on all three charts. Generally, these also match similar peaks in the vacuum distilled oil and appear to be partial distillation products flashed in the high pressure, high temperature separator. The light oil composite appears to contain modest amounts of phenolic material not present in the vacuum distillate oil but which matches peaks seen in the short contact time light oil. The presence of these substances suggests that the short contact time SRC still retains oxygen which can be eliminated as promptly formed phenolic compounds which are also volatile.

The chromatograms for the light oil blends from DOE 498A and 498B conclude this series (Figures A-22 and A-23). These match each other reasonably well but differ significantly from the light oils made with the HDS catalyst. When pyrite is used, its lower efficiency is evident, first in a lowered concentration of saturates and second in a tendency for a more aromatic rich distribution of hydrocarbons to be formed. The pattern of basic nitrogen compounds is shifted significantly also. The strong peak at about 121 minutes retention time is preceded by a moderate sized peak appearing at about 119 to 120 minutes retention time. At the same time, the peak at about 110 minutes retention time has not developed in the way that it is observed with the HDS catalyst system. Finally, more phenolic material is observed at both 415°C and at 430°C operating conditions. Here it seems evident that phenolic material originates in the filtrate conversion step and that the efficiency of the catalyst for oxygen reduction has an influence on the amount which escapes reaction.

## A2.6 Discussion

The chromatographic analysis of the whole suite of oils involved in these runs has allowed observation of the effect of catalysis and operating condition changes on a variety of substances in the solvent array or derived by conversion of the coal. The source of a particular material can be deduced in many cases by noting the location with regard to boiling range and the response to varying catalyic potentials. Thus, the phenols are predominantly a product from the coal conversion step but seem to be made at some rate from the low conversion SRC material as well. Certain materials are not very stable and reduce first and, in some instances, may be the precursors for more stable substances which appear at intermediate stages. At high reduction potentials these are the last to be consumed. Products tend to move to saturated hydrocarbons as a limit. This can be best observed by reference to charts from materials made on the trickle-bed catalyst system reported in the previous section or to the material made on the vapor phase hydrotreating reactor system reported in the second quarter of 1983* (see DOE 484R).

It seems evident that one of the problems in reduction of functional groups is design of a system which will maintain the material in contact with the catalyst for long enough at suitable conditions. The volatile substances which can escape promptly and which carry a heteroatom out account for much of the low product quality that is evident in coal conversion materials. The vapor phase reactor intercepts these and finishes the reaction. Perhaps this can be done with a trickle bed of sufficient length. The prospect for efficient heteroatom removal in systems with powdered catalyst suspensions or ebullating pellets of catalyst appears poor because of mixing effects. Those materials made near the top of the reactor will likely escape from the primary reaction (though a following vapor phase reactor could polish the finish well, most likely).

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* "Advanced Coal Liquefaction Research," Quarterly Technical Progress Report for the Period April 1, 1983 through June 30, 1983; December 1983, PC50001-18.

Figure A-1
Liquid Chromatogram of Run DOE 493 Light Oil Composite

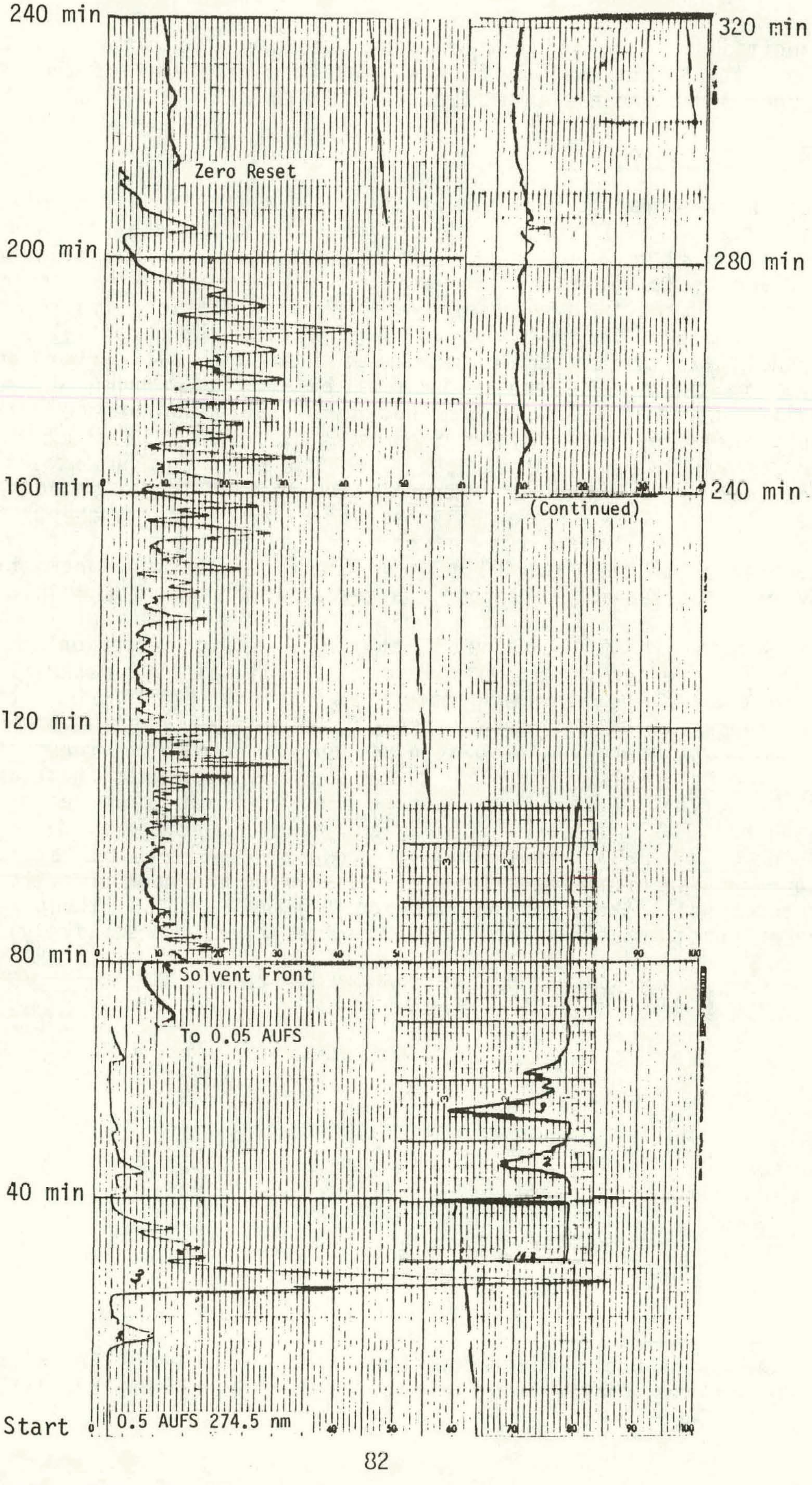


Figure A-2
Liquid Chromatogram of Run DOE 494 Light Oil Composite

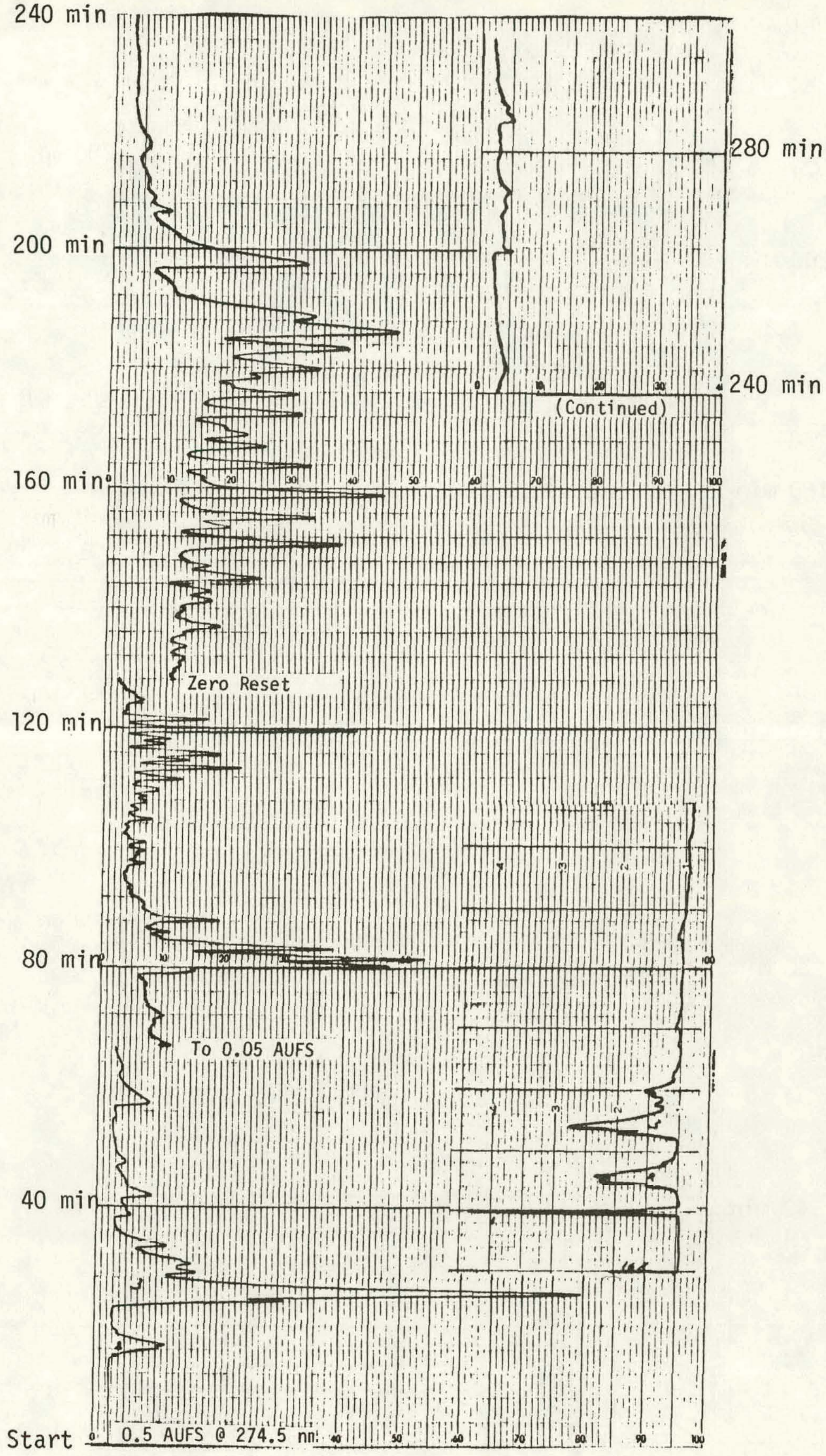


Figure A-3
Liquid Chromatogram of Run DOE 495A Light Oil Composite

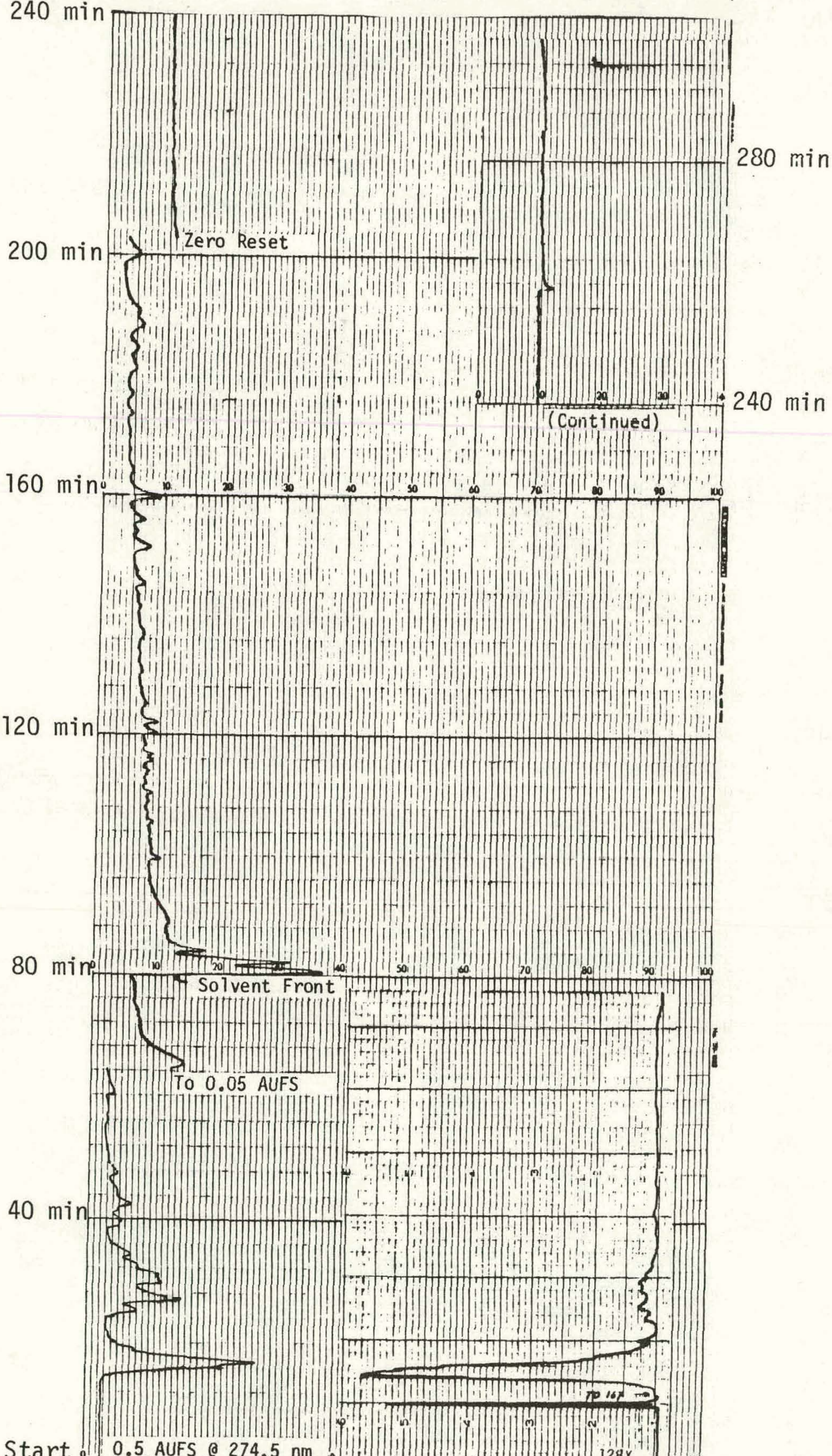


Figure A-4
Liquid Chromatogram of Run DOE 495B Light Oil Composite

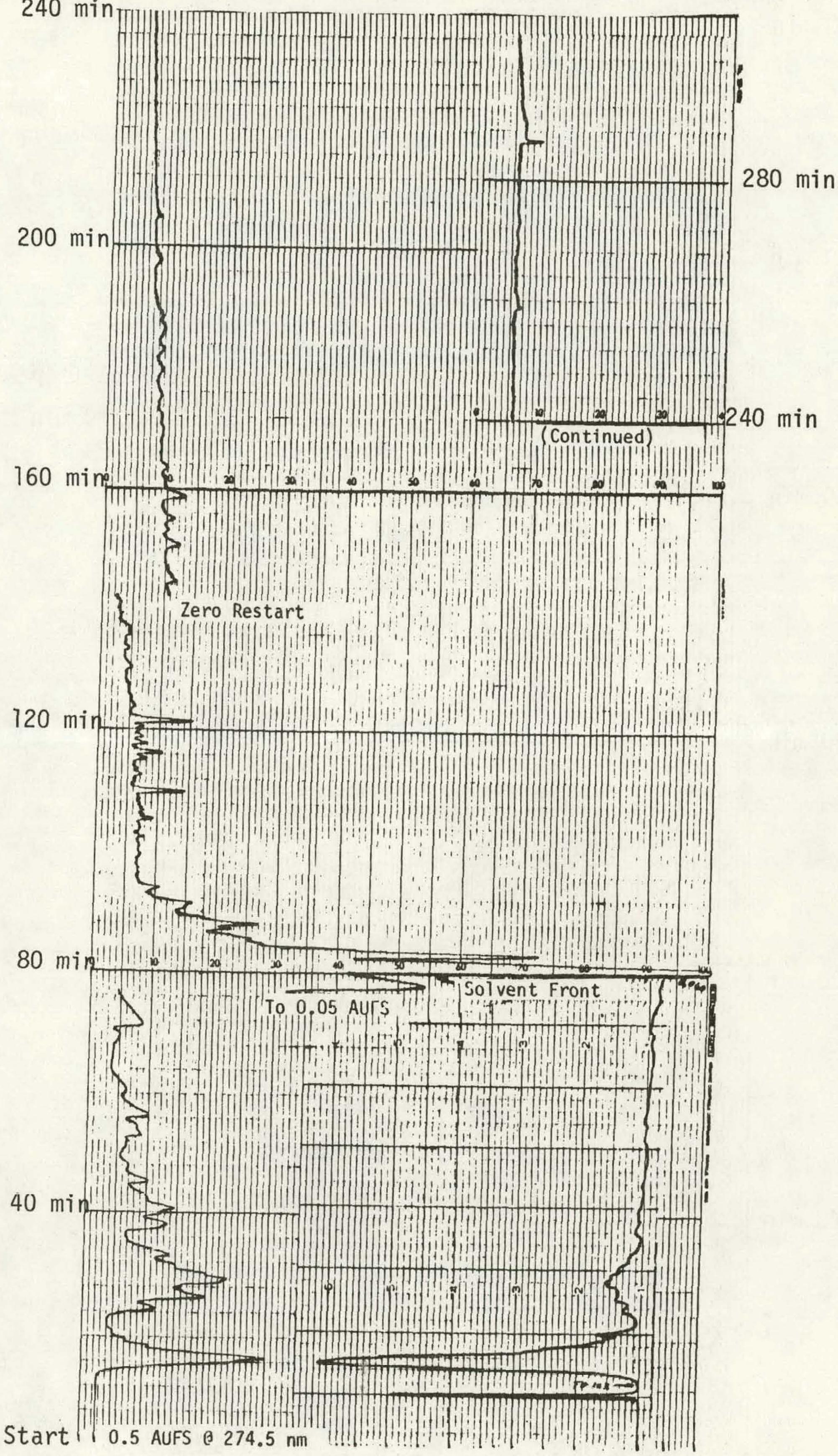


Figure A-5
Liquid Chromatogram of Run DOE 495C Light Oil Composite

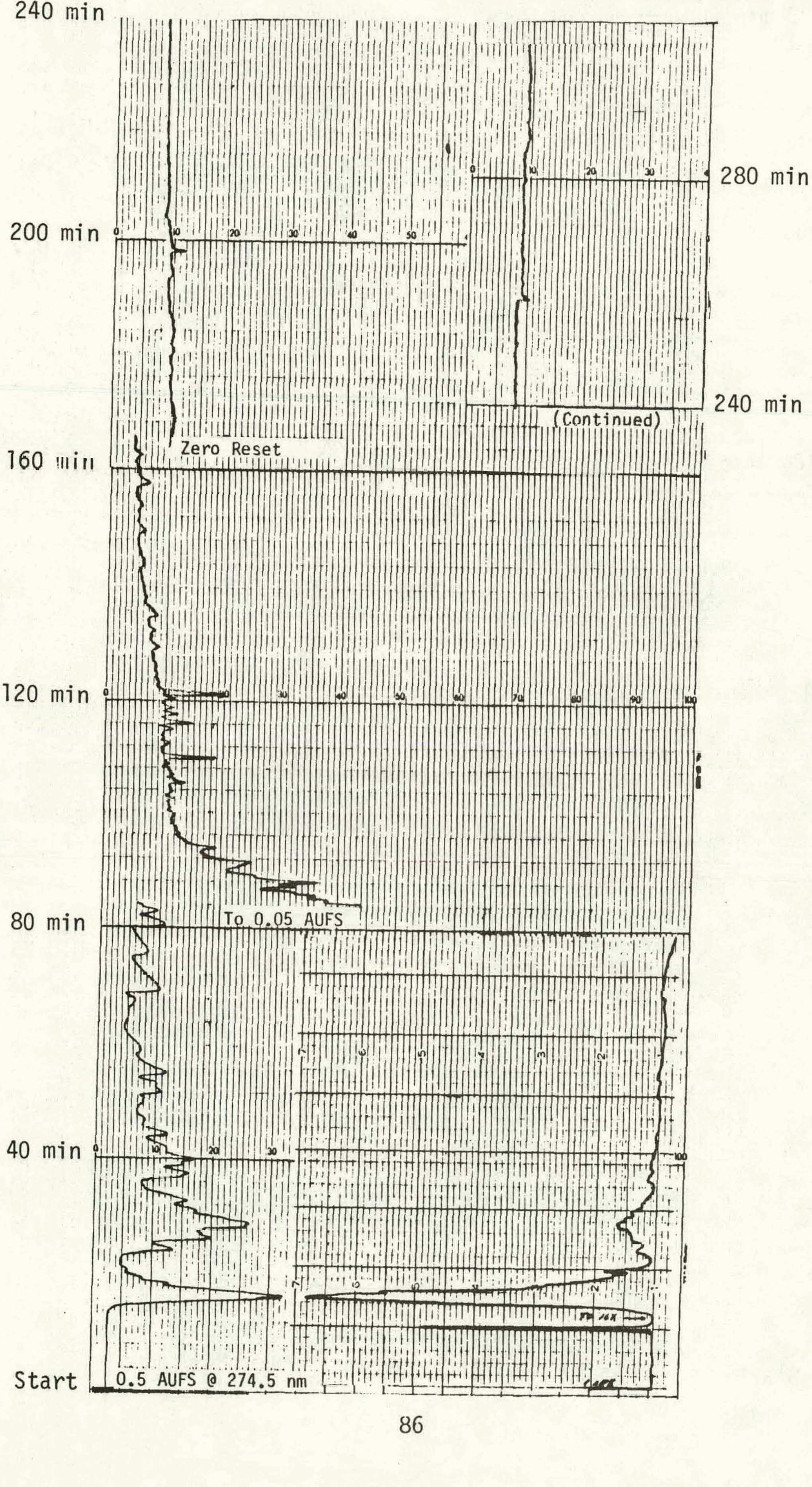


Figure A-6
Liquid Chromatogram of Run DOE 495D Light Oil Composite

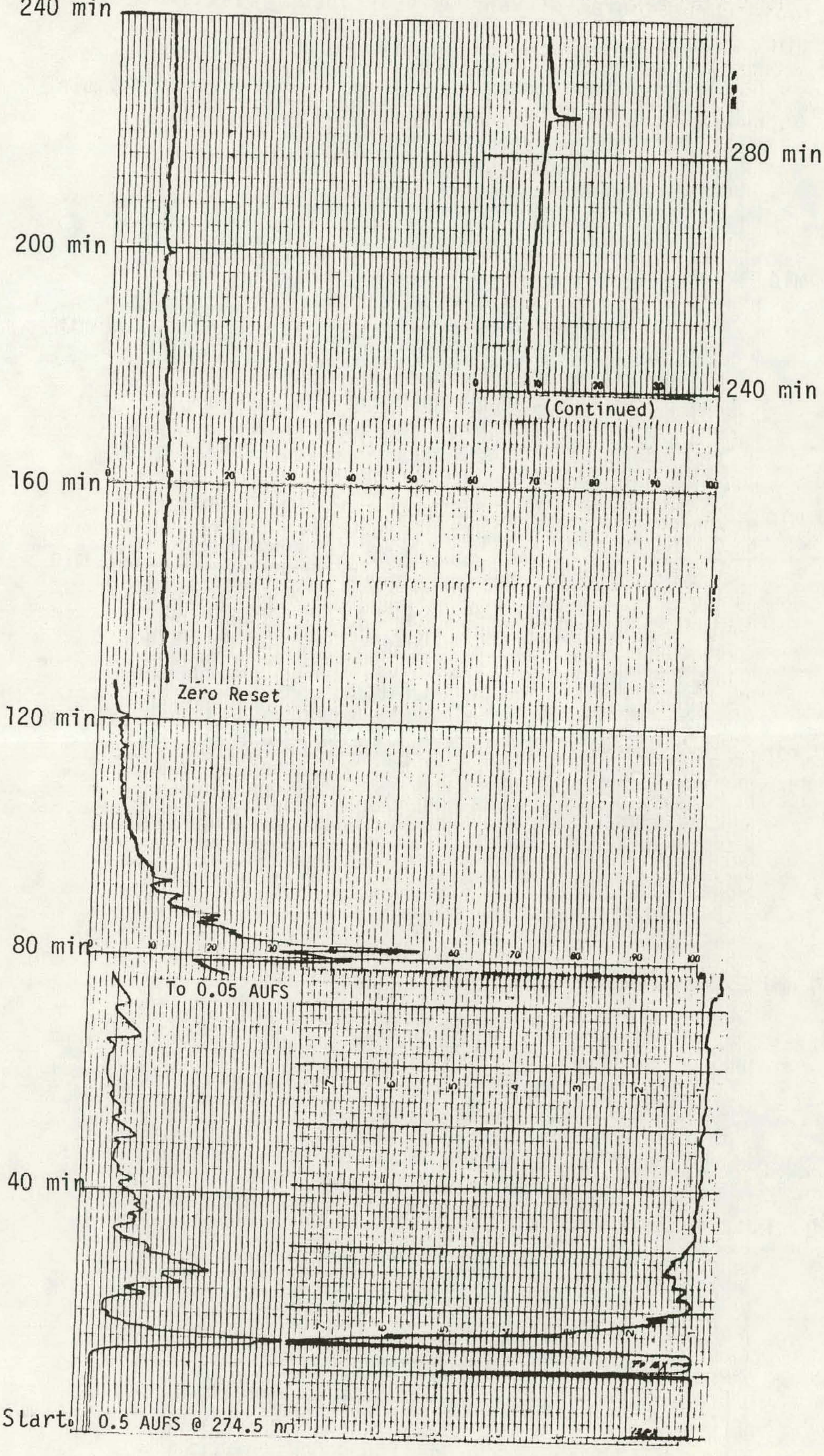


Figure A-7
Liquid Chromatogram of Run DOE 495A Vacuum Distillate

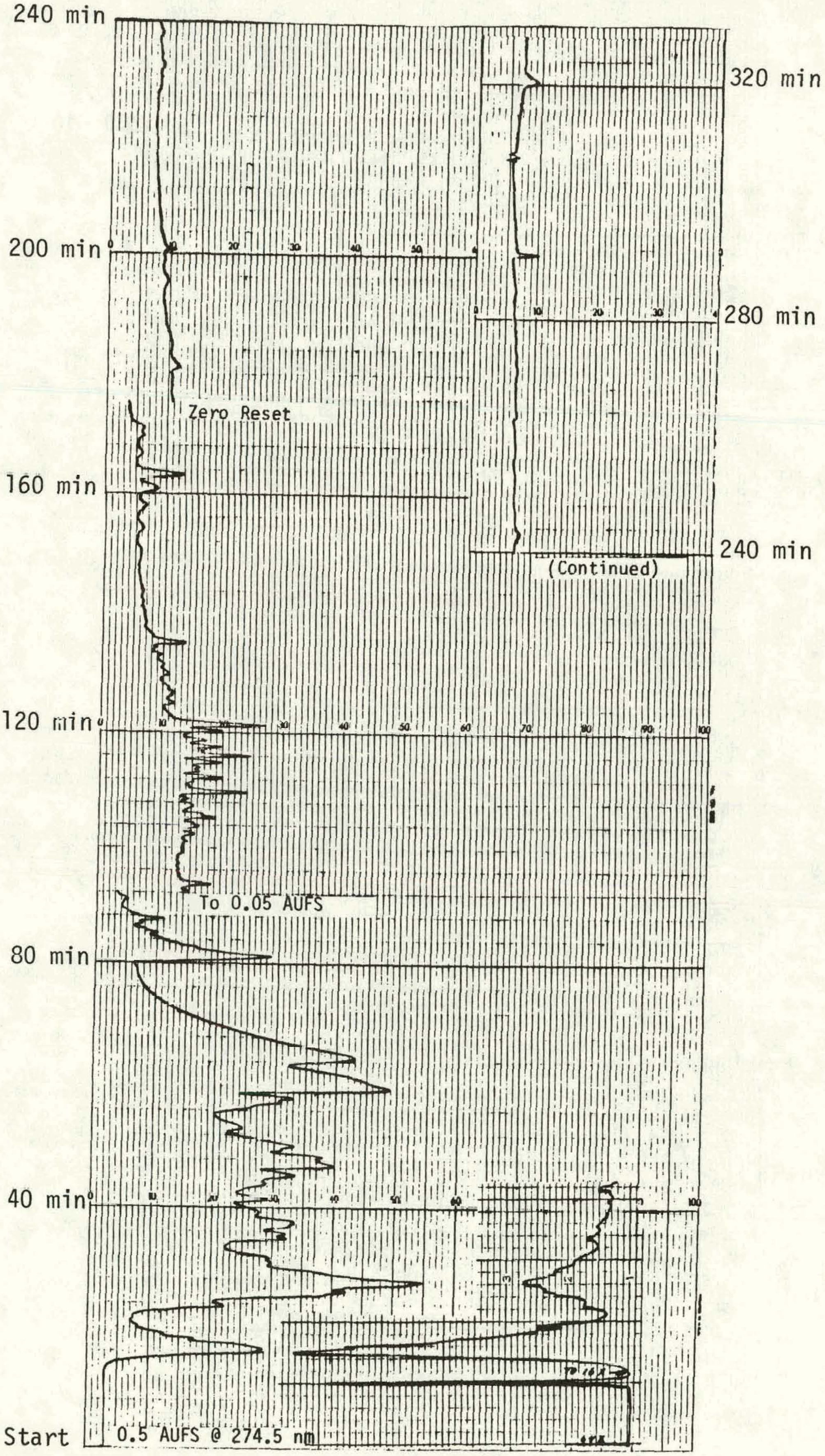


Figure A-8
Liquid Chromatogram of Run DOE 495B Vacuum Distillate

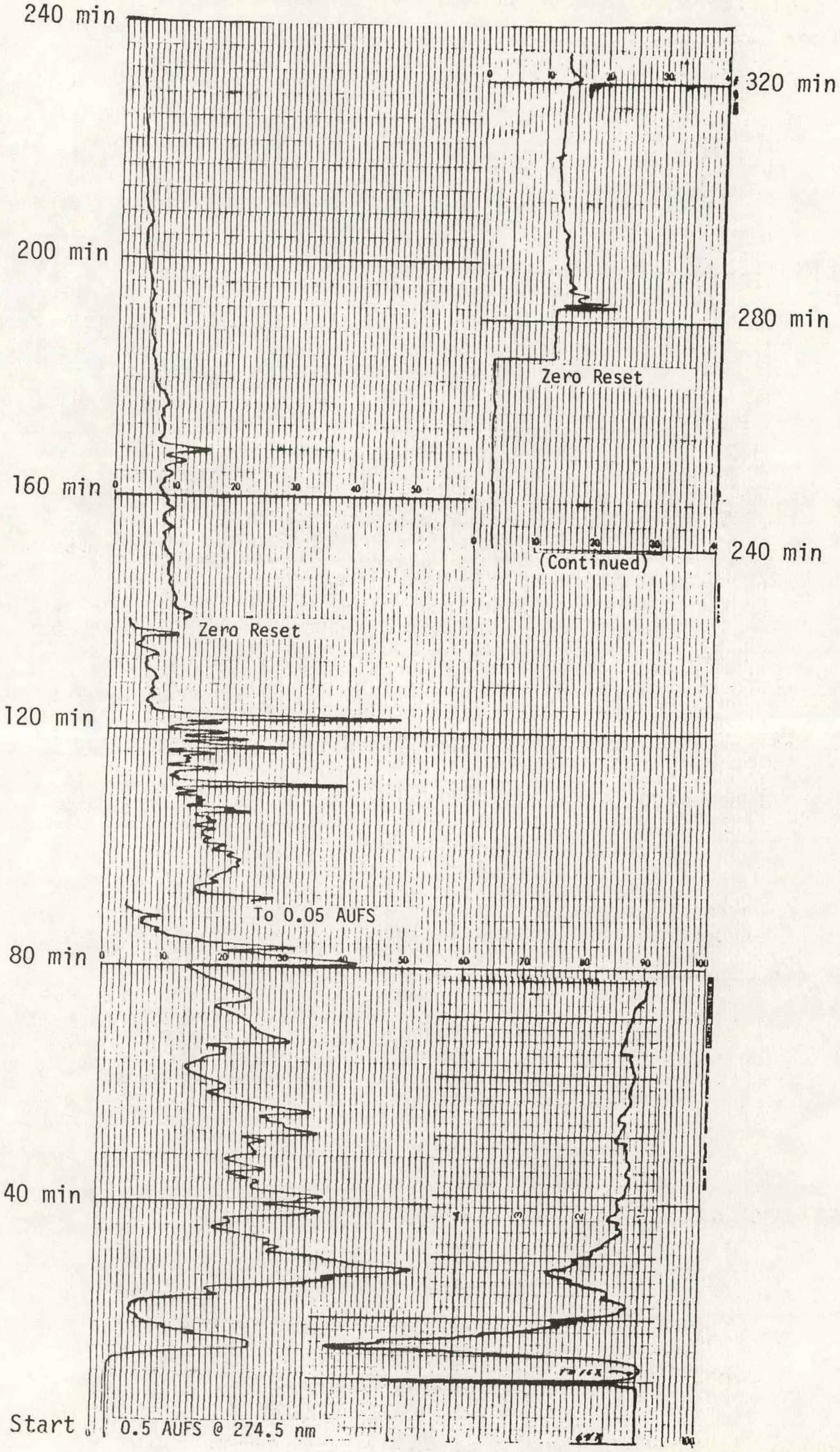


Figure A-9
Liquid Chromatogram of Run DOE 495C Vacuum Distillate

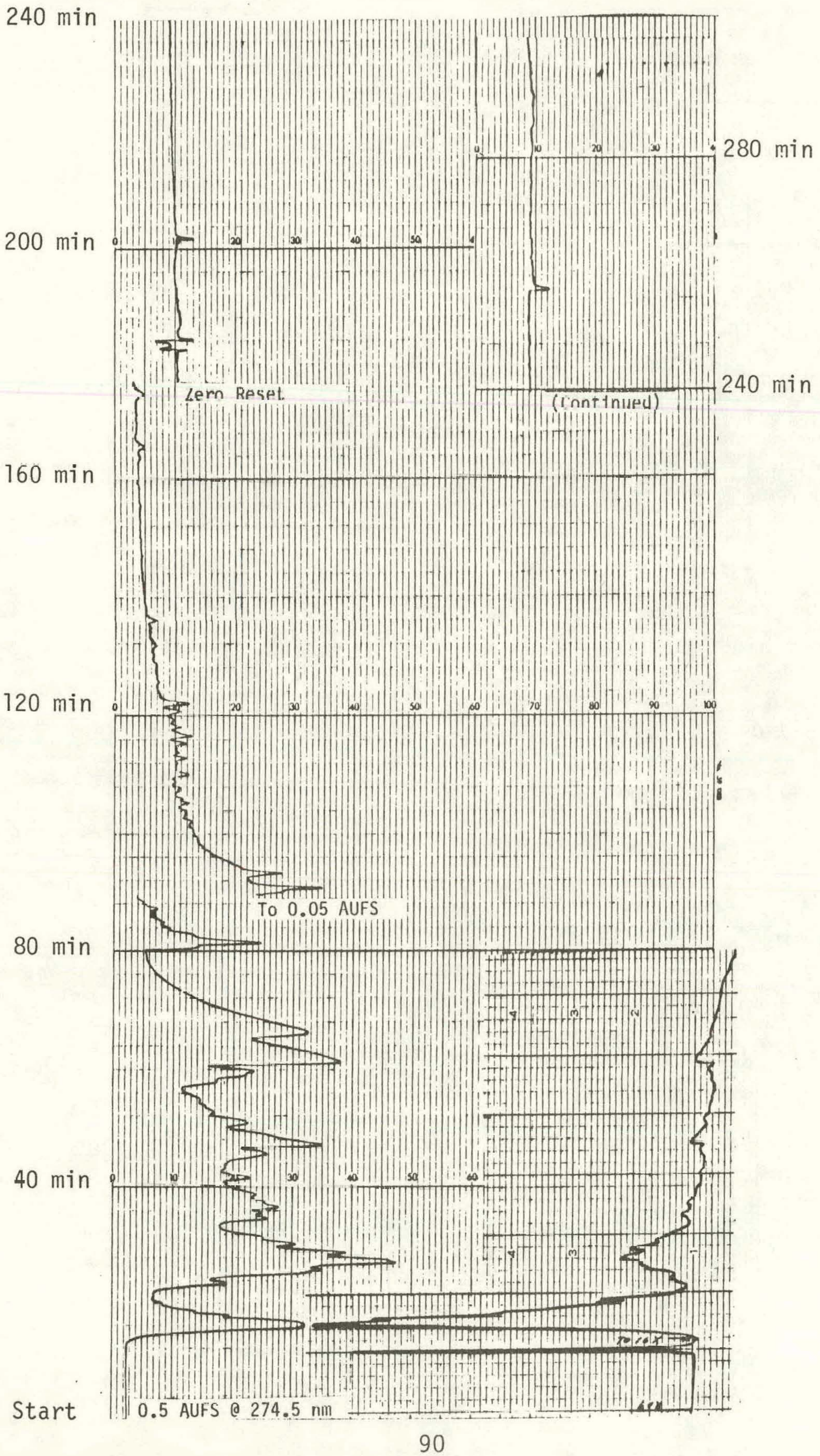


Figure A-10
Liquid Chromatogram of Run DOE 495D Vacuum Distillate

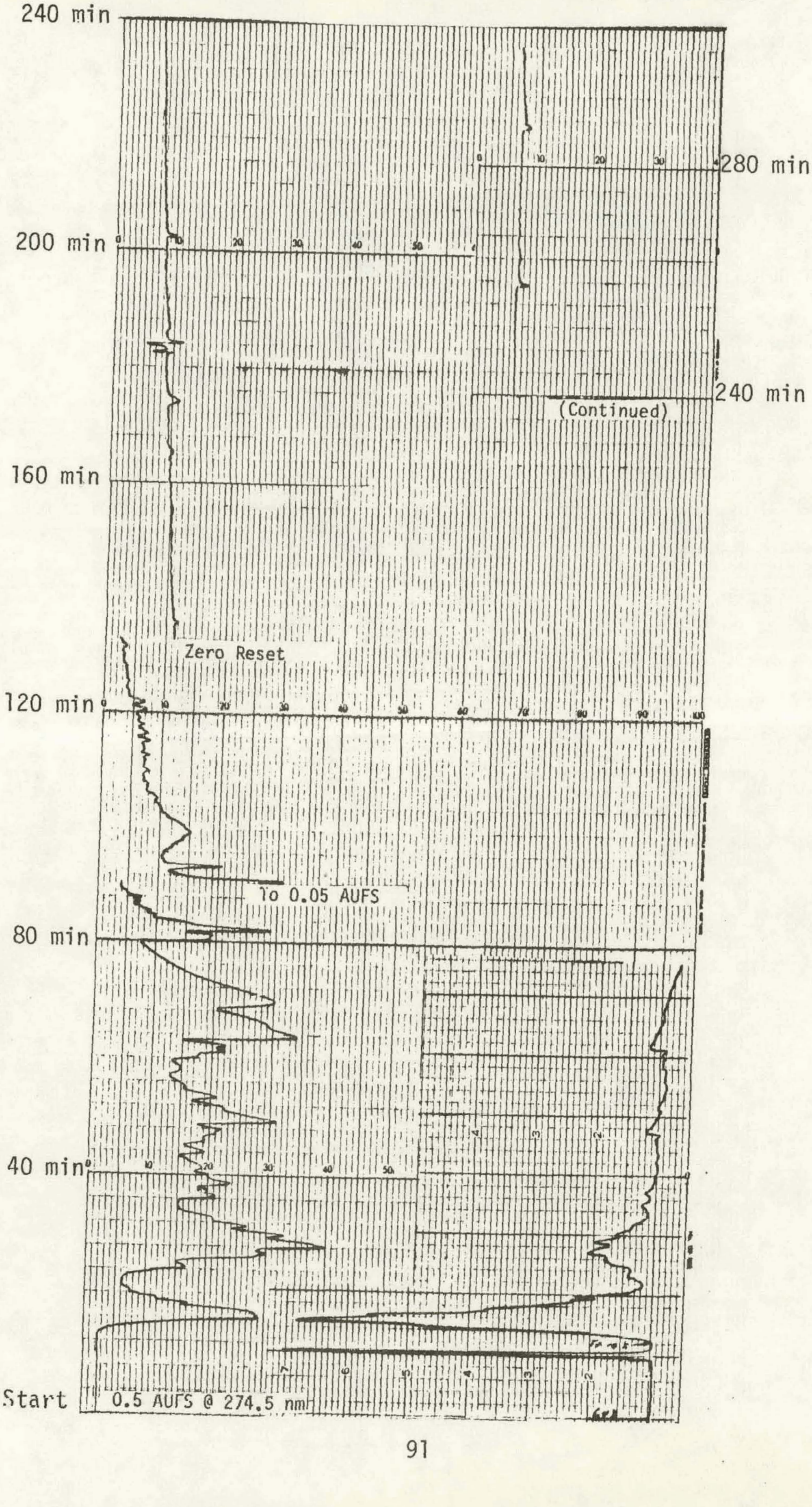
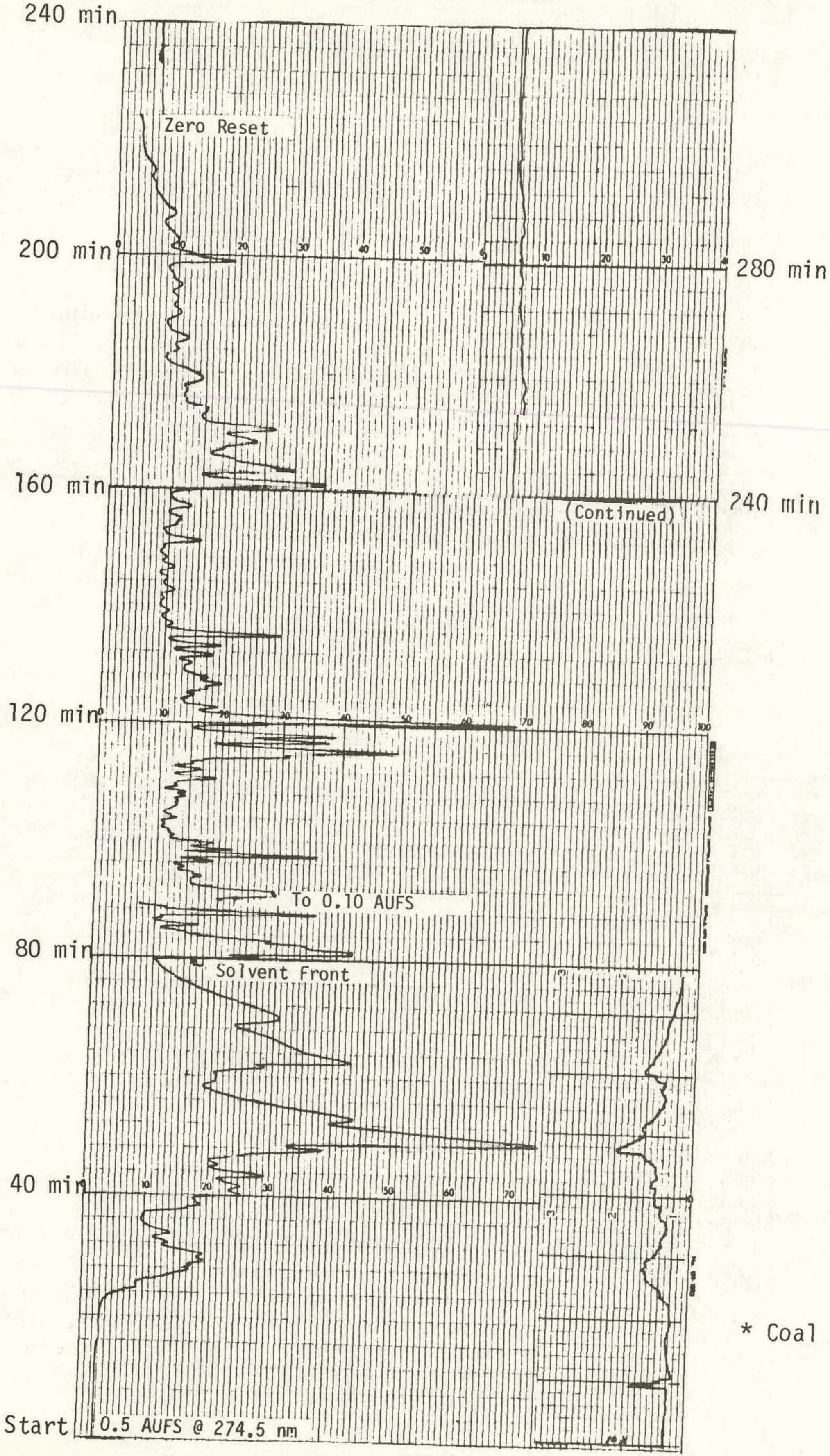


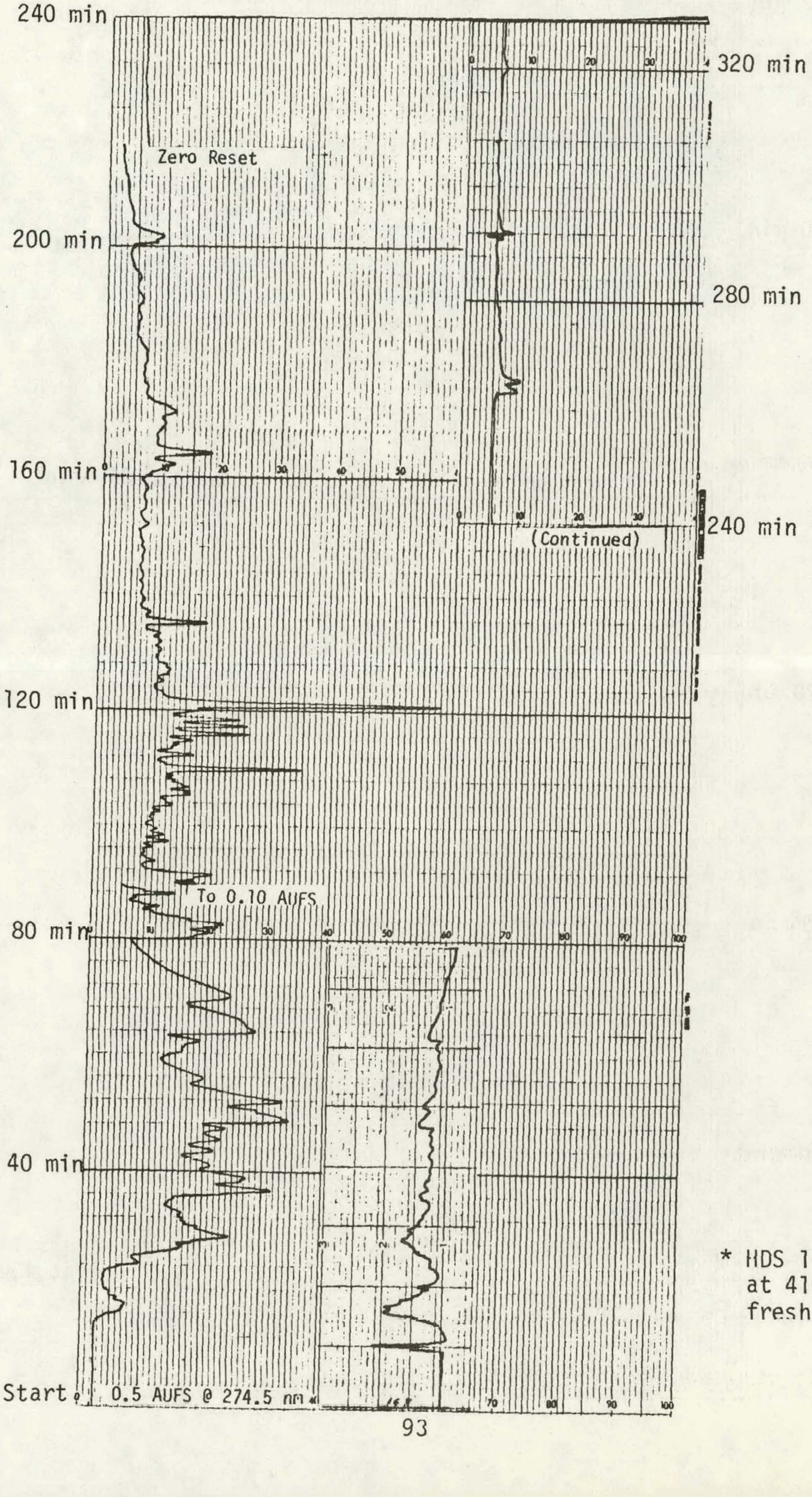
Figure A-11

Liquid Chromatogram of Run DOE 496*
Vacuum Distillate



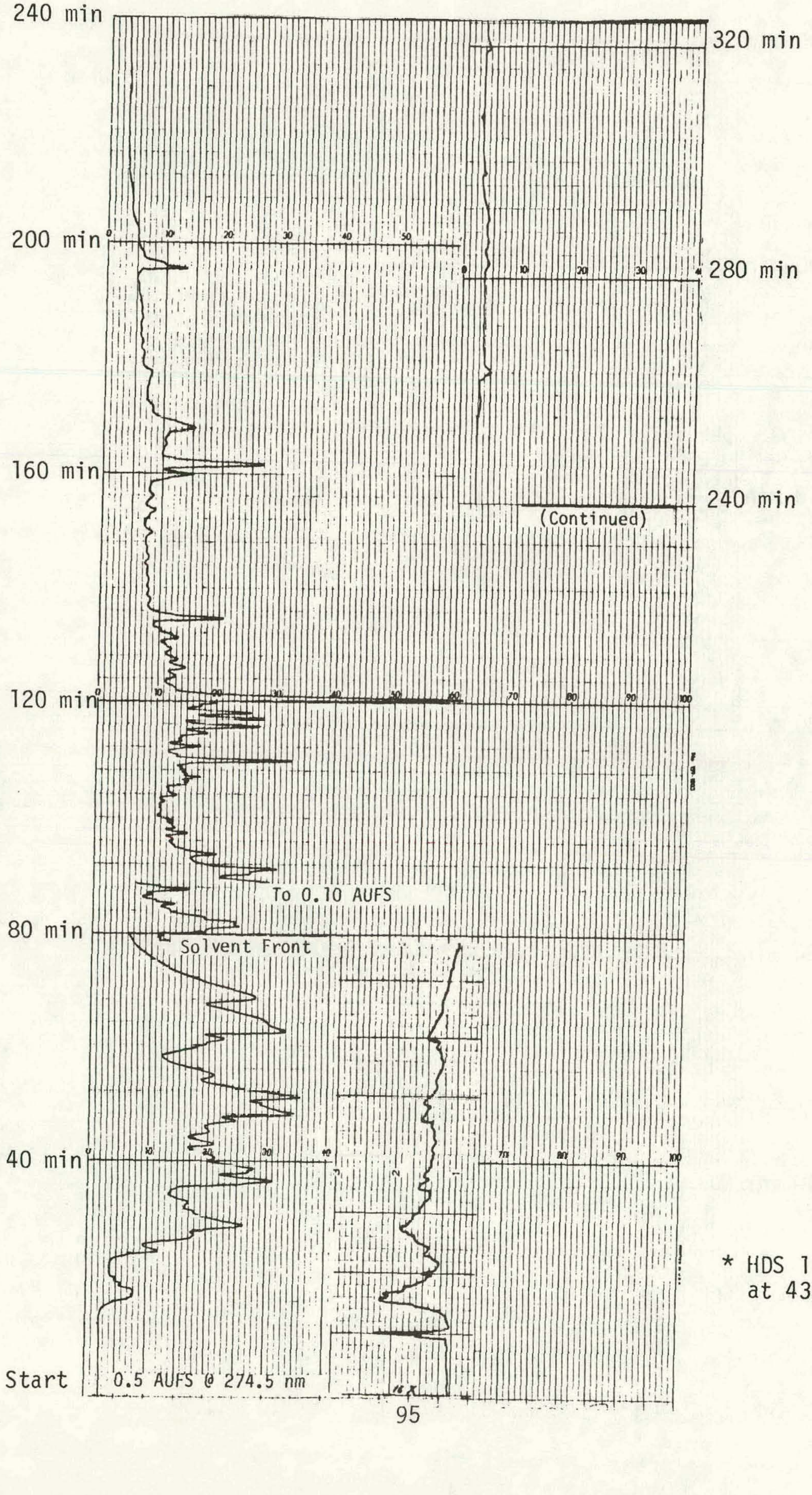
* Coal Dissolution

Figure A-12
Liquid Chromatogram of Run DOE 497B-1*
Vacuum Distillate



* HDS 1443 Catalyst at 415°C (with fresh catalyst)

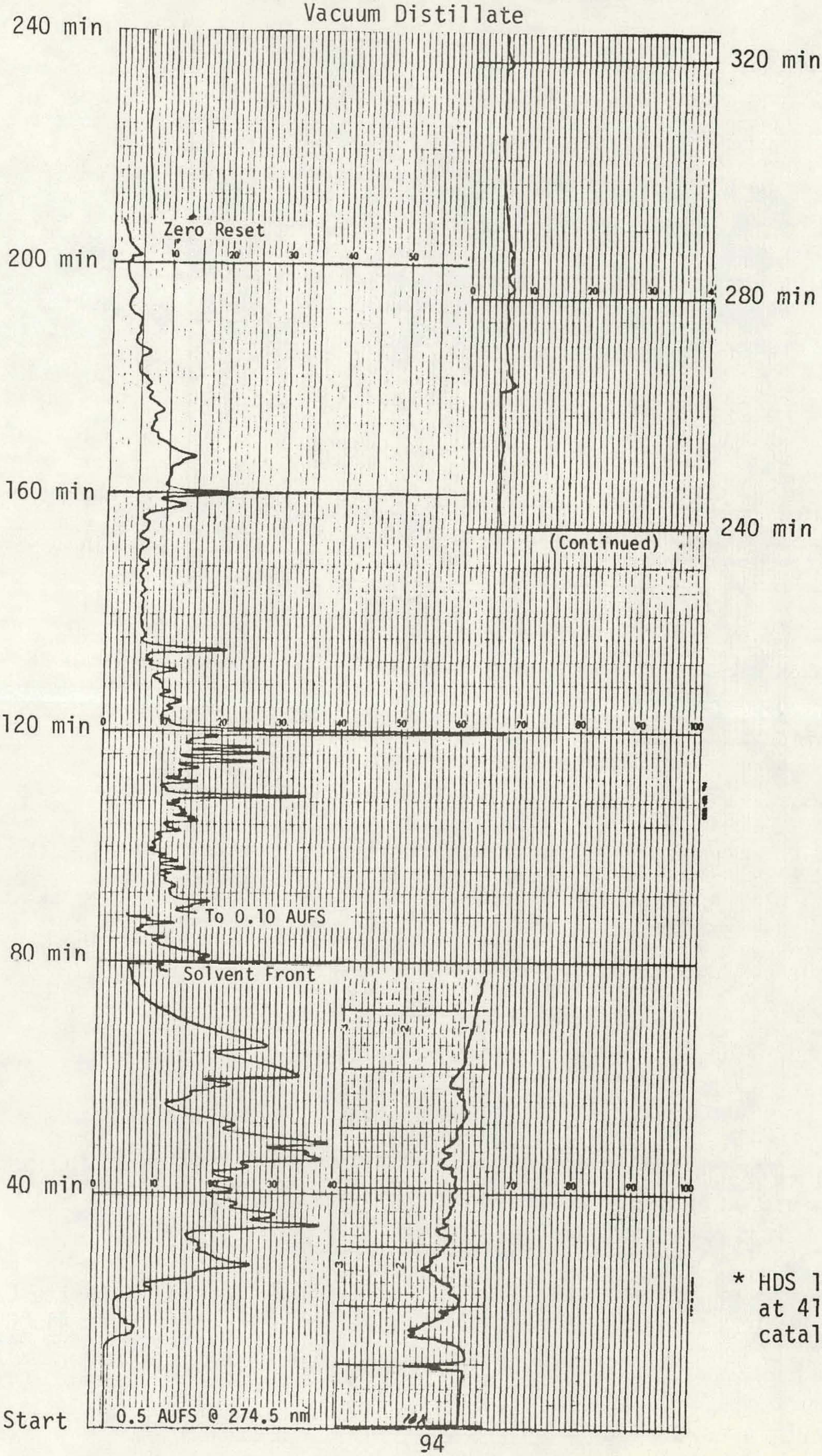
Liquid Chromatogram of Run DOE 497C*
Vacuum Distillate



* HDS 1443 Catalyst
at 430°C

Figure A-13

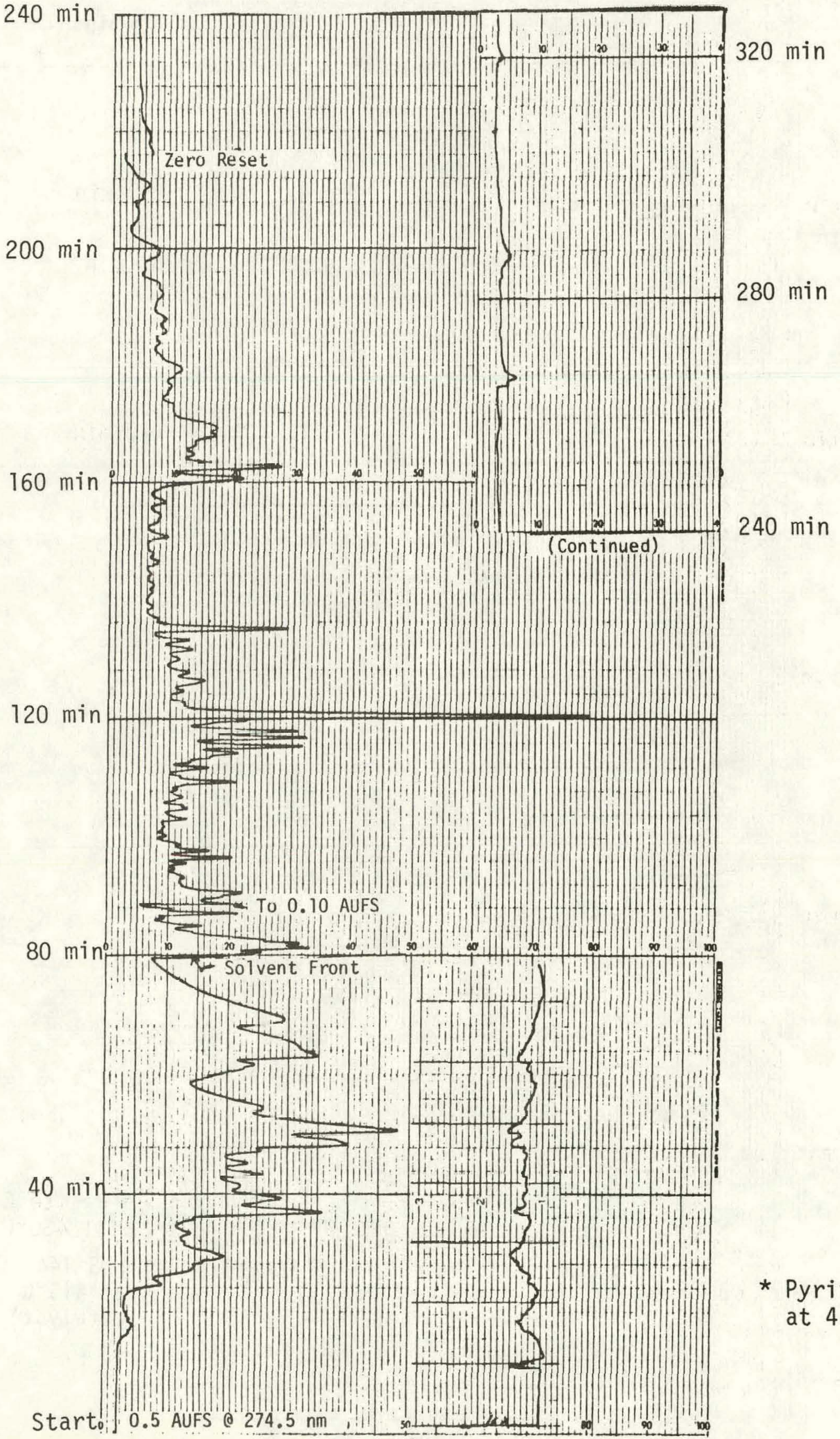
Liquid Chromatogram of Run DOE 497B-2*
Vacuum Distillate



* HDS 1443 Catalyst at 415°C (aged catalyst)

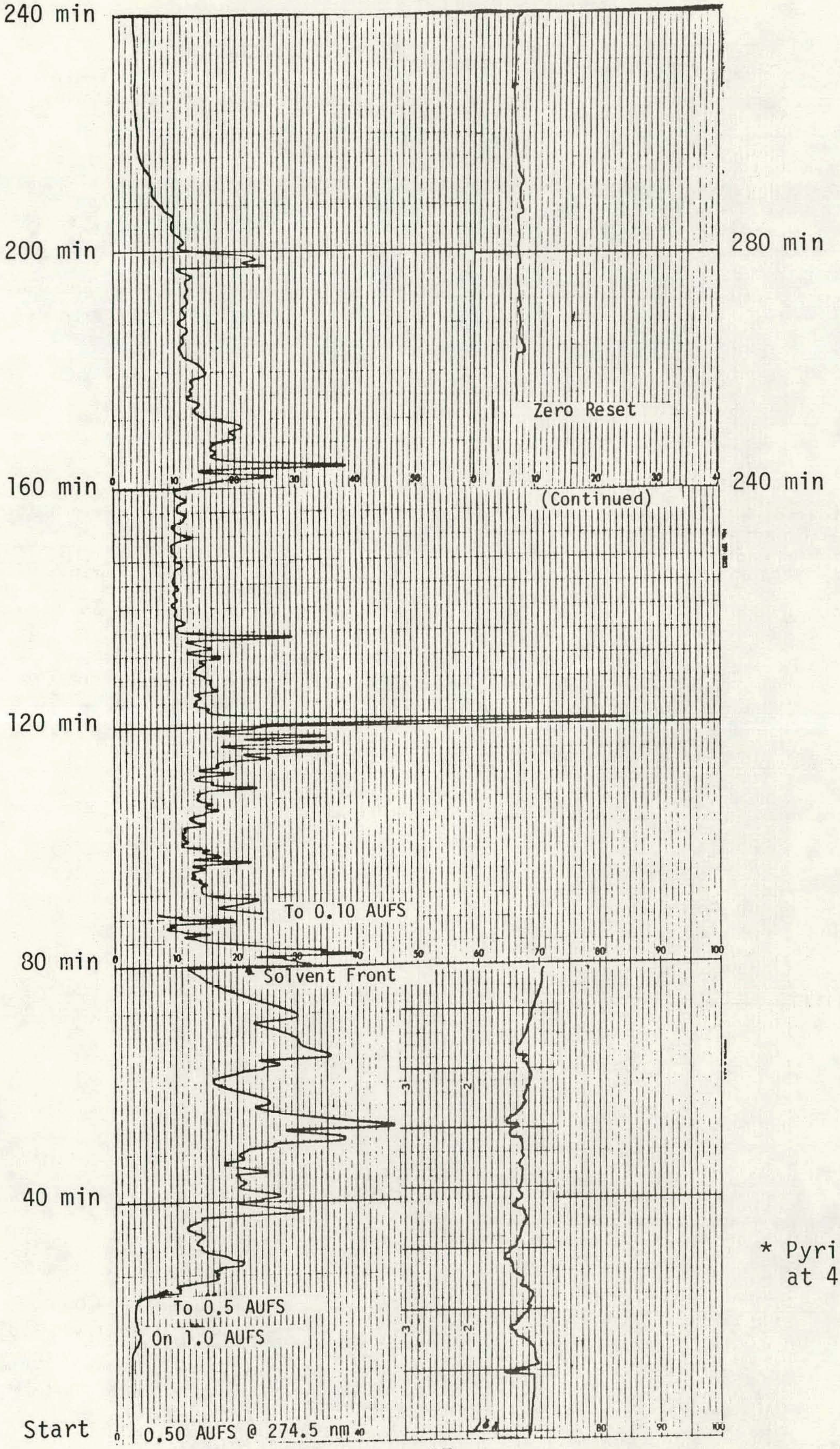
Figure A-15

Liquid Chromatogram of Run DOE 498A*
Vacuum Distillate



* Pyrite Catalyst
at 415°C

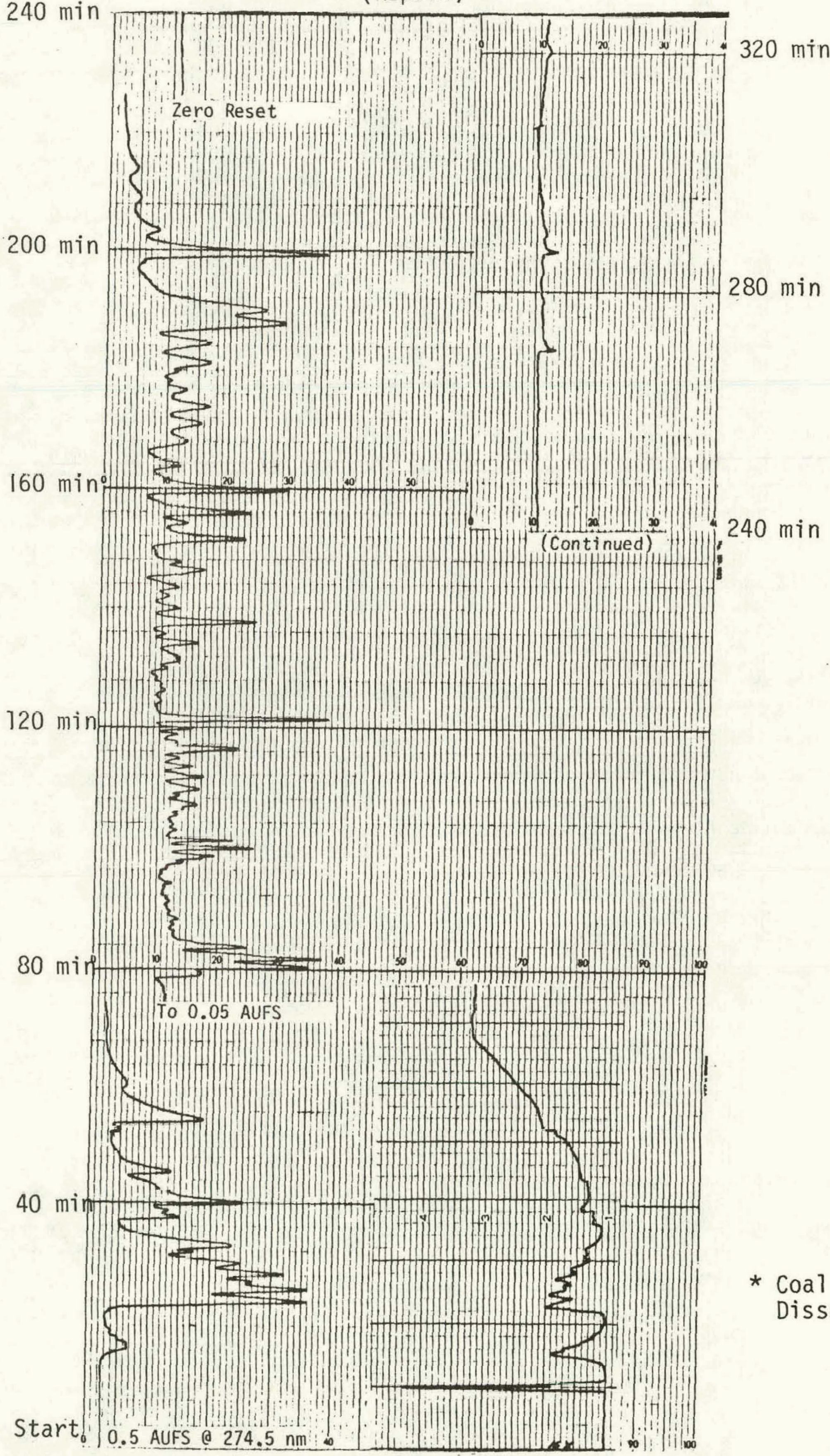
Liquid Chromatogram of Run DOE 498B*
Vacuum Distillate



* Pyrite Catalyst
at 430°C

Figure A-17

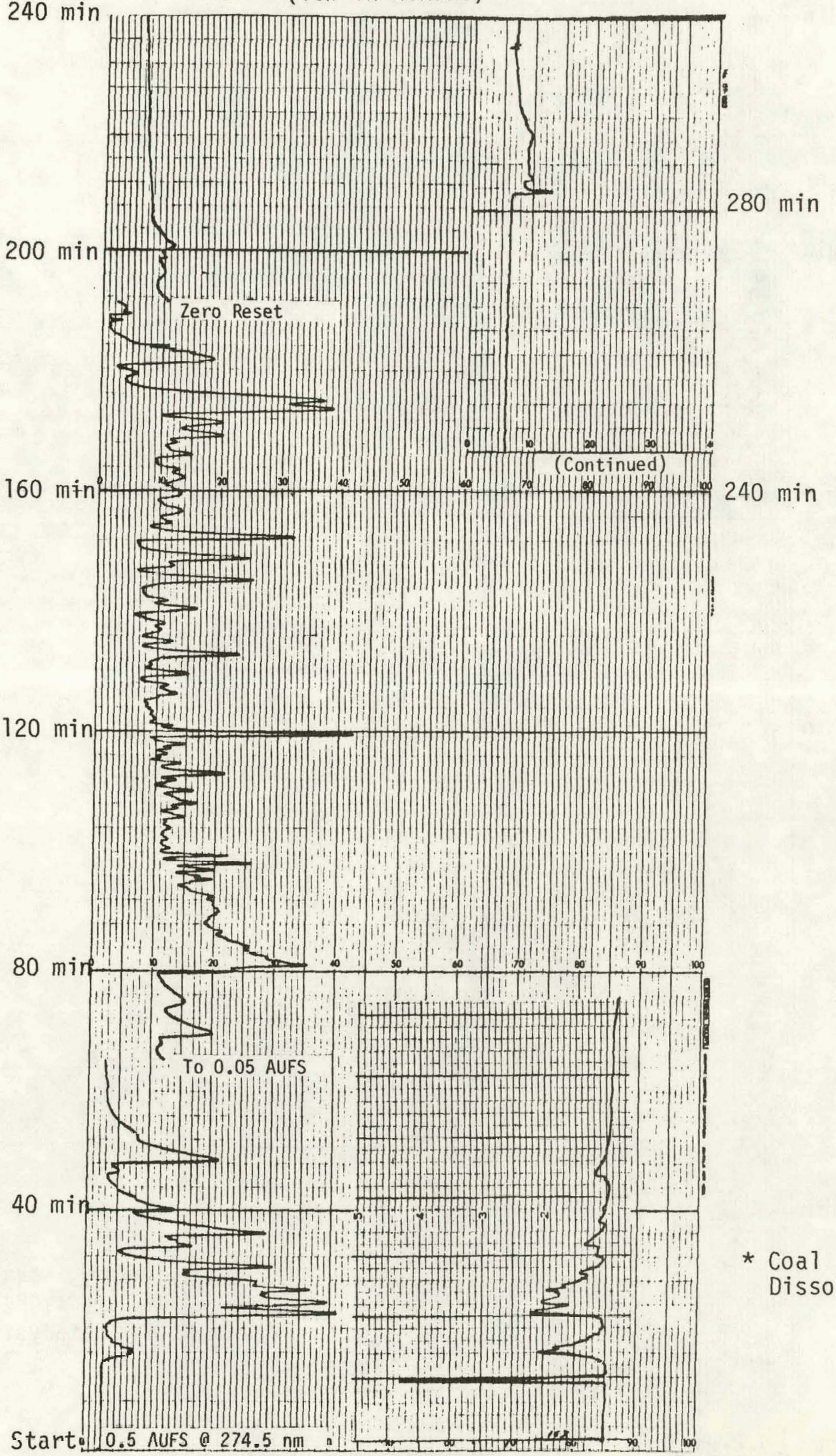
Liquid Chromatogram of Run DOE 496*
Light Oil Composite
(Repeat)



* Coal Dissolution

Figure A-18

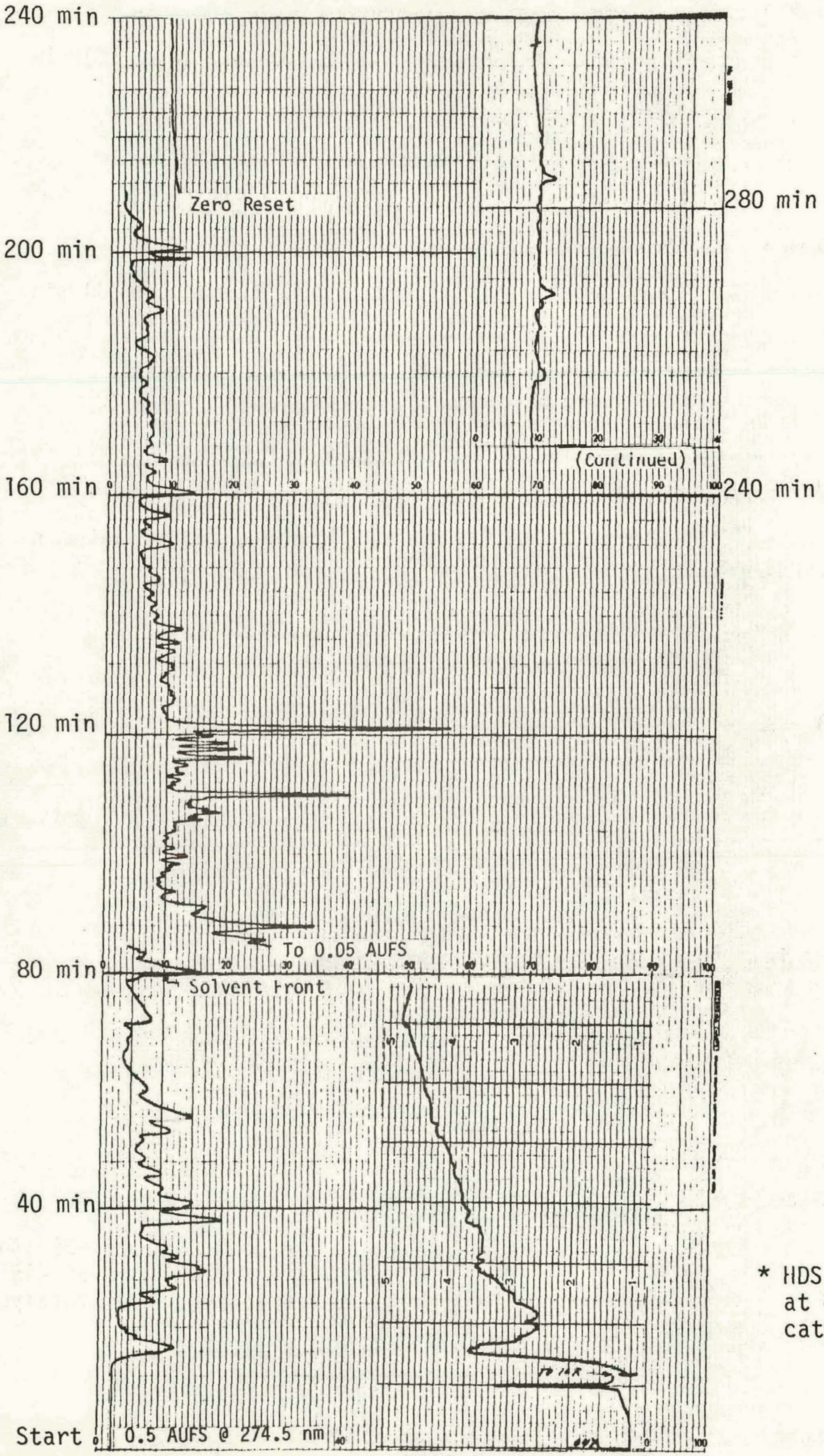
Liquid Chromatogram of Run DOE 496*
Light Oil Composite
(10% in hexane)



* Coal
Dissolution

Figure A-19

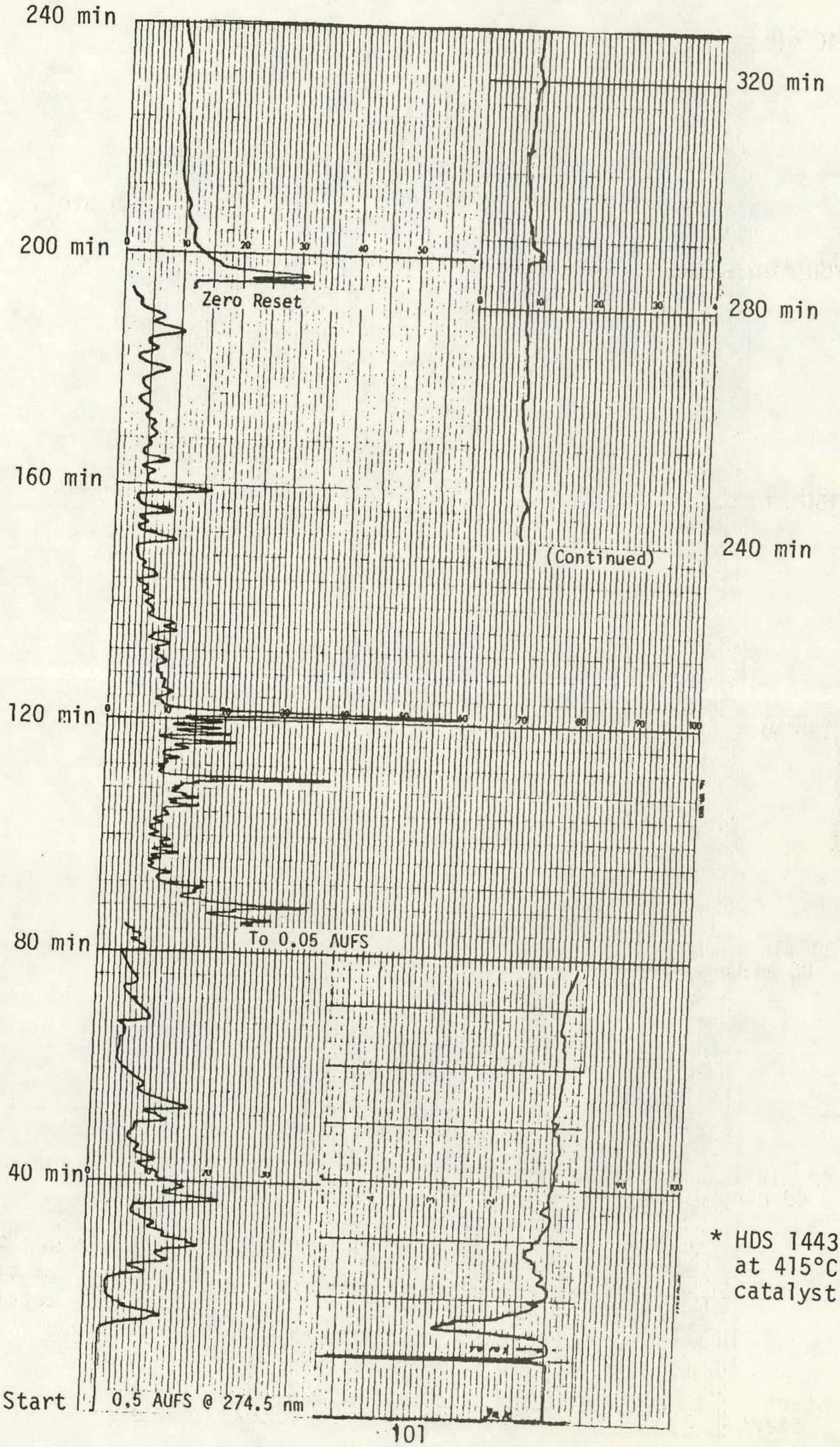
Liquid Chromatogram of Run DOE 497B-1*
Light Oil Composite



* HDS 1443 Catalyst at 415°C (fresh catalyst)

Figure A-20

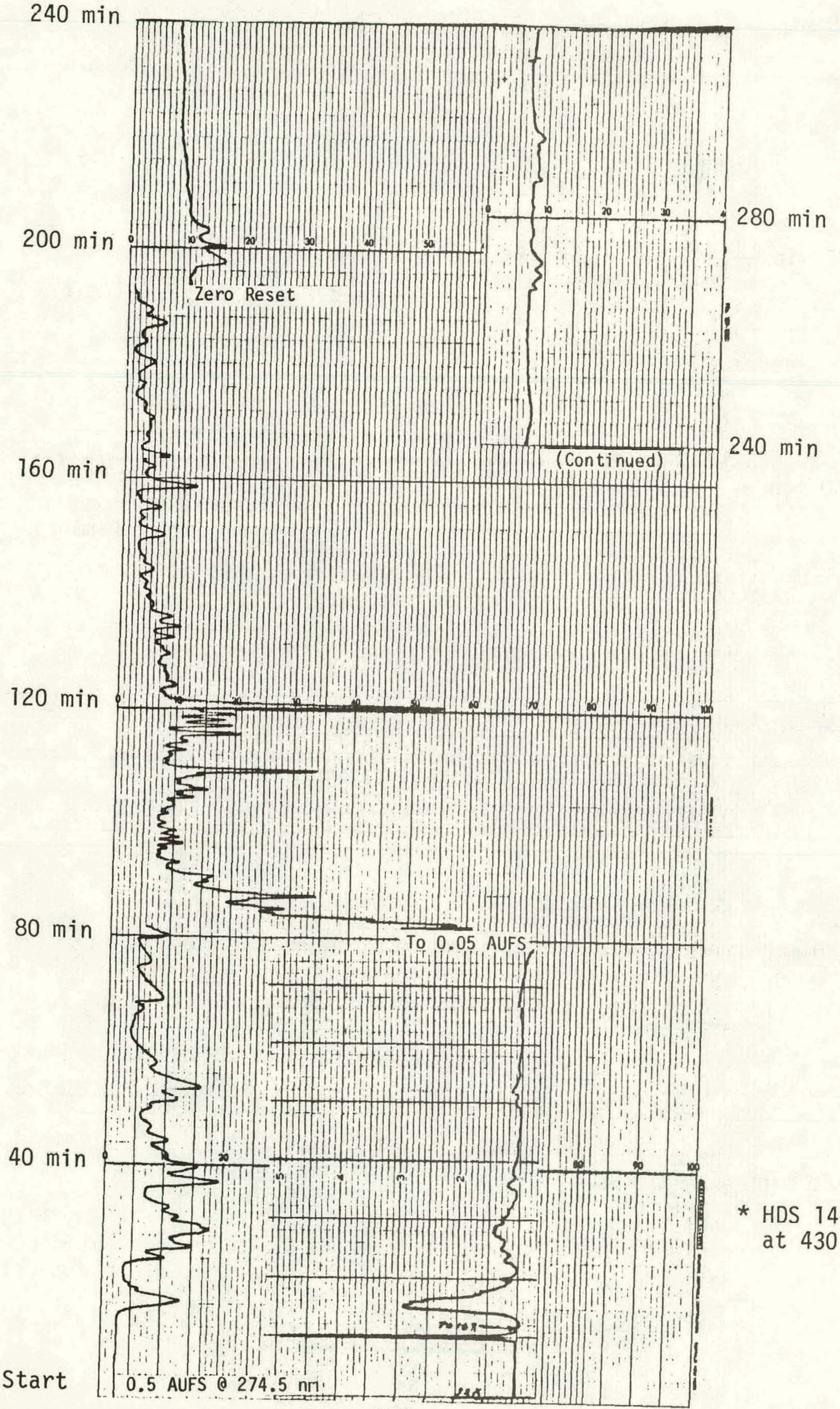
Liquid Chromatogram of Run DOE 497B-2*
Light Oil Composite



* HDS 1443 Catalyst at 415°C (aged catalyst)

Figure A-21

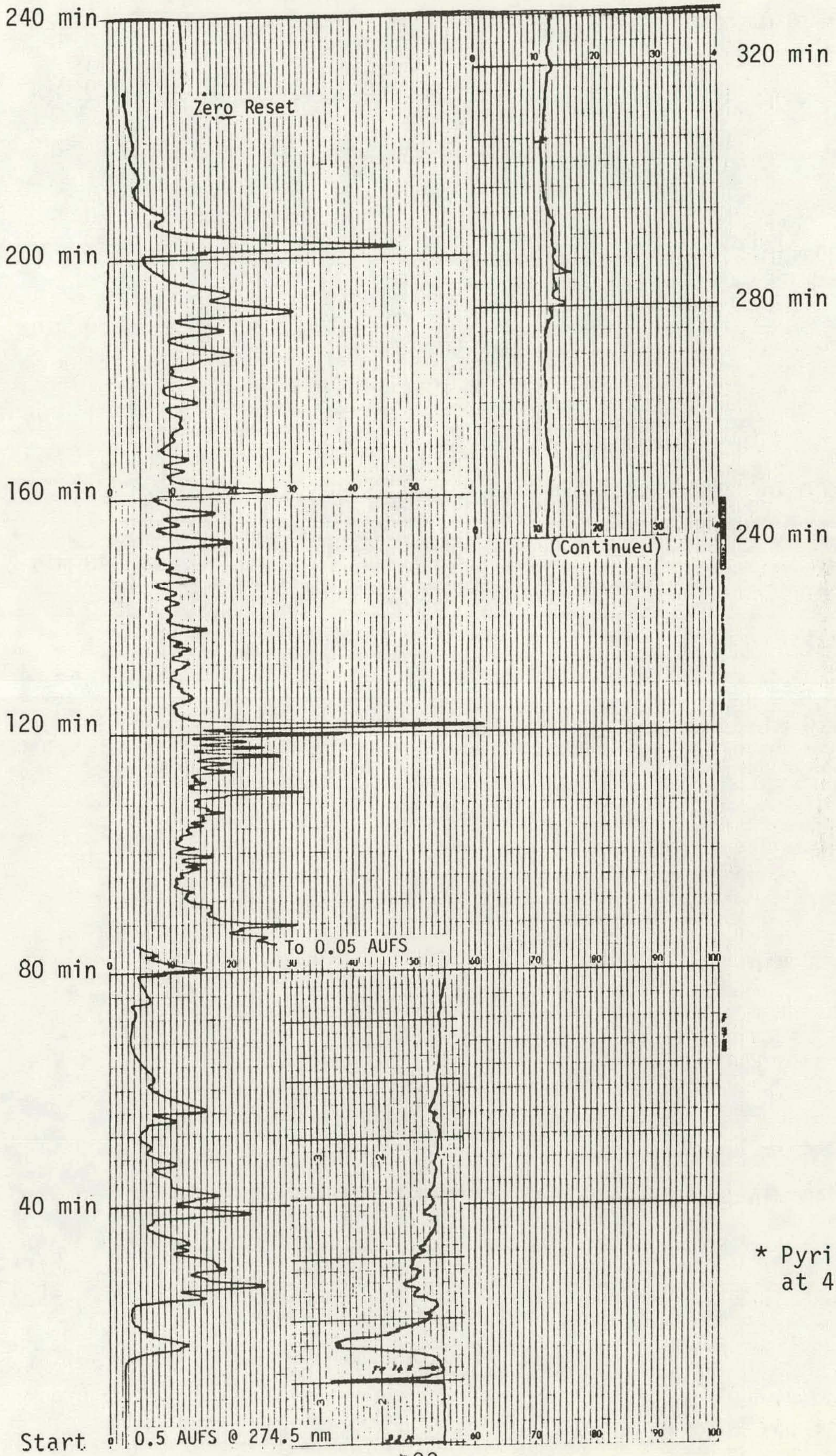
Liquid Chromatogram of Run DOE 497C*
Light Oil Composite



* HDS 1443 Catalyst
at 430°C

Figure A-22

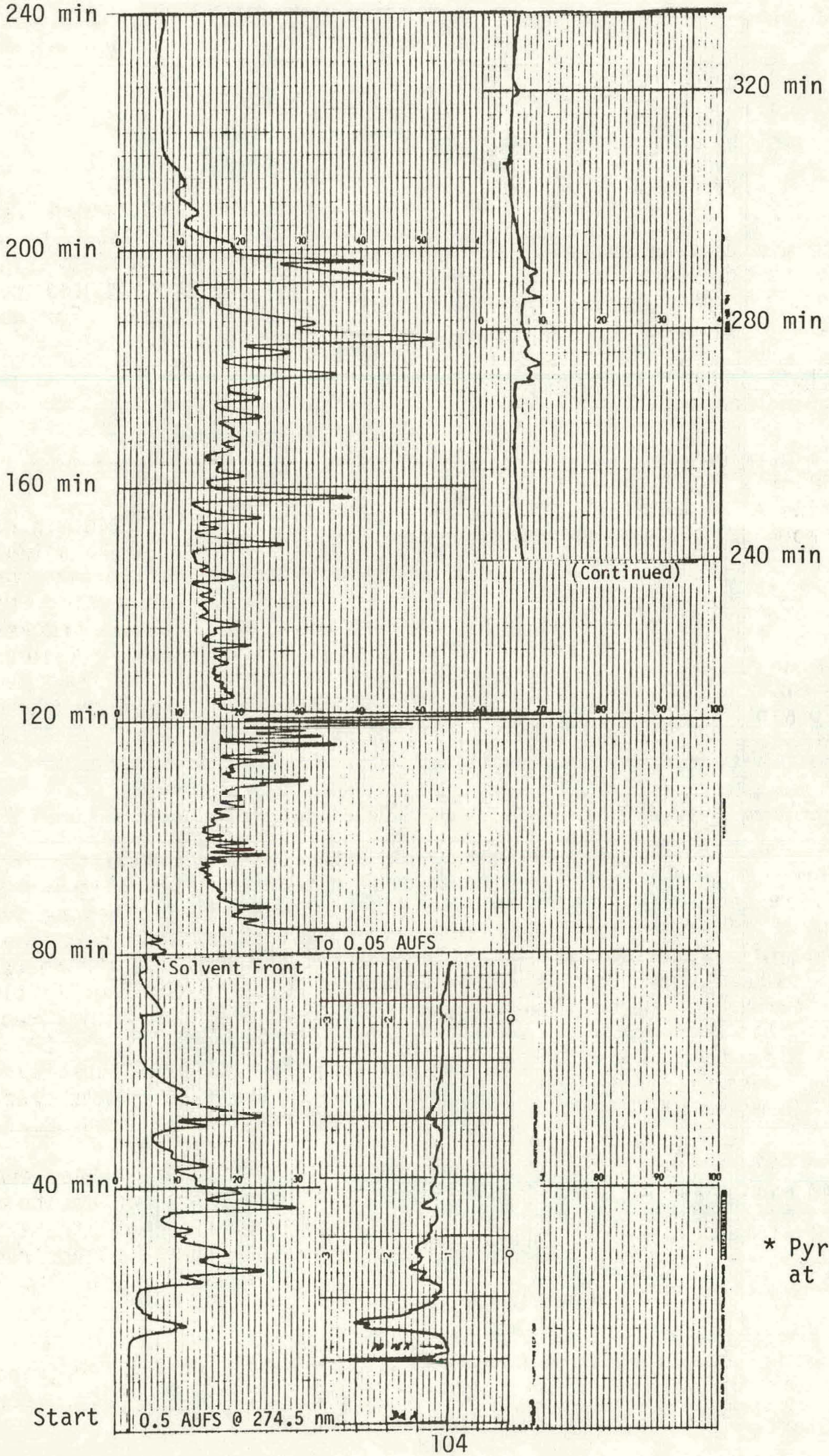
Liquid Chromatogram of Run DOE 498A*
Light Oil Composite



* Pyrite Catalyst
at 415°C

Figure A-23

Liquid Chromatogram of Run DOE 498B*
Light Oil Composite



* Pyrite Catalyst
at 430°C

# APPENDIX B

# CHARACTERIZATION OF RESIDUE PRODUCTS

The solubility of distillation residues has been determined using 5% increments of pyridine mixed with hexane as test reagents. The samples were dissolved in pyridine and the mixtures were prepared by pipetting these stock solutions into volumetric flasks containing the required amounts of pyridine and filling to the mark with hexane. For details, see the first quarter 1983 progress report, Appendix C*.

## B1 Short Contact Time Coal Liquefaction (Runs DOE 499A-C)

### B1.1 Introduction

A series of experiments was run with Belle Ayr coal in the short contact time mode to explore ways to obtain increased conversion to soluble material. Run DOE 499 was a base case experiment in which the coal was reacted in the presence of pyrite as a catalyst and increasing reaction times at 440°C and 2250 psig hydrogen pressure were used as process conditions. Each experiment resulted in the preparation of a number of filtered samples and these were distilled to obtain the SRC component for evaluation. Solubility of these residues was determined in the graded series of hexane-pyridine test reagents to study the effect of extending the reaction time.

### B1.2 Solubility Data

Charts are presented showing the solubility of the distillation residues obtained at 15, 30 and 45 minute nominal retention times (Figures B-1, 2 and 3, respectively). An increase in the solubility in hexane was observed as the reaction time increased. At the conditions chosen, the yield of oil increased with reaction time and the yield of IOM decreased. It must be presumed that the SRC component is being continually altered by the removal of material to make distillate and by the partial replacement of this with material moving from the IOM category to the SRC category. This tends to hold the level of material in the solubility array roughly constant, therefore no large shifts in the size of the fractions at each concentration of pyridine in the test reagent are evident.

When individual fractions are compared, it is seen that the tendency is for the less soluble fractions to decrease in concentration as the reaction time is increased. In a few instances, the peak solubility is found at an intermediate time, again suggesting movement from locations requiring higher concentrations of pyridine to dissolve the material to locations requiring less pyridine.

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* "Advanced Coal Liquefaction Research," Quarterly Technical Progress Report for the Period January 1, 1983 through March 31, 1983; December 1983, PC50001-15.

## B2 Multiple Stage Liquefaction

### B2.1 Short Contact Time versus SRC I Coal Dissolution Stages (Runs DOE 493 and 494)

#### B2.1.1 Introduction

A short contact time (SCT) and a normal contact time were used to prepare feedstock for conversion in the trickle-bed reactor to determine if the preparative step had any substantive effect on the upgrading. The coal used in both cases was conventionally cleaned Burning Star (Illinois No. 6) and the same drum of solvent was used to make both stocks. The short contact time run was DOE 493 (at 6 minutes nominal retention time) and the normal contact time run was DOE 494 (at 30 minutes nominal retention time). When the oil yields in the coal dissolution step were compared, the 30 minute retention time reaction produced more oil, as would be expected. When the oil yields in the catalyzed upgrading step were compared, the yield from the SCT feedstock was a little larger than the yield from the 30 minute retention time feedstock. When the first and second stages were taken together, the oil from the sum of the steps was nearly the same in both cases.

It is therefore of interest to compare the solubility distribution of the distillation residues from each feedstock to see if some difference can be found that would explain the difference in reactivity.

#### B2.1.2 Solubility Data

Figures B-4 and B-5 show that the solubility of the distillation residue increased in the hexane rich test reagents when the reaction time was increased from 6 minutes nominal to 30 minutes nominal. This behavior is accompanied by elimination of some of the fractions soluble only in the higher concentrations of pyridine. Thus, on the basis of solubility behavior, it is demonstrated that progressive reaction of the vacuum distillation residue material is taking place as the reaction time is increased.

### B2.2 Comparison of Fixed Bed and Slurry Catalysts (Runs DOE 496-498B)

#### B2.2.1 Introduction

Run DOE 496 was a short contact time coal dissolution run which was used to prepare filtered high temperature, high pressure separator bottoms for upgrading studies. This feed was used with HDS 1443 ($NiMo/Al_2O_3$) and pyrite slurry catalysts in runs DOE 497 and 498, respectively.

#### B2.2.2 Solubility Data

The solubility curves were determined for the DOE 496, 497B and 497C distillation residues (Figures B-6, B-7 and B-8). This was done because the solubility pattern reported by the Soxhlet extraction method was peculiar in the sense that the toluene solubility seemed high relative to the hexane solubility. The extraction by hexane appeared incomplete and it appears necessary to use the precipitation method (this study) to check the results.

The chart obtained for the DOE 496 distillation residue (Figure B-6) compares favorably with the chart presented for DOE 479A* with conventionally cleaned Burning Star coal at 6 minutes retention time and with 2000 psig hydrogen pressure. When the pressure was increased to 2250 psig in DOE 496, the distillation residue was slightly more soluble in hexane and in the lower percentages of pyridine added to hexane. These are small shifts but are believed to be significant.

When the filtrate was reacted in the presence of HDS 1443 catalyst, the SRC component of the feedstock was hydrogenated and the solubility of the distillation residue was substantially increased. The solubility in hexane was found to be 74% for the material processed at 415°C and 80% for the material processed at 430°C. See Figures B-7 and B-8. The least soluble fractions in the feedstock have been eliminated and the residual material has been shifted to more soluble fractions in both cases. More shift is observed at the 430°C temperature than at the 415°C temperature. Thus, in addition to removal of sulfur and nitrogen from the SRC component of the reaction product, a substantial alteration in the solubility of this material has been obtained. It should be noted that the hexane solubility by this method is substantially different from the solubility by the Soxhlet extraction method. It is believed that the Soxhlet result is not dependable for this kind of material, though the cause is obscure. The powdered sample forms a gummy mass in the thimble and it appears that the solvent is not able to penetrate the material. The clue that trouble is present in this extraction is that the solubility in toluene is very high while the solubility in hexane is not very high by the method.

When the filtrate was reacted in the presence of pyrite, the increase in solubility was also substantial (Figures B-9 and B-10). The hexane solubility was 64.5% at 415°C and 70.0% at 430°C. This is reasonable based on the observation that the hydrogen content of the distillation residue was nearly the same as the hydrogen content of the residue processed with the HDS catalyst. Thus, the modification of the distillation residue by hydrogenation was largely accomplished with either catalyst, the difference in behavior being mainly the efficiency with which heteroatoms were removed. The lower efficiency of pyrite is evident since the solubility for materials in hexane is about 10% less at each temperature than the solubility in the corresponding HDS processed material. A lessor shift in the solubility of higher fractions is also evident in the case of pyrite catalysis.

It has been estimated that both the HDS 1443 catalyst powder and the pyrrhotite derived from the pyrite tended to accumulate in the upflow

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* "Advanced Coal Liquefaction Research," Quarterly Technical Progress Report for the Period January 1, 1983 through March 31, 1983; December 1983, PC50001-15.

reactor to establish solids levels in the vicinity of 30%. Neither of these catalysts has done as well as the Shell 324 catalyst working in the trickle-bed mode. There are several differences in the mode of operation which are likely to account for this behavior. First: the ratio of catalyst solids to substrate is lower for the powdered material, though the dwell time in the trickle bed is likely shorter than in the upflow reactor. Second: the back mixing in the upflow reactor will substantially alter the contact time pattern allowing a partly reacted fraction to exit the reactor fairly soon after it is introduced. Finally, it is evident that pyrite alone does not have the heteroatom removing potential (and possibly the cracking potential, as well) of the more active metal sulfides on alumina.

### B2.2.3 Conclusions

In the experiments from run DOE 484 through the present series, we have explored the use of several catalysts in various operating modes. It is evident that the best potential for heteroatom removal lies in the vapor-phase reactor and that after that the trickle-bed reactor is most effective. Each of these systems has stringent requirements for feedstock in terms of volatility and absence of solids. These requirements can be satisfied by processing distillate or carefully filtered material. Distillate can be made in the SRC II mode using pyrite as the catalyst, either as a natural component of the coal or as an additive where it is absent. The production of short contact time filtrate has been demonstrated as a method for making a feedstock which can be processed on a trickle-bed reactor. The catalytic reactions are run at mild conditions and do not generate much hydrocarbon gas. All of the heteroatoms are removed as hydrogenated products except for that part of the oxygen which is eliminated as carbon monoxide and carbon dioxide. These are taken out in the initial solution reaction and only minor amounts are made in the catalytic step.

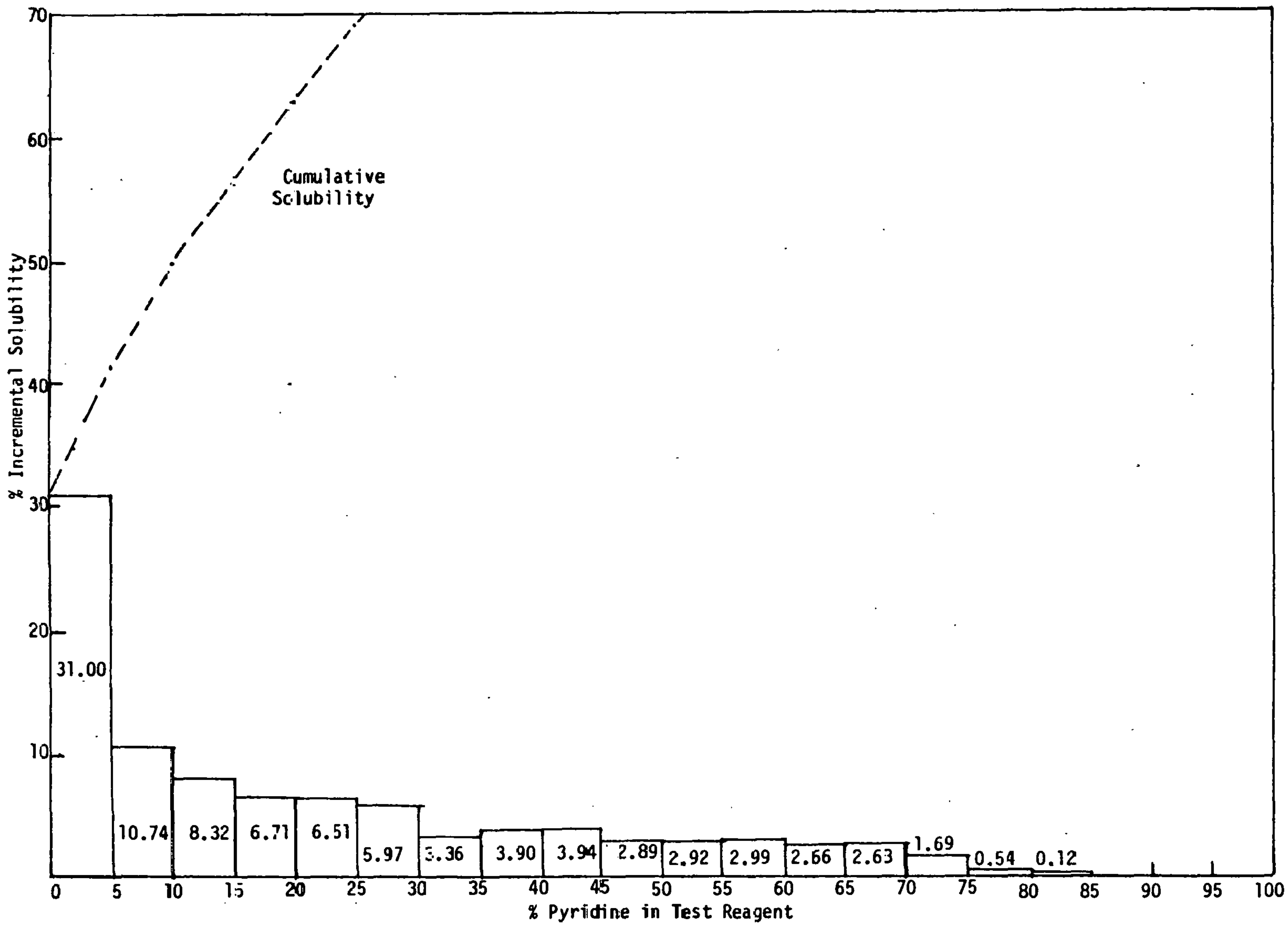
Use of the powdered catalysts or of ebullating pellets in the upflow mode appears to develop a much lower potential for finishing the heteroatom removal reactions. It would appear that the only advantage in this system is the tolerance for mineral matter which can be allowed to remain in the feedstock. The same advantages and disadvantages apply to emulsion generated catalysts, with the added disadvantage that concentrations are inherently low and that considerable oil and water have to be added to sustain the catalyst addition rate.

It is evident that the most reactive species added is the raw coal and that the next most reactive species is the preasphaltene derived from the coal. As material is reacted, thermal bond breaking and hydrogenation of the resultant free radicals appear to be the dominant reaction mechanism. This results in a progressively more thermally stable and hydrogenated product array (which is progressively more soluble in hexane) approaching saturated hydrocarbons as a limit. Not much difference is observed from one catalyst to another in this regard, the more potent catalysts tending to cause more effect at a given operating condition but products at equivalent stages of conversion appear to be available even with crude catalysts if these are used in suitable ways. It appears that hydrogenation requires some kind of catalyst, and it appears that cracking to make distillate also requires catalysis. Coal minerals must supply some of each function since the SRC II process is operable on coal minerals alone, given sufficient iron in the feed coal. By inference, the clays are the other component of natural catalysis. The studies with Burning Star coal washed in various ways tend to support this conclusion, particularly since the unwashed sample made one of the highest distillate yields.

Working with natural catalysis has been a difficulty since the activities are low. The question is then, how can more active catalysts be applied? Generally, this means a separation of the mineral matter, construction of a mineral tolerant catalyst system, or reprocessing of distillate from a crudely catalysed reaction in recycle mode (SRC II or even EDS type distillate). It does not appear that catalysis applied out of direct contact with the coal derived material is as effective as catalysis in the dissolution reactor. The turnover rate for the catalyst in the reactor outruns the effect of a reaction conducted only to improve the solvent. This seems to be the main chemical problem in the EDS strategy while backmixing is likely the main chemical problem in any of the processes using an ebullating bed of catalyst.

Figure B-1

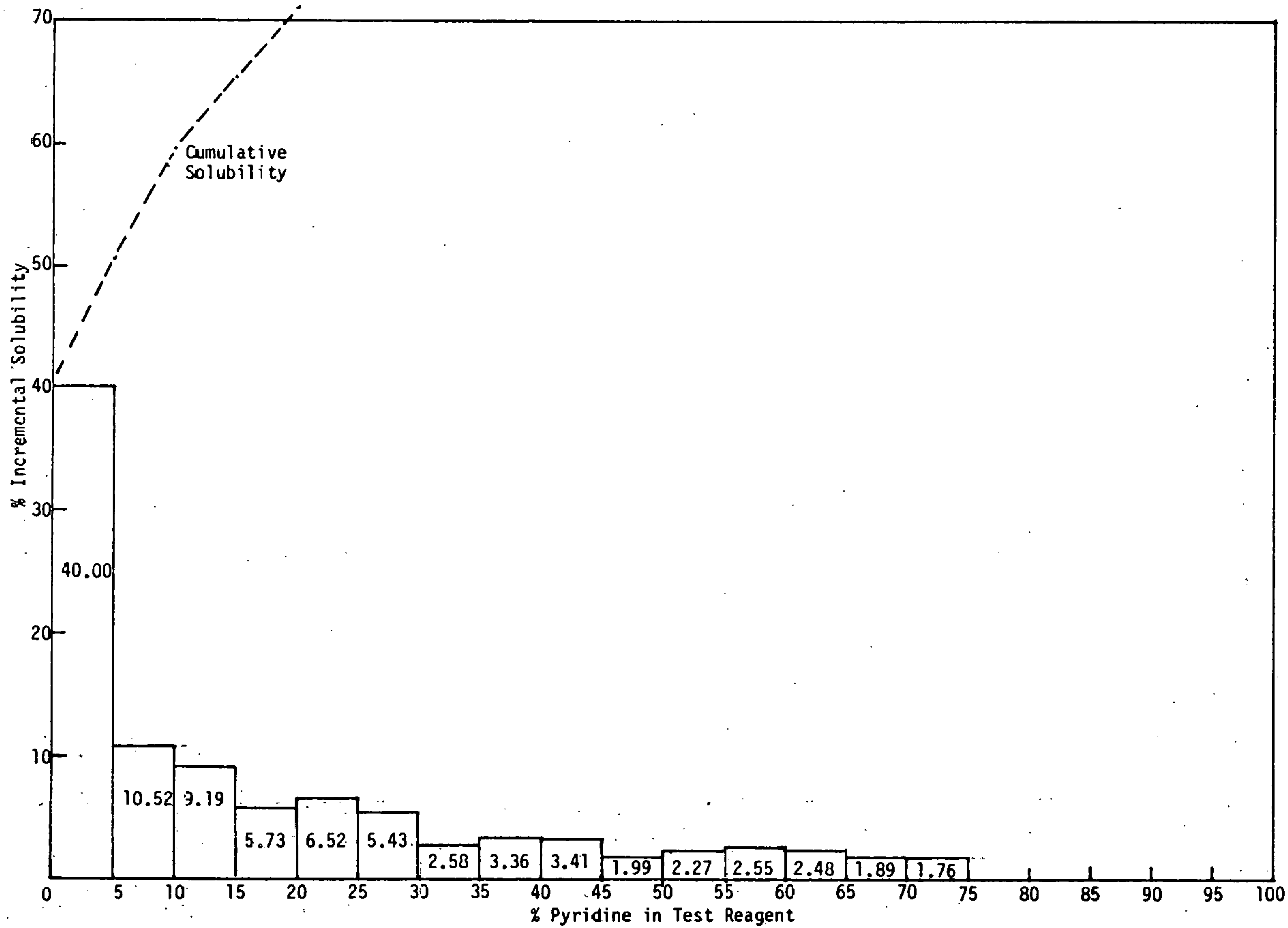
Solubility of Residue from Vacuum Distillation of High Temperature, High Pressure Separator Bottoms. Run DOE 499A*



* 15 minutes residence time

Figure B-2

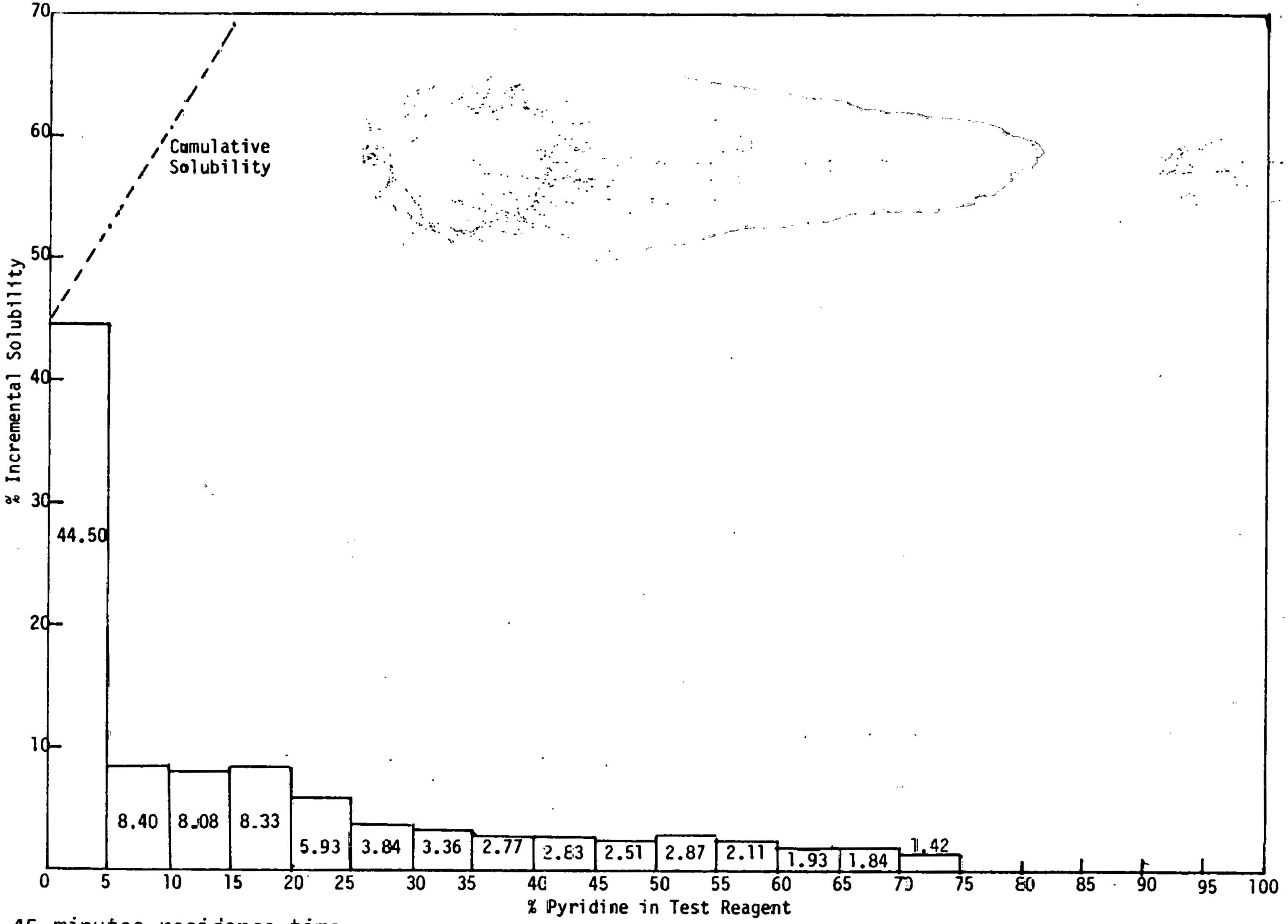
Solubility of Residue from Vacuum Distillation of High Temperature, High Pressure Separator Bottoms. Run DOE 499B*



* 30 minutes residence time

Figure B-3

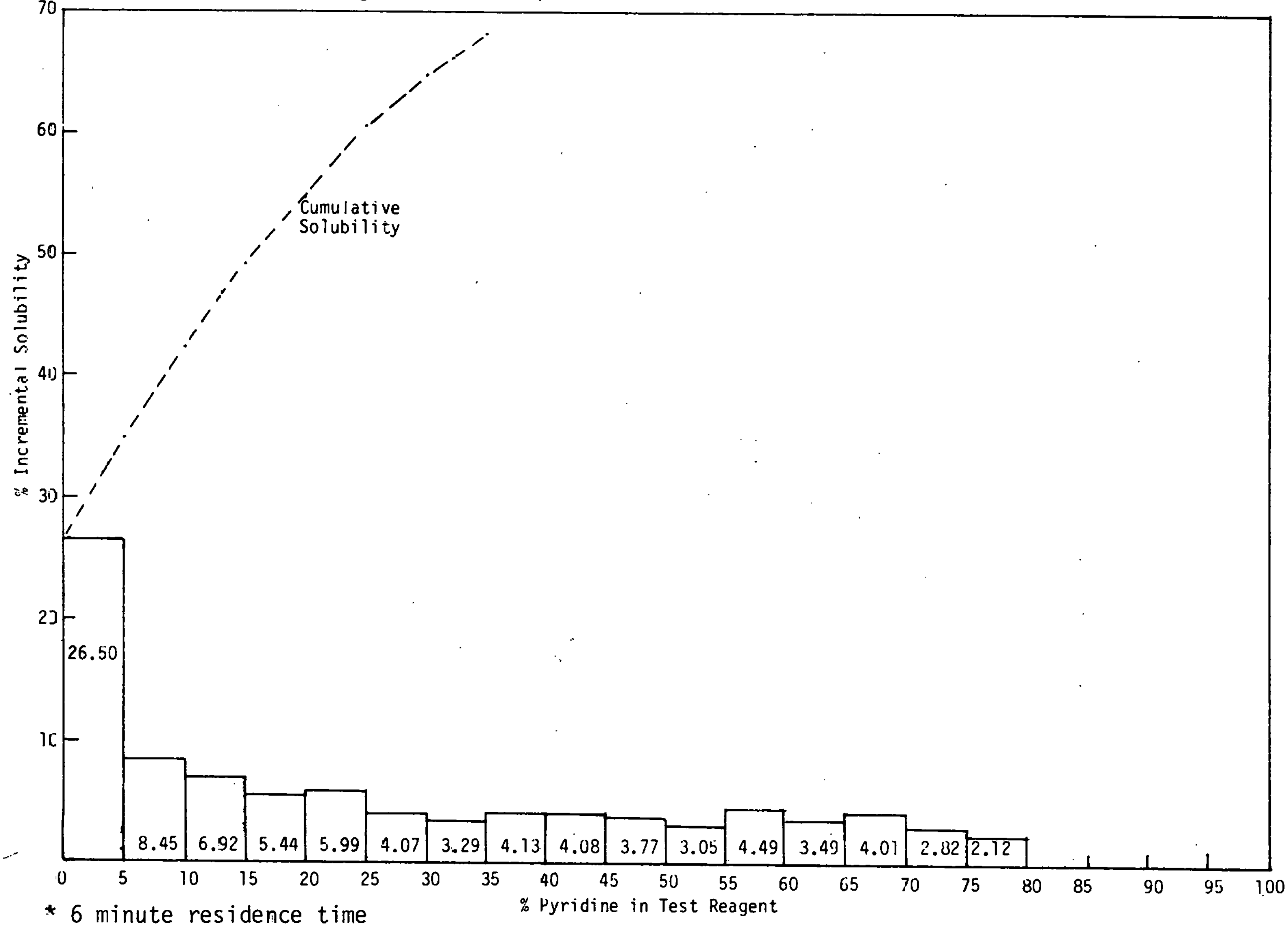
Solubility of Residue from Vacuum Distillation of High Temperature, High Pressure Separator Bottoms. Run DOE 499C*



* 45 minutes residence time

Figure B-4

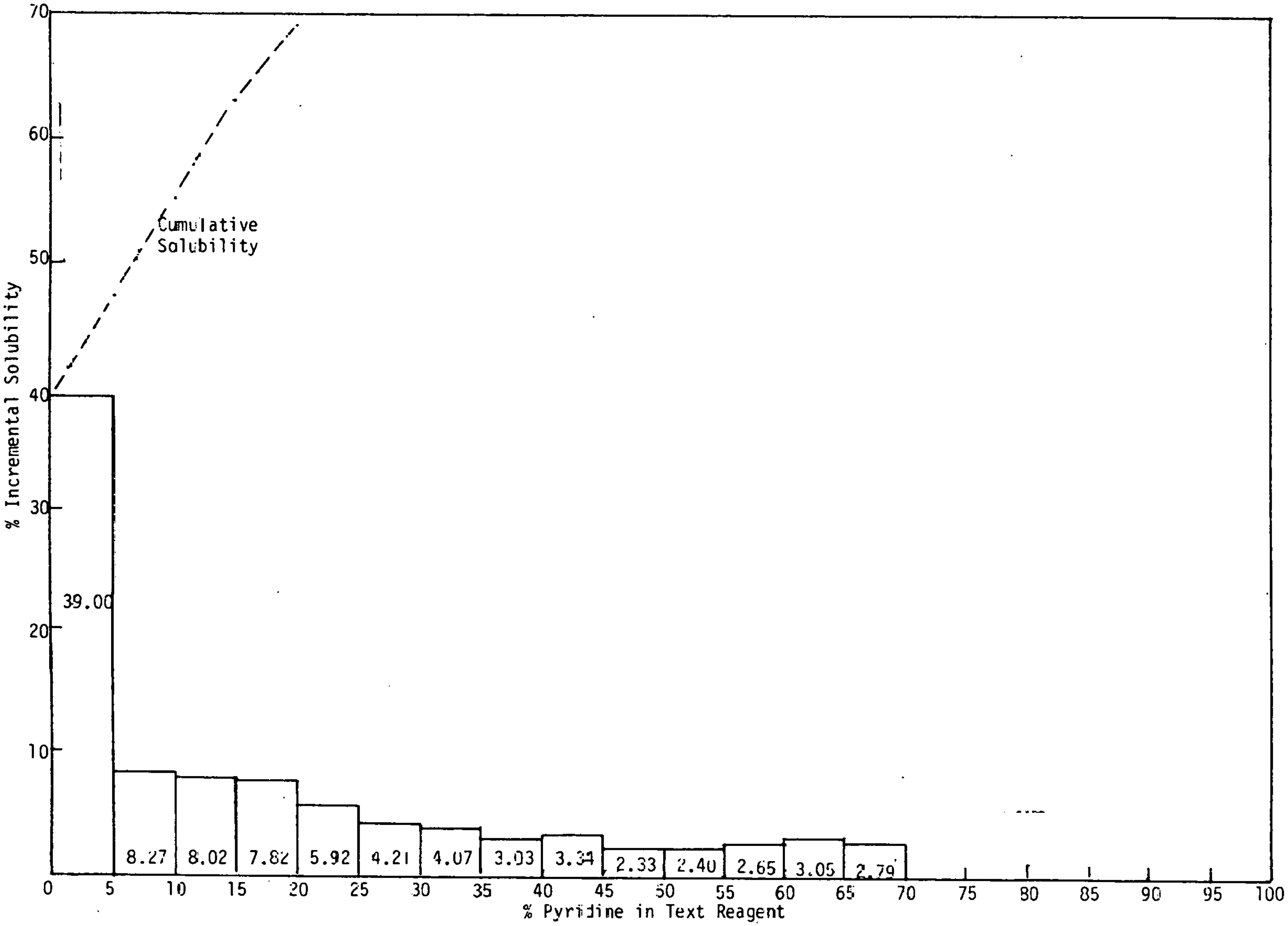
Solubility of Residue from Vacuum Distillation of High Temperature, High Pressure Separator Bottoms. Run DOE 493*



* 6 minute residence time

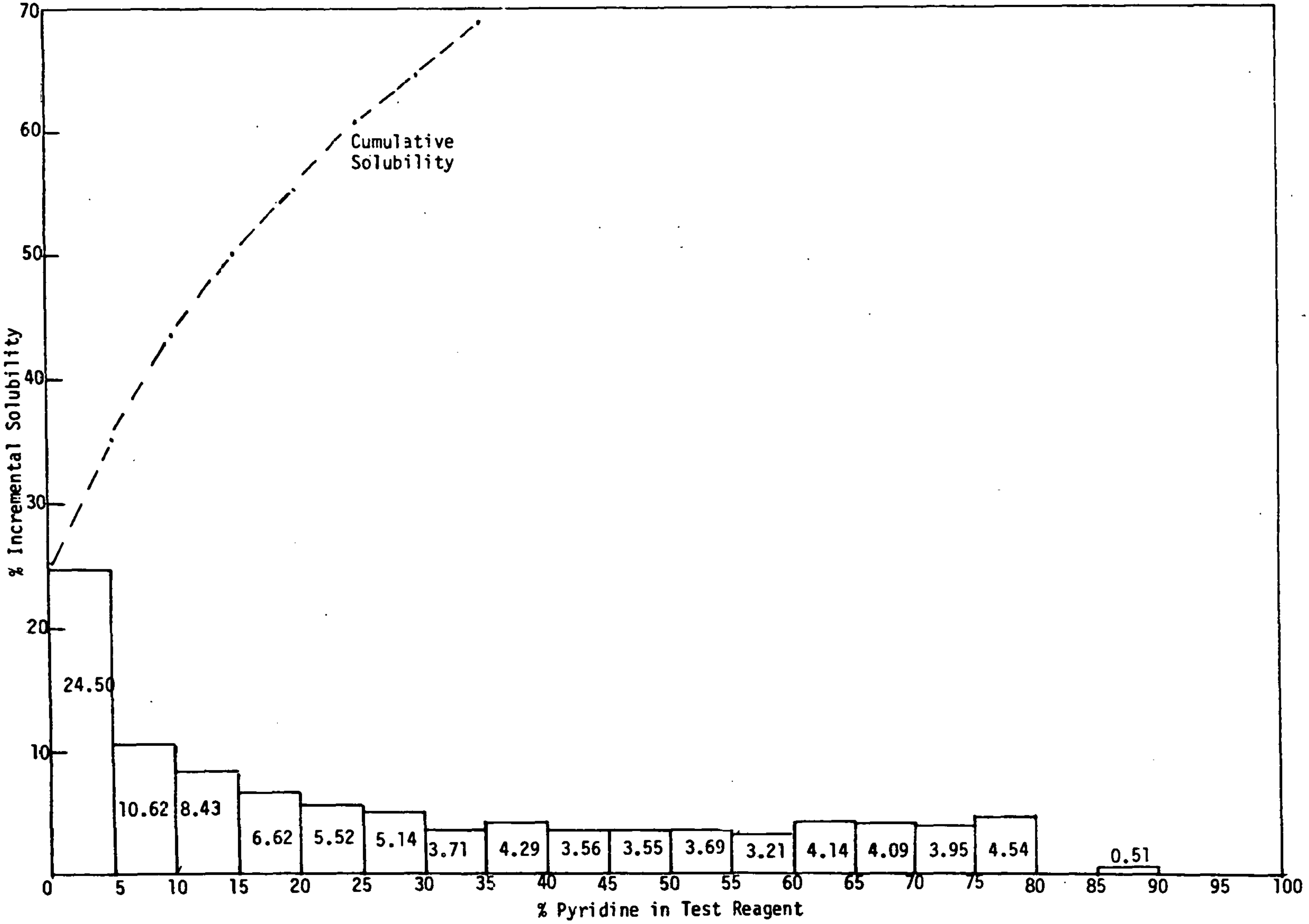
Figure B-5

Solubility of Residue from Vacuum Distillation of High Temperature, High Pressure Separator Bottoms. Run DOE 494*



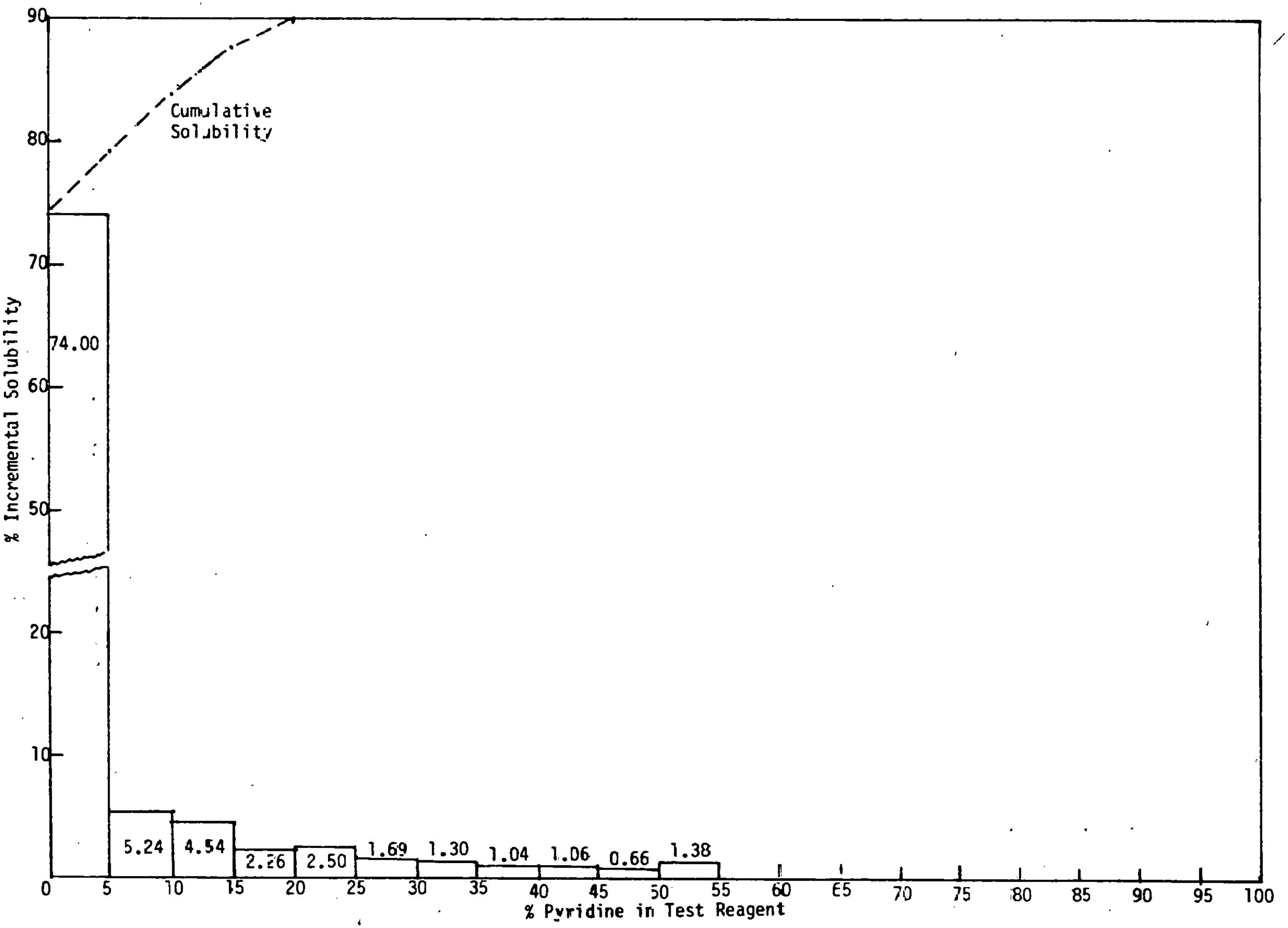
* 30 minutes residence time

Figure B-6
Solubility of Residue from Vacuum Distillation of High Temperature, High Pressure Separator Bottoms. Run DOE 496*



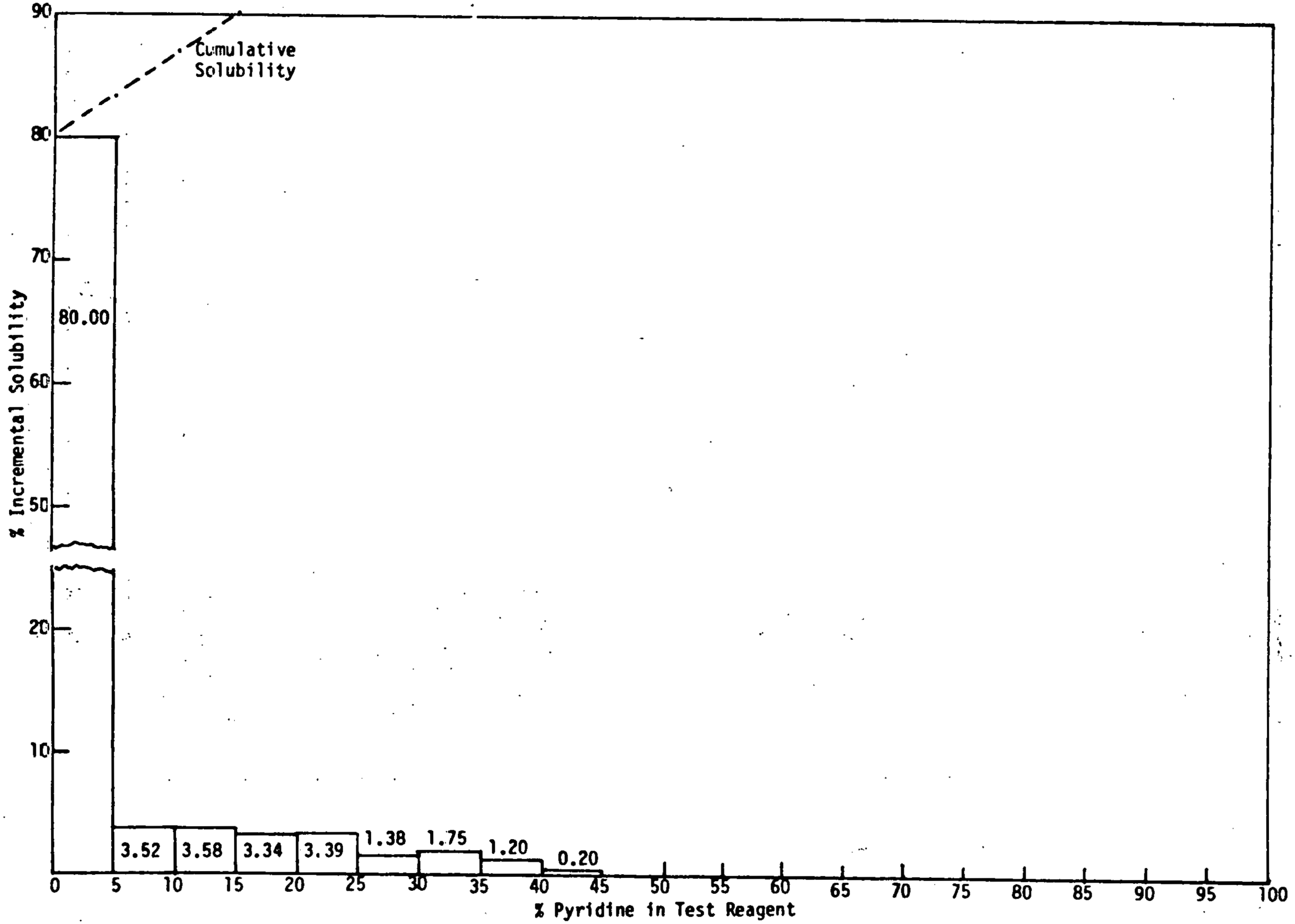
* Coal Dissolution

Figure B-7
Solubility of Residue from Vacuum Distillation of High Temperature, High Pressure Separator Bottoms. Run DOE 497B-2*



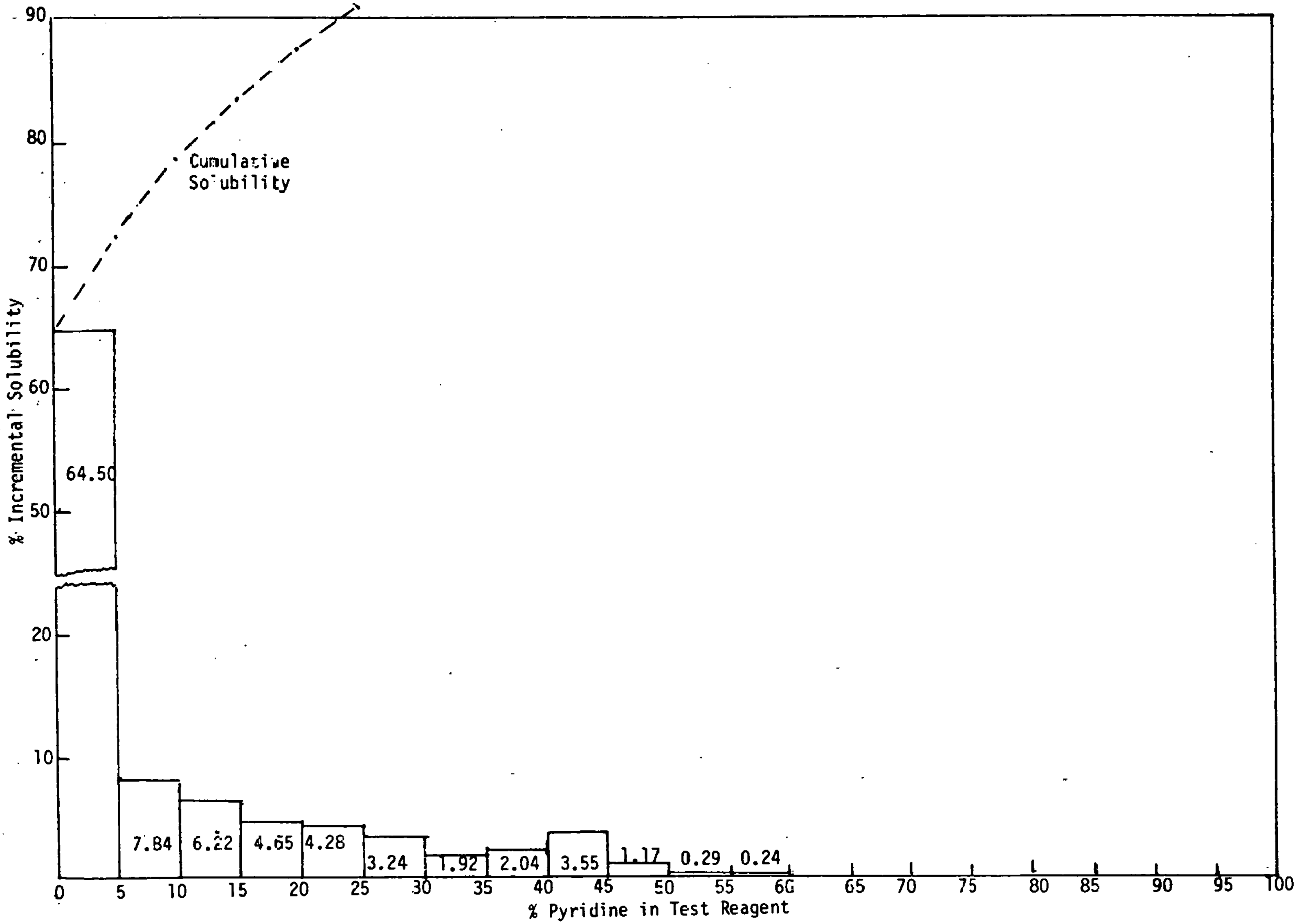
* HDS Catalyst at 415°C

Figure B-8
Solubility of Residue from Vacuum Distillation of High Temperature, High Pressure Separator Bottoms. Run DOE 497C*



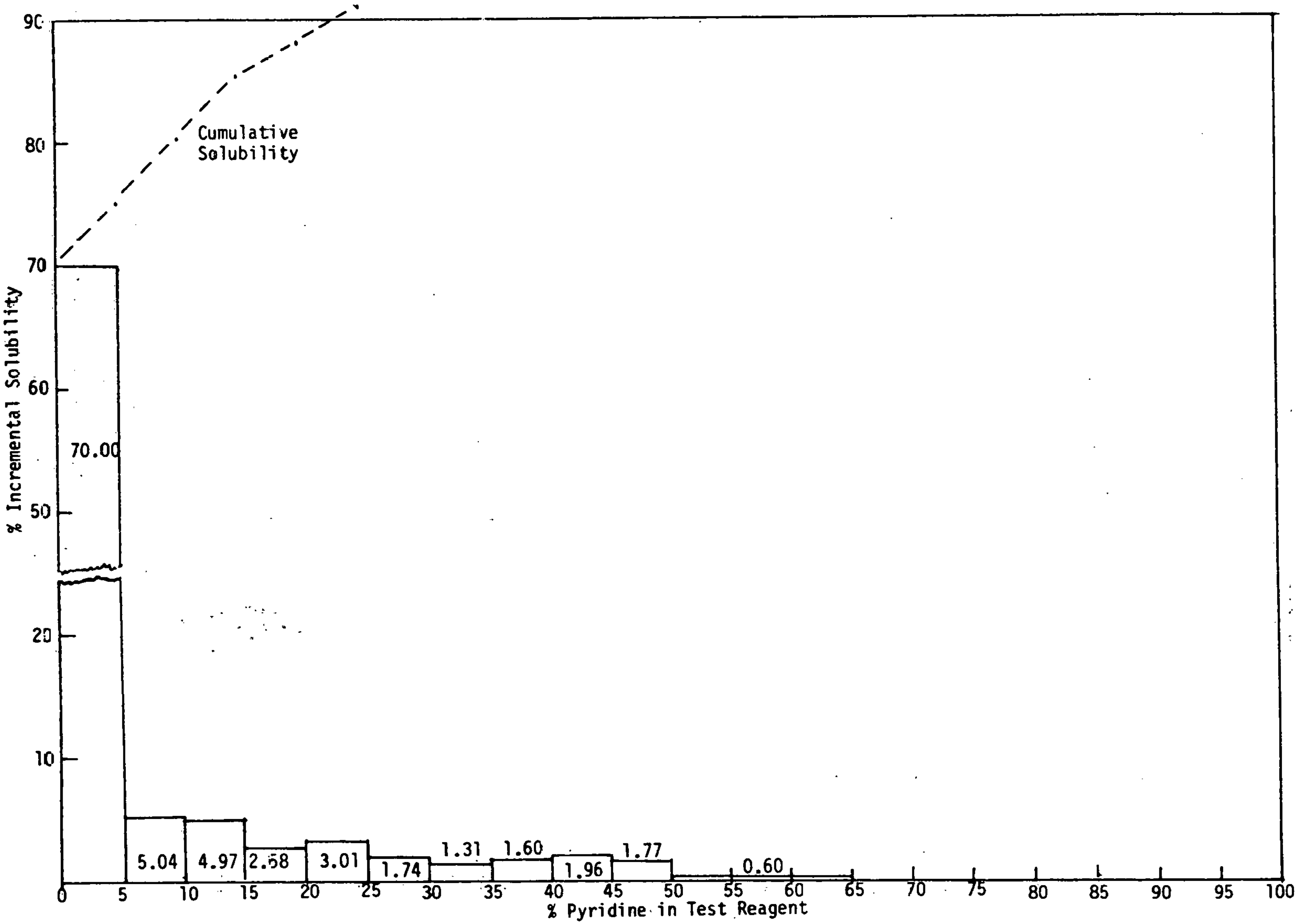
* HDS Catalyst at 430°C

Figure 3-9
Solubility of Residue from Vacuum Distillation of High Temperature, High Pressure Separator Bottoms. Run DOE 498A*



* Pyrite Catalyst at 415°C

Figure B-10
Solubility of Residue from Vacuum Distillation of High Temperature, High Pressure Separator Bottoms. Run DOE 498B*



* Pyrite Catalyst at 430°C

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