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# COAL-LIQUEFACTION-CATALYST DEVELOPMENT

## QUARTERLY PROGRESS REPORT NO. 4

BY

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# FOREWARD

The H-Coal process, developed by Hydrocarbon Research, Incorporated (HRI), involves the direct catalytic hydroliquefaction of coal to low-sulfur boiler fuel or synthetic crude oil. A 200-600 ton/day H-Coal pilot plant has been constructed next to the Ashland Oil, Incorporated refinery at Catlettsburg, Kentucky under DOE contract to Ashland Synthetic Fuels, Incorporated. The heart of the process is the catalyst; therefore, it is desirable to optimize the specific functions of the catalyst as well as minimize its cost. The objective of this program is to develop improved catalysts for coal liquefaction with the overall objective of improving the H-Coal process. This project is the continuation of the catalyst development program previously funded by the Electric Power Research Institute (EPRI).

The program was originally divided into five project tasks:

Task 1 - Catalyst Preparation and Screening
Task 2 - Catalyst Aging Tests--Eastern Coal
Task 3 - Catalyst Aging Tests--Western Coal
Task 4 - Development Support Studies--Synthetic Coal
Task 5 - Application of New Catalysts--H-Coal

The object of this report is to outline and summarize progress in all the project tasks during the last quarter of the project plus convey new information concerning earlier quarters that has since become available.

Utilization of the flexibility originally built into Task 2 was made to determine the feasibility of using Amoco's continuous aging unit to test SRC I upgrading catalysts. This work will be reported under Tasks 2 and 3.

# COAL LIQUEFACTION CATALYST DEVELOPMENT

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JULY 1 - SEPTEMBER 30, 1980

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## TASK 1 - CATALYST PREPARTATION AND SCREENING

Under Task 1 of the Coal Liquefaction Catalyst Development Program, new experimental catalysts will be prepared, characterized, and tested in a batch screening unit. Most of the experimental catalysts are prepared in our Amoco laboratories. The activities under Task 1 focus on the development of highly improved catalysts by structuring the experimental program to areas which offer the most promise. The most promising areas consist of the following:

Modified aluminas
Alternate catalytic materials
Multifunctional catalysts
Novel catalyst system

During this quarter 42 batch screening runs were successfully completed. Catalysts from all key areas were tested with a large emphasis on the retesting and refining of thos systems reported to show promise in the 1st annual report. A categorization of our 42 runs is presented below and indicates that much of our effort was directed toward novel catalyst systems and modified aluminas. This reflects an effort to improve performance of molten stannous chloride systems and samarium for support stabilization.

TABLE I

CLASSIFICATION OF BATCH RUNS (5th Quarter)

| | |
|---|---|
| Base Runs | 7 |
| Modified Aluminas | 15 |
| Alternate Materials | 2 |
| Two Catalyst Systems | 6 |
| Novel Catalyst Systems | 10 |
| Miscellaneous | 2 |
| Total | 42 |

Unless otherwise noted, all runs were performed under idential conditions and with materials specified previously in the annual report. Product work-up techniques were also identical. An updated list of all catalysts tested to date and a tabulation of our latest run results are presented in Appendix Tables A-I and A-II respectively. All new runs will be discussed according to category with reference to material in the annual report where applicable.

The relative activity index was described in the annual report and will be used throughout this discussion to evaluate catalyst performance. However, heteroatom removal will be discussed in terms of the reciprocals of the relative sulfur and nitrogen levels. This modification is made so that improved catalyst performance will be reflected by an increase in the performance indices.

## Base Case Runs

During this quarter, seven base runs were completed using HDS-1442A as our reference catalyst. These runs were made as a check against any unintentional changes in test conditions or procedures that could affect catalyst evaluation. The results of these tests are summarized in Table II.

TABLE II

BASE RUN RESULTS

| Run Number | Catalyst | R.A. | 1/R.S. | 1/R.N. |
|---|---|---|---|---|
| 3660-195 | HDS-1442A | 1.05 | 1.45 | 1.11 |
| 3859-7 | " | 0.98 | 1.11 | 1.15 |
| 3859-14 | " | 1.02 | 1.15 | 1.09 |
| 3859-17 | " | 0.89 | 0.98 | .96 |
| 3859-18 | " | 0.96 | 1.08 | 1.03 |
| 3859-19 | " | 1.04 | 1.30 | 1.06 |
| 3859-23 | " | 1.04 | 1.14 | 1.37 |
| Average | | 1.00±6% | 1.17±13% | 1.11±12% |

By definition, the relative performance indices obtained with the reference catalyst should all be equal to 1.0 and, in fact, our earlier base runs discussed in the annual report all had average indices of unity. Base runs completed this quarter again show relative activities that average out to 1.0 with a standard deviation of 6%--about the same as before. However sulfur and nitrogen analyses indicate that our base catalyst is doing better this quarter than over the past year. Thus performance indices, 1/RS and 1/RN are significantly greater than unity. Reasons for this drift are unknown but may reflect a change to a new batch of Illinois No. 6 coal that occurred earlier in the quarter. On evaluating experimental catalyst this bias toward better heteroatom removal will have to be taken into account.

## Modified Aluminas

Fifteen modified aluminas were tested in the batch unit to determine the effect of samarium on nickel-moly catalyst and to evaluate a cobalt-moly-samarium catalyst prior to and following a pilot plant testing. The rare earth, gadolinium, was also retested as a possible support stabilizer.

Results obtained with samarium modified nickel-moly system are summarized below:

TABLE III

EFFECTS OF SAMARIUM ON NIMO SYSTEMS

| Run No. | Catalyst No. | Description | R.A. | 1/R.S. | 1/R.N. |
|---|---|---|---|---|---|
| 3660-122 | 3651-82 | $NiMo/Al_2O_3$ (Fresh) | 1.10 | 1.08 | .86 |
| 3660-199 | 3768-173-1 | (Steamed) | 1.07 | 1.39 | 1.09 |
| 3660-198 | 4367-44 | $NiMoSm/Al_2O_3$ (Fresh) | 1.13 | 1.52 | 1.10 |
| 3660-201 | 3768-173-4 | (Steamed) | 1.01 | .93 | 1.33 |
| 3660-194 | 3651-81+4367-5-1 | $Mo/Al_2O_3+Ni/Al_2O_3$ (Fresh) | 1.07 | 1.15 | 1.15 |
| 3859-9 | 3861-2+3768-173-5 | (Steamed) | 1.04 | 1.18 | 1.33 |
| 3660-197 | 4367-43+3651-81 | $NiSm/Al_2O+Mo/Al_2O_3$ (Fresh) | 1.13 | 1.18 | 1.10 |
| 3859-8 | 3762-173-2+3861-2 | (Steamed) | 1.05 | .98 | 1.23 |

Here we see the effect of samarium on cosupported nickel-moly as well as on the nickel component of nickel-alumina/moly-alumina mixture. Results are presented for both the fresh and steamed version of the catalyst. Steaming was conducted at 1200°F for 24 hours. For comparison, the fresh and steamed performance of samarium-free nickel-moly system is also presented.

The unmodified NiMo catalyst, Amocat 1C loses very little liquefaction activity due to steaming and actually gains desulfurization and denitrogenation activity. This behavior differs from CoMo catalysts such as Amocat 1A and HDS-1442A which more significantly deactivated. This difference suggests that cobalt may be catalyzing support degradation to $CoAl_2O_4$ spinel under steaming conditions. During steaming the following reaction predominates:

$$CoO+Al_2O_3 \longrightarrow CoAl_2O_4$$

No stabilization is observed when adding samarium to the cosupported NiMo. While fresh activities are higher, the samarium catalyst loses desulfurization and liquefaction activity after steaming. A mixture of nickel-alumina and moly-alumina is about as active as the cosupported catalyst (as noted in the annual report). Like the cosupported catalyst it is unaffected by steaming except for a slight gain in denitrogenation activity. Samarium addition to the nickel component produces no stabilization. We conclude there is no advantage to adding samarium to nickel-moly systems and that nickel-moly shows far less steam sensitivity than similar cobalt-moly catalysts.

Because of the promising result obtained with the cobalt-samarium-moly system, a large batch was prepared in extrudate form for testing on the continuous aging unit. Prior to our pilot plant run (described under Task 3 of this report) batch testing was performed to evaluate the fresh and steamed activity of a ground portion (60/100 mesh) of this samarium promoted extrudate. Result of these tests are shown in Table IV. For comparison, results obtained with a CoSmMo catalyst prepared on 60/100 mesh powder are also presented.

## TABLE IV

## COBALT SAMARIUM MOLY CATALYST

Fresh Activity

| Run No. | Catalyst No. | Description | R.A. | 1/R.S. | 1/R.N. |
|---|---|---|---|---|---|
| 3889-20 | 4367-51-0 | From Extrudates | 1.08 | 1.25 | 1.14 |
| 3660-173 | 4367-76-0 | From Powder | 1.08 | 1.20 | 1.20 |

Steamed Activity

| Run No. | Catalyst No. | Description | R.A. | 1/R.S. | 1/R.N. |
|---|---|---|---|---|---|
| 3859-21 | 3861-34-1 | From Extrudates | 1.09 | .88 | .85 |
| 3660-184 | 3768-145-2 | From Powder | 1.08 | 1.20 | 1.16 |

The fresh activity for both extrudate and powder forms are identical and similar to our reference catalyst HDS-1442A. The steamed version of the powdered catalyst has lost no activity. The catalyst prepared on extrudate has good denitrogenation activity. Unfortunately sulfur and nitrogen product analyses were not available in time to cancel a pilot plant test which also showed poor extrudate performance. (See Task 3). The steamed extrudate catalyst was also tested using slurry oil in place of Panasol in one batch run and using Wyodak coal in place of Illinois No. 6 in another run. These results are shown in Table V. Our data for reference catalyst, HDS-1442A, is also presented for comparison.

## TABLE V

## EFFECT OF SLURRY OIL AND WYODAK COAL

| Run No. | Catalyst No. | Description | R.A. | 1/R.N. | 1/R.N. |
|---|---|---|---|---|---|
| Slurry Oil + Illinois No. 6 | | | | | |
| 3859-33 | 3861-34-1 | CoMoSm/Extrudates | 1.20 | na | na |
| 3859-31 | 2392-5-0 | HDS-1442A | 1.16 | na | na |
| Wyodak Results + Panasol | | | | | |
| 3859-38 | 3861-34-1 | CoMoSm/Extrudate | 1.00 | na | na |
| 3889-39 | 2392-5-0 | HDS-1442A | .97 | na | na |
| 3859-37 | 2392-5-0 | " | .97 | na | na |
| Illinois No. 6 + Panasol | | | | | |
| 3889-21 | 3861-34-1 | SnCoMo/Extrudate | 1.09 | .88 | .85 |
| Average | 2392-50 | HDS-1442A | 1.00 | 1.17 | 1.11 |

na = unavailable

Pilot plant tests were run using slurry oil and Wyodak coal in place of Panasol and Illinois No. 6. The batch runs summarized in Table V show that neither changing coal type nor the liquefaction media changes the ranking of the catalyst with respect to activity for liquefaction. Thus poor pilot plant performance is not related to either of these factors.

More recent results obtained by electron microscopy and X-ray line scanning indicate that the samarium catalyst prepared on extrudates has very poor cobalt and samarium distribution. This may account for the poor performance since much of the metals may be unavailable to the reactor environment. The catalyst prepared on powdered alumina is less vulnerable to poor metal distribution and should perform better as noted in our batch runs.

Finally gadolinium, a rate earth, was evaluated as a support stabilizer. The fresh and steamed activities of a cobalt, gadolinium, molybdenum catalyst are shown in Table VI.

## TABLE VI

## CoGdMo PERFORMANCE

| Run No. | Catalyst No. | Description | R.A. | 1/R.S. | 1/R.N. |
|---|---|---|---|---|---|
| 3660-172 | 4367-27-0 | CoMoGd Fresh | .93 | 1.08 | 1.19 |
| 3660-200 | 3768-173-1 | " Steamed | 1.12 | .89 | .75 |

While liquefaction activity is improved by steaming, heteroatom removal activity is lost. The improved liquefaction is probably due to a steam opening of pores and does not reflect stabilization imparted by gadolinium.

## Alternate Catalytic Materials

Two catalysts prepared from alternate materials were tested during this quarter. Both Tests were repeats of earlier runs and were performed to confirm the promising results previously observed. Our observations are summarized in Table VII.

TABLE VII

ALTERNATE MATERIALS

| Run No. | Catalyst No. | Description | R.A. | 1/R.S. | 1/R.N. |
|---|---|---|---|---|---|
| 3889-26 | 4367-1-1 | $Co_2BMoB_2$ in $Al_2O_3$ Matrix | 1.0 | 1.01 | 1.41 |
| 3660-117 | " | " | 0.9 | .87 | 1.32 |
| 3660-203 | 4367-1-3 | $Co_2BMO_2N$ in $Al_2O_3$ Matrix | 1.0 | .95 | 1.23 |
| 3660-104 | " | " | 1.32 | .63 | .74 |

Both catalysts performed well in our latest experiments showing high denitrogenation activity and acceptable liquefaction and desulfurization activity. The reproducibility of the cobalt boride-moly boride tests is good and confirms the low nitrogen product observed earlier. Tests with the moly nitride were not as reproducible but our earlier results were probably in error due to poor flow control during that run. On the basis of these results, the cobalt boride-moly boride system can be recommended for pilot plant testing.

## Multifunctional Catalysts

Seven mixtures were tested during this quarter to determine the effect of varying metal loadings and catalyst ratios on cobalt sodium and moly mixtures. The effect of co-extruding mixed catalysts to overcome possible diffusion barriers was also examined.

The effect of increasing cobalt metal loading is demonstrated in Table VIII.

## TABLE VIII

## COBALT LOADING EFFECTS

| Run No. | Catalysts | Description* | R.A. | 1/R.S. | 1/R.N. |
|---|---|---|---|---|---|
| 3660-192 | 2392-143+3651-81 | 2.3%Co,1.0% Na 15% $MoO_3$ | 1.07 | 1.05 | 1.02 |
| 3859-13 | 4367-46+3651-81 | 6.0% Co, 1.3% Na + 15% $MoO_3$ | 1.11 | 1.12 | 1.23 |
| 3859-30 | " " | " " | 1.07 | 1.02 | 1.32 |

*Results were obtained at a constant catalyst ratio of one part cobalt-sodium to 4 parts molybdenum catalyst. Sodium and molybdenum loadings were also kept constant at 1 and 15%, respectively. Increasing the cobalt loading from 2.3% to 6.0% has little effect on liquefaction or desulfurization activity but significantly improves nitrogen removal. A duplicate run shows this improvement is reproducible.

In other tests we examined the effect of increasing the cobalt-sodium to molybdenum catalyst ratio. This ratio study was performed with both high and low cobalt catalyst and results are summarized in Table IX.

## TABLE IX

## CATALYST RATIO EFFECTS

At 2.3% Cobalt Loading

| Run No. | Catalysts | Ratio | R.A. | 1/R.S. | 1/R.N. |
|---|---|---|---|---|---|
| 3660-192 | 2392-143 + 3651-81 | 1/4 | 1.07 | 1.05 | 1.02 |
| 3859-12 | " " | 2/3 | 1.07 | 1.02 | 1.11 |
| 3889-11 | " " | 3/2 | 1.06 | 1.10 | 1.27 |
| At 6.0% Cobalt Loading | | | | | |
| 3889-30 | 4367-46 + 3651-81 | 1/4 | 1.07 | 1.02 | 1.32 |
| 3889-24 | " " | 2/3 | 1.05 | 1.02 | 1.33 |

At the low cobalt loading, the ratio of cobalt to moly catalysts has little effect on liquefaction or desulfurization activity. However nitrogen removal is improved as the ratio is increased. This observation agrees with our cobalt loading experiments of Table VIII showing that increasing the cobalt content of the mixture improves denitrogenation. It apparently makes little difference if cobalt is added by increasing the metal loading or by increasing the cobalt to moly catalyst ratio. The overall cobalt content of the mixture is the important factor. At the high, 6.0% cobalt level, denitrogenation activity is already high for the 1 to 4 mix. Increasing the ratio to 2/3 yields no further improvement.

Conceivably, diffusion limitations may exist between the cobalt sodium and molybdenum catalyst particles used in the batch tests reported in Table VIII and IX. In these tests catalyst particles of 60 to 100 mesh size were loosely mixed and slurried in the reaction media. The existence of diffusion limitations might be detected by reducing the particle size of each mixture component to pass 100 mesh and co-extruding the mixture to give close contact between the two catalysts. The co-extrudate is then ground to give 60/100 mesh particles. We have now tested this mixture, prepared by co-extrusion and summarize the results in Table X. For comparison, we also show results obtained with a loose mixture having the same catalyst ratio metal loadings and final particle size.

TABLE X

CO-EXTRUDED MIXTURE

| Run No. | Catalyst No. | Description | Ratio | Preparation | RA | 1/RS | 1/RN |
|---|---|---|---|---|---|---|---|
| 3859-29 | 4367-52 | (6.0% Co 1% Na) + ($15\%$ $MoO_3$) | 1/4 | Co-extruded | 1.05 | 1.02 | 1.32 |
| 3889-30 | 4367-46+<br>3651-81 | " " | 1/4 | Mixed | 1.07 | 1.02 | 1.41 |

Except for a slight increase in denitrogenation activity both loosely mixed and co-extruded mixtures perform identically. No apparent diffusion limitations exist for our batch unit. Diffusion may be a problem in the continuous aging unit where much larger particles are tested. Here the co-extruded catalyst would be expected to perform best.

## Novel Catalyst Systems

Ten novel catalyst systems were tested in the batch unit during this quarter. tests were directed at optimizing the nickel graphite and stannous chloride catalyst that showed promise in our earlier work.

A preliminary test showed nickel graphite had superior desulfurization activity when compared to nickel supported on alumina. The result of these tests are summarized in Table XI.

## TABLE XI

### NICKEL GRAPHITE

| Run No. | Catalyst No. | Description | RA | 1/RS | 1/RN |
|---|---|---|---|---|---|
| 3660-96 | 4367-34-4 | Ni/Graphite | .92 | .73 | .91 |
| 3660-120 | 4367-5-1 | Ni/$Al_2O_3$ | .80 | .55 | .89 |

Neither of these catalysts have acceptable overall performance when compared to our reference. However, when nickel graphite is mixed with moly alumina, a superior catalyst is obtained. Its performance is summarized in Table XII. For comparison, results obtained with a nickel-alumina/moly-alumina mixture and cosupported nickel-moly are also presented.

## TABLE XII

### NICKEL GRAPHITE MIXTURE

| Run No. | Catalysts | Description | Ratio | RA | 1/RS | 1/RN |
|---|---|---|---|---|---|---|
| 3859-24 | 4367-34-4 +<br>3651-81 | Ni/Graphite/Mo/$Al_2O_3$ | 1/4 | 1.08 | 1.04 | 1.32 |
| 3660-130 | 4367-5-1 +<br>3651-81 | Ni/$Al_2O_3$ + Mo/$Al_2O_3$ | 1/4 | 1.15 | .98 | 1.00 |
| 3660-132 | 3651-82 | NiMo/$Al_2O_3$ | -- | 1.10 | 1.08 | .86 |

The graphite containing mixture shows a significant increase in denitrogenation activity and acceptable liquefaction and desulfurization activity.

Several experiments were aimed at optimizing our molten stannous chloride system. Our initial studies showed that the tin and chloride functions could be separated while maintaining significant liquefaction activity. This result suggests bifunctional catalysis in which chloride promoter acid catalyzed cracking reactions while tin catalyzer hydrogenation. It also suggests that non-volatile substitutes for chloride may exist which when mixed with tin yield thermally stable high performance catalysts. During this quarter we have tested molybdenum oxide as a chloride substitute. Not only is molybdena an acidic oxide, it obviously has catalytic activity of its own. Several tin oxide-moly oxide mixtures have now been tested. The results of these tests are summarized in Table XIII. In order to better observe the activity of tin in tin-moly mixtures, Table XIII also shows data for an unpromoted moly catalyst, Amocat 1B and for pure tin oxide.

TABLE XIII

TIN MXODE MOLYBDENUM OXIDE MIXTURES

| Run No. | Description | | RA | 1/RS | 1/RN |
|---|---|---|---|---|---|
| 3859-5 | 4367-38 + 3651-81 | $SnO_2/Al_2O_3+MoO_3/Al_2O_3$ | 1.09 | 1.08 | 1.18 |
| 3660-204 | 4367-34-8+ | $SnO_2+MoO_3/Al_2O_3$ | 1.04 | 1.05 | 1.22 |
| 3660-177 | 4367-38-0 | $SnO_2$ | .79 | .72 | 1.10 |
| 3660-123 | 3651-81 | $MoO_3/Al_2O_3$ | .99 | .81 | .76 |

The tin-moly mixtures are clearly superior to pure tin oxide or to umpromoted moly-alumina. Again this strongly suggests bifunctional catalysis. These mixed systems are about equivalent to our reference HDS-1442A for heteroatom removal while exhibiting 4 to 9% better liquefaction activity.

Several experiments were directed at finding the optimum tin loading in the tin-moly system. Thus three catalysts were prepared by impregnating moly alumina, Amocat 1B with 5, 12 and 25% stannous chloride. The resulting catalysts were dried and tested uncalcined and then calcined and retested. The results of these experiments are summarized in Table XIV.

## TABLE XIV

## SN LOADING EFFECTS

| Run No. | Catalyst No. | Description | % $SnCl_2$ | RA | 1/RS | 1/RN |
|---|---|---|---|---|---|---|
| | | Uncalcined Catalysts | | | | |
| 3660-123 | 3651-81 | $Mo/Al_2O_3$ | 0% | .99 | .81 | .76 |
| 3889-15 | 4367-49 | $SnCl_2$-$Mo/Al_2O_3$ | 5% | 1.07 | 1.04 | 1.18 |
| 3889-15 | 4367-50 | " | 12% | 1.08 | 1.06 | 1.12 |
| 3859-6 | 4367-45 | " | 25% | 1.10 | .95 | 1.22 |
| | | Calcined Catalysts | | | | |
| 3660-123 | 3651-81 | $Mo/Al_2O_3$ | 0* | .99 | .81 | .76 |
| 3859-27 | 4367-49 | $SnO_x$-$Mo/Al_2O_3$ | 5* | 1.03 | 1.03 | 1.37 |
| 3859-22 | 4367-50 | $SnO_x$-$Mo/Al_2O_3$ | 12* | 1.04 | 1.06 | 1.35 |
| 3859-10 | 4367-45 | $SnO_x$-$Mo/Al_2O_3$ | 25* | 1.08 | 1.05 | 1.15 |

*$SnCl_2$ Loading Before Calcination

Results show that the largest increase in activity is obtained in going from 0 to 5% stannous chloride. Further increases produce only slightly improved liquefaction activity and no change in heteroatom removal. Therefore 5% $SnCl_2$ on Amocat 1B is probably the optimum composition. Behavior of the calcined catalyst should reflect these thermal stability. Table XIV shows that calcination produces almost no change in liquefaction or desulfurization activity and activity improves denitrogenation. The activity of the calcined catalyst is still clearly superior to unpromoted moly and far superior to calcined moly-free stannous chloride alumina.

## CONCLUSIONS AND RECOMMENDATIONS

### Modified Aluminas

Samarium does not stabilize the nickel-moly system against hydrothermal aging. In fact, samarium free catalyst resist aging better than the corresponding modified catalyst, showing no signs of activity loss after treatment in steam at 1200°F for 24 hours. Since cobalt catalysts lose much activity after this treatment cobalt may be catalyzing support breakdown.

The cobalt samarium moly catalyst prepared on extrudates had very poor metal distributions. This may be responsible for the poor performance of this batch of catalyst. If metals can be successfully distributed throughout an extrudate, the samarium modified catalyst should be retested in the pilot plant.

### Alternate Materials

The catalyst prepared by dispersing cobalt boride and moly boride in an alumina matrix continues to exhibit acceptable liquefaction and desulfurization activity and superior denitrogenation activity. If an extrudate can be prepared from these materials having the correct pore structure, pilot plant testing should be conducted to evaluate activity maintenance.

### Two Catalyst Mixtures

The cobalt sodium alumina/moly alumina mixed system has been optimized to give superior liquefaction and denitrogenation activity. A larger batch of coextruded mixture has been prepared and screened and is available for pilot plant testing.

### Novel Catalyst Systems

A thermally stable supported tin chloride catalyst has been prepared and exhibits superior liquefaction and denitrogenation activity. An optimized catalyst contains 5% stannous chloride supported on a molybdenum alumina catalyst such as Amocat 1B. The system maintains its superior performance even after calcination at 1000°F for 3 hours. A large batch is now being prepared for pilot plant testing.

# TABLE A-I

## CATALYST COMPOSITIONS

| CATALYST | COMPOSITION | SUPPORT | COMMENTS | |
|---|---|---|---|---|
| 2392- 5-0 | CO MO | ALUMINA | HDS-1442A | |
| 2392-135-0 | MO | ALUMINA | COMPONENT | |
| 2392-138-0 | CO | ALUMINA | COMPONENT | |
| 2392-143-0 | CO NA | ALUMINA | COMPONENT | |
| 2392-144-0 | CO B | ALUMINA | COMPONENT | |
| 3639- 22-0 | | US SIEVE | COMPONENT | |
| 3651- 80-0 | CO MO | ALUMINA | AMOCAT 1A | |
| 3651- 81-0 | MO | ALUMINA | AMOCAT 1B | |
| 3651- 82-0 | NI MO | ALUMINA | AMOCAT 1C | |
| 3651- 83-0 | | ALUMINA | G120B | |
| 3651-120-3 | CO NI MO | ALUMINA | | |
| 3768- 63-1 | MO | ALUMINA | AMOCAT 1B | STEAMED |
| 3768- 63-2 | CO MO SM | SAMARIUM ALUMINA | COGELLED | STEAMED |
| 3768- 63-3 | CO MO GD | GD ALUMINA | COGELLED | STEAMED |
| 3768- 67-1 | CO MO MG | MAGNESIA ALUMINA | COGELLED | STEAMED |
| 3768- 67-2 | CO MO CE | CERIUM ALUMINA | COGELLED | STEAMED |
| 3768- 87-1 | CO MO U | URANIUM ALUMINA | COGELLED | STEAMED |
| 3768- 87-2 | CO MO BA | BARIUM ALUMINA | IMPREGNATED | STEAMED |
| 3768- 87-3 | CO MO PR | PR ALUMINA | COGELLED | STEAMED |
| 3768- 93-1 | CO MO | ALUMINA | AMOCAT 1A | STEAMED |
| 3768- 93-2 | CO MO | ALUMINA | HDS-1442A | STEAMED |
| 3768-145-1 | CO MO GD | GD ALUMINA | IMPREGNATED | STEAMED |
| 3768-145-2 | CO MO SM | SAMARIUM ALUMINA | IMPREGNATED | STEAMED |
| 3768-145-3 | CO MO PR | PR ALUMINA | IMPREGNATED | STEAMED |
| 3768-173-1 | NI MO | ALUMINA | AMOCAT 1C | STEAMED |
| 3768-173-2 | NI SM | SAMARIUM ALUMINA | COMPONENT | STEAMED |
| 3768-173-4 | NI MO SM | SAMARIUM ALUMINA | IMPREGNATED | STEAMED |
| 3768-173-5 | NI | ALUMINA | COMPONENT | STEAMED |
| 3861- 2-0 | MO | ALUMINA | AMOCAT 1B | STEAMED |
| 3861- 17-1 | SN CL MO | ALUMINA | MOLTEN SALT | CALCINED |
| 3861- 17-2 | SN CL MO | ALUMINA | MOLTEN SALT | CALCINED |
| 3861- 34-1 | SM CO MO | SAMARIUM ALUMINA | IMPREGNATED | STEAMED |
| 4367- 1-1 | CO MO B | ALUMINA | BORIDES | |
| 4367- 1-2 | CO B MO C | ALUMINA | BORIDES | CARBIDES |
| 4367- 1-3 | CO B MO N | ALUMINA | BORIDES | NITRIDES |
| 4367- 2-0 | CO MO CE | CERIUM ALUMINA | COGELLED | |
| 4367- 3-0 | CO MO U | URANIUM ALUMINA | COGELLED | |
| 4367- 4-0 | CO MO BA | BARIUM ALUMINA | IMPREGNATED | |
| 4367- 5-1 | NI | ALUMINA | COMPONENT | |
| 4367- 5-2 | W | ALUMINA | COMPONENT | |
| 4367- 6-0 | CO MO PR | PR ALUMINA | COGELLED | |
| 4367- 7-0 | CO MO SM | SAMARIUM ALUMINA | COGELLED | |
| 4367- 8-0 | CO MO GD | GD ALUMINA | COGELLED | |
| 4367- 10-0 | CO MO MG | MAGNESIA ALUMINA | COGELLED | |
| 4367- 11-0 | NI B W C | ALUMINA | BORIDES | CARBIDES |
| 4367- 12-0 | NI B W B | ALUMINA | BORIDES | |
| 4367- 14-0 | NI MO MO | ALUMINA | PRE-MIXED | |
| 4367- 17-0 | SN | ALUMINA | MOLTEN SALT | CHLORIDE |
| 4367- 18-0 | ZN | ALUMINA | MOLTEN SALT | NITRATE |
| 4367- 19-0 | CO MO CE | CERIUM ALUMINA | COGELLED | |
| 4367- 20-0 | AL CL | ALUMINA | MOLTEN SALT | CHLORIDE |
| 4367- 21-0 | SN | ALUMINA | MOLTEN SALT | CALCINED |
| 4367- 22-0 | SN | ALUMINA | MOLTEN SALT | CALCINED |
| 4367- 23-0 | SN GA | ALUMINA | MOLTEN SALT | CALCINED |
| 4367- 24-0 | SN GA | ALUMINA | MOLTEN SALT | CALCINED |
| 4367- 25-0 | CO MO PR | PR ALUMINA | IMPREGNATED | |
| 4367- 26-0 | CO MO SM | SAMARIUM ALUMINA | IMPREGNATED | |
| 4367- 27-0 | CO MO GD | GD ALUMINA | IMPREGNATED | |
| 4367- 28-0 | SN | ALUMINA | MOLTEN SALT | CHLORIDE |
| 4367- 29-0 | SN | ALUMINA | MOLTEN SALT | CHLORIDE |
| 4367- 30-0 | GA | ALUMINA | | |
| 4367- 31-0 | ZN | ALUMINA | MOLTEN SALT | CHLORIDE |
| 4367- 32-0 | SN GA | GALLIUM ALUMINA | MOLTEN SALT | CHLORIDE |
| 4367- 33-0 | SN GA | GALLIUM ALUMINA | MOLTEN SALT | CHLORIDE |
| 4367- 34-1 | CO B | | BORIDES | |
| 4367- 34-2 | MO B | | BORIDES | |
| 4367- 34-3 | CO | GRAPHITE | INTERCALATED | |
| 4367- 34-4 | NI | GRAPHITE | INTERCALATED | |
| 4367- 34-5 | AL CL | GRAPHITE | INTERCALATED | |
| 4367- 34-6 | CR CL | GRAPHITE | INTERCALATED | |
| 4367- 34-7 | | GRAPHITE | | |
| 4367- 34-8 | SN O2 | | COMPONENT | |
| 4367- 38-0 | SN | ALUMINA | MOLTEN SALT | CALCINED |
| 4367- 39-0 | SN | ALUMINA | MOLTEN SALT | CALCINED |
| 4367- 40-0 | SN CL | SILICA ALUMINA | MOLTEN SALT | |
| 4367- 41-0 | ZN CL | SILICA ALUMINA | MOLTEN SALT | |
| 4367- 42-0 | ZN CL CU CL | SILICA ALUMINA | MOLTEN SALT | |
| 4367- 43-0 | NI SM | ALUMINA | IMPREGNATED | |
| 4367- 44-0 | NI MO SM | ALUMINA | IMPREGNATED | |
| 4367- 45-0 | SN CL MO | ALUMINA | MOLTEN SALT | AMOCAT 1B |
| 4367- 46-0 | CO NA | ALUMINA | | |
| 4367- 47-1 | H- CO AL 1 | ALUMINA | | |
| 4367- 47-2 | H- CO AL 2 | ALUMINA | | |
| 4367- 47-3 | H- CO AL 5 | ALUMINA | | |
| 4367- 48-0 | SN CL MO | ALUMINA | MOLTEN SALT | CALCINED |
| 4367- 49-0 | SN CL MO | ALUMINA | MOLTEN SALT | AMOCAT 1B |
| 4367- 50-0 | SN CL MO | ALUMINA | MOLTEN SALT | AMOCAT 1B |
| 4367- 51-0 | SM CO MO | SAMARIUM ALUMINA | IMPREGNATED | |
| 4367- 52-0 | CO NA MO | ALUMINA | PRE-MIXED | |

# TABLE A-II

## RUN INFORMATION

| RUN | CATALYSTS | | TIME | F.R. | CONV. | H/C | S | N | O |
|---|---|---|---|---|---|---|---|---|---|
| 3660-175 | 0- 0-0 | | 31.00 | 3.14 | 35.29 | 1.03 | 2.03 | 1.42 | 8.32 |
| 3660-176 | 0- 0-0 | | 31.00 | 2.79 | 34.04 | 1.03 | 2.53 | 1.45 | 6.91 |
| 3660-177 | 4367- 38-0 | | 31.00 | 2.57 | 44.43 | 1.02 | 2.17 | 1.65 | 9.04 |
| 3660-178 | 4367- 39-0 | | 31.00 | 2.85 | 38.65 | 1.03 | 2.04 | 1.50 | 8.50 |
| 3660-179 | 4367- 40-0 | | 31.00 | 2.63 | 56.77 | 1.04 | 1.70 | 1.50 | 6.58 |
| 3660-180 | 4367- 41-0 | | 31.00 | 2.90 | 32.79 | 1.00 | 3.29 | 2.10 | 15.26 |
| 3660-181 | 4367- 42-0 | | 31.00 | 2.98 | 33.49 | 1.02 | 2.09 | 1.47 | 9.66 |
| 3660-182 | 2392- 5-0 | | 31.00 | 2.28 | 51.23 | 1.05 | 1.36 | 1.59 | 9.12 |
| 3660-183 | 3768-145-1 | | 31.00 | 2.98 | 49.43 | 1.08 | 6.46 | 7.45 | 37.04 |
| 3660-184 | 3768-145-2 | | 31.00 | 2.55 | 60.84 | 1.04 | 1.30 | 1.56 | 5.18 |
| 3660-185 | 3768-145-3 | | 31.00 | 2.53 | 58.88 | 1.07 | 1.42 | 1.57 | 8.38 |
| 3660-187 | 2392- 5-0 | | 31.00 | 3.05 | 58.57 | 1.05 | 1.25 | 1.67 | 6.11 |
| 3660-188 | 4367- 20-0 | 4367- 24-0 | 31.00 | 2.59 | 52.56 | 1.04 | 1.77 | 1.62 | 7.94 |
| 3660-189 | 4367- 34-8 | 3639- 22-0 | 31.00 | 3.14 | 42.79 | 1.02 | 1.91 | 1.55 | 6.39 |
| 3660-190 | 3651- 81-0 | 2392-138-0 | 31.00 | 2.79 | 59.90 | 1.05 | 1.49 | 1.79 | 7.76 |
| 3660-191 | 2392- 5-0 | | 31.00 | 2.94 | 60.13 | 1.05 | 1.34 | 1.49 | 5.29 |
| 3660-192 | 2392-143-0 | 3651- 81-0 | 31.00 | 3.10 | 62.71 | 1.05 | 1.36 | 1.60 | 6.72 |
| 3660-143 | 4367- 47-1 | | 31.00 | 3.23 | 65.14 | 1.05 | 1.43 | 1.77 | 2.01 |
| 3660-146 | 4367- 47-2 | | 31.00 | 2.83 | 64.43 | 1.01 | 2.29 | 1.67 | 7.47 |
| 3660-186 | 4367- 47-3 | | 31.00 | 3.06 | 57.95 | 1.07 | 1.33 | 1.58 | 5.62 |
| 3660-194 | 3651- 81-0 | 4367- 5-1 | 31.00 | 2.98 | 62.32 | 1.04 | 1.36 | 1.59 | 7.13 |
| 3660-195 | 2392- 5-0 | | 31.00 | 3.04 | 60.84 | 1.06 | 1.07 | 1.64 | 7.34 |
| 3660-196 | 3651- 81-0 | | 31.00 | 3.27 | 63.26 | 1.04 | 1.39 | 1.65 | 6.14 |
| 3660-197 | 3651- 81-0 | 4367- 43-0 | 31.00 | 2.67 | 64.35 | 1.05 | 1.33 | 1.65 | 6.92 |
| 3660-198 | 4367- 44-0 | | 31.00 | 2.96 | 65.53 | 1.04 | 1.03 | 1.66 | 8.89 |
| 3660-199 | 3768-173-1 | | 31.00 | 2.96 | 62.24 | 1.04 | 1.12 | 1.67 | 7.86 |
| 3660-200 | 3768-145-1 | | 31.00 | 3.14 | 65.45 | 1.04 | 1.74 | 2.44 | 10.82 |
| 3660-201 | 3768-173-4 | | 31.00 | 2.79 | 62.56 | 1.04 | 1.24 | 1.63 | 5.99 |
| 3660-202 | 4367- 20-0 | 4367- 34-8 | 31.00 | 3.06 | 58.88 | 1.03 | 1.69 | 1.37 | 3.59 |
| 3660-203 | 4367- 1-3 | | 31.00 | 2.77 | 57.01 | 1.05 | 1.64 | 1.47 | 3.65 |
| 3660-204 | 4367- 34-8 | 3651- 81-0 | 31.00 | 3.00 | 60.29 | 1.04 | 1.49 | 1.49 | 5.25 |
| 3859- 5 | 4367- 38-0 | 3651- 81-0 | 31.00 | 2.79 | 62.71 | 0.96 | 1.46 | 1.54 | 5.89 |
| 3859- 6 | 4367- 45-0 | | 31.00 | 3.19 | 64.82 | 1.05 | 1.64 | 1.49 | 6.33 |
| 3859- 7 | 2392- 5-0 | | 31.00 | 3.21 | 57.48 | 1.06 | 1.40 | 1.58 | 9.58 |
| 3859- 8 | 3861- 2-0 | 3768-173-2 | 31.00 | 2.98 | 60.76 | 1.04 | 1.59 | 1.48 | 9.39 |
| 3859- 9 | 3861- 2-0 | 3768-173-5 | 31.00 | 2.86 | 60.13 | 1.05 | 1.33 | 1.37 | 9.70 |
| 3859- 10 | 4367- 48-0 | | 31.00 | 2.90 | 62.09 | 1.04 | 1.49 | 1.59 | 13.18 |
| 3859- 11 | 2392-143-0 | 3651- 81-0 | 31.00 | 2.88 | 60.92 | 1.04 | 1.42 | 1.43 | 11.13 |
| 3859- 12 | 3651- 81-0 | 2392-143-0 | 31.00 | 3.23 | 62.87 | 1.05 | 1.52 | 1.64 | 12.00 |
| 3859- 13 | 3651- 81-0 | 4367- 46-0 | 31.00 | 2.90 | 63.96 | 1.04 | 1.39 | 1.47 | 11.62 |
| 3859- 14 | 2392- 5-0 | | 31.00 | 3.08 | 59.59 | 1.04 | 1.35 | 1.68 | 6.47 |
| 3859- 15 | 4367- 49-0 | | 31.00 | 2.73 | 61.23 | 1.03 | 1.50 | 1.55 | 4.67 |
| 3859- 16 | 4367- 50-0 | | 31.00 | 2.77 | 61.70 | 1.03 | 1.48 | 1.62 | 5.53 |
| 3859- 17 | 2392- 5-0 | | 31.00 | 3.27 | 52.71 | 1.04 | 1.59 | 1.89 | 8.25 |
| 3859- 18 | 2392- 5-0 | | 31.00 | 2.79 | 55.29 | 1.04 | 1.46 | 1.77 | 7.15 |
| 3859- 19 | 2392- 5-0 | | 31.00 | 3.19 | 60.84 | 1.04 | 1.20 | 1.71 | 6.42 |
| 3859- 20 | 4367- 51-0 | | 31.00 | 2.88 | 62.32 | 1.04 | 1.25 | 1.61 | 7.81 |
| 3859- 21 | 3861- 34-1 | | 31.00 | 2.85 | 62.56 | 1.02 | 1.77 | 2.15 | 6.78 |
| 3859- 23 | 2392- 5-0 | | 31.00 | 2.83 | 59.98 | 1.06 | 1.37 | 1.32 | 11.80 |
| 3859- 24 | 4367- 46-0 | 3651- 81-0 | 31.00 | 2.81 | 60.53 | 1.06 | 1.53 | 1.37 | 10.66 |
| 3859- 25 | 3651- 81-0 | 4367- 34-4 | 31.00 | 2.85 | 62.09 | 1.07 | 1.50 | 1.39 | 13.13 |
| 3859- 26 | 4367- 1-1 | | 31.00 | 3.45 | 59.35 | 1.06 | 1.54 | 1.29 | 10.74 |
| 3859- 27 | 3861- 17-1 | | 31.00 | 3.08 | 60.21 | 1.06 | 1.52 | 1.32 | 11.20 |
| 3859- 28 | 3861- 17-2 | | 31.00 | 3.00 | 60.45 | 1.06 | 1.47 | 1.34 | 8.77 |
| 3859- 29 | 4367- 52-0 | | 31.00 | 2.79 | 60.06 | 1.06 | 1.54 | 1.30 | 11.95 |
| 3859- 30 | 3651- 81-0 | 4367- 46-0 | 31.00 | 2.83 | 61.54 | 1.05 | 1.54 | 1.38 | 13.12 |
| 3859- 31 | 2392- 5-0 | | 31.00 | 3.08 | 67.48 | 1.04 | 2.57 | 6.02 | 11.68 |
| 3859- 33 | 3861- 34-1 | | 31.00 | 3.19 | 70.29 | | | | |
| 3859- 37 | 2392- 5-0 | | 31.00 | 3.23 | 57.01 | | | | |
| 3859- 38 | 3861- 34-1 | | 31.00 | 3.50 | 59.43 | | | | |
| 3859- 39 | 2392- 5-0 | | 31.00 | 3.00 | 56.38 | | | | |
| 3859- 40 | 3651-120-3 | | 31.00 | 3.12 | 58.96 | | | | |

## TASKS 2 AND 3. CATALYST AGING TESTS

### Solvent Refined Coal (SRC)

At the beginning of May an experiment was run using a mixture of 33% SRC (FCL-15) and 67% creosote oil (FSN-11). Compositions of these are listed in Table I.

TABLE I

COMPOSITIONS OF SRC AND CREOSOTE OIL

| | SRC (FCL-15) | Creosote Oil (FSN-11) |
|---|---|---|
| Water | 0.85 wt% | 0.02 wt% |
| Basic N | N.D. | 0.14 |
| N | 1.96 | 0.36 |
| H | 5.81 | 8.11 |
| O, Direct | 6.14 | 0.71 |
| C | 85.31 | 91.20 |
| Oxide Ash | 0.12 | N.D. |
| Viscosity, 40°C | N.D. | 28.6 CST |
| Sp. Gravity, 60°/60°F | N.D. | 1.026 |
| Distn. Residue, D1160 | N.D. | 1.83 wt% |

N.D.: Not Determined

This SRC solution is too thick to pump at room temperature, but if it is heated too much, it becomes too thin for the Bran-Lubbe to pump; the Bran-Lubbe is a piston metering pump using ball check valves, and the balls do not seat well enough to prevent back flow of thin liquids. This made it necessary to carefully trace the feed lines and experiment with the feed tank temperature until the correct conditions were found for reliable pumping. After some difficulty the experiment (51108) was successfully completed and a product sample was obtained under steady state operation.

Then the concentration of SRC in the feed was increased to 50% and experiments 51109, 51110 and 51111 were run. However, it was not possible to run long enough at one time to obtain product at fully lined out conditions. One major problem was the inability to control the feed temperature because of the electrical tracing of the feed lines. Either the feed was too cold and the lines froze or the feed got too hot for the pump to handle. At times the rupture disk at the pump would blow out when the section of line between the pump and reactor would plug. A second major problem was the open top feed tank which allowed the light ends of the heated feed to evaporate. This resulted in the feed composition changing and the feed becoming thicker as the run proceeded until the feed line froze or plugged. A third problem was a tendency of the feed to be sticky enough to hold the pump check balls either open or closed so that pumping would stop.

After about a month of frustrating effort, it was decided that a major revision of the system would be needed to allow using the 50% SRC feed with any degree of success. At the least, it would be necessary to obtain a heated, closed feed tank to control the evaporation of the creosote light ends, and to trace all the feed lines with a heated oil system so that the feed temperature could be controlled. No decision has been reached on how to handle the sticking pump check ball problem if the 50% SRC experiments are resumed.

It was decided to finish out the balance of the experiments using a 33% SRC feed. The system was modified to include more high pressure relief valves to reduce the frequency of blowing out rupture disks, and a constant pressure was maintained on the Bran-Lubbe pump inlet by using a Moyno pump to circulate the feed from the feed tank, past the Bran-Lubbe, and through a 20 psi relief valve back into the feed tank. The second modification tended to overcome the check ball sticking problem and to maintain a more constant feed temperature as the feed would not have a chance to lie in the lines during startup. These modifications made it possible to run experiments 51112 through 51115 and obtain good steady state data.

## SRC Experiments and Results

The SRC experiments were run using the revised experimental conditions listed in Table II.

TABLE II

REVISED EXPERIMENTAL CONDITIONS FOR SRC I UPGRADING

| | |
|---|---|
| Catalyst: | 70 cc |
| Feed: | 33% SRC in Creosote Oil |
| Pressure: | 2000 psi |
| Temperature: | 750°F ( 1 day)<br>810°F (balance of exp.) |
| Feed Rate: | 100 cc/hr |
| Reactor Volume: | 295 cc |
| Hydrogen Rate: | 7.5 SCFH |
| Residence Time: | 180 min. in reactor |

The reactor volume listed is the active liquid volume and does not include the volumes occupied by the catalyst, basket, agitator, or thermowell. Before an experiment was started the catalyst was presulfided using the same procedure that is used with H-Coal experiments. After sulfiding at 500°F, the reactor was heated to the 750°F reaction temperature using a feed of hydrogenated anthracene oil containing 0.7% dimethyl disulfide. When the reaction temperature was reached, the feed was switched to the SRC feed solution. This startup procedure, which is the same as that used in H-Coal experiments, does not subject the catalyst to feed conditions which might cause catalyst fouling or deactivation. The experiments conducted in this revised SRC program are listed in Table III. The properties of the catalysts are listed in the appendix.

## TABLE III

## SRC HYDROGENATION EXPERIMENTS

| Experiment No. | Catalyst | Remarks |
|---|---|---|
| 51112 | 3651-1182 | American Cyanamid 1442B |
| 51113 | 3651-1183 | Shell 324 |
| 51114 | 3651-131 | 1/32" Dia Amocat 1C |
| 51115 | 3651-83 | Amocat Alumina Support |

The reaction products leaving the reactor is distilled into three fractions using the ASTM D1160 procedure. The fractions obtained in this distillation are: (a) a cut boiling below 650°F at atmospheric pressure, (b) a cut boiling between 650°F at atmospheric pressure and 560°F at 1 mm of mercury, and (c) the distillation residue remaining in the distillation flask. Both distillate cuts and the residue receive an elemental analysis. Based on these analyses and the weight fraction each cut is of the total, the composition of the reaction product, the percentages of the heteroatoms removed, and the hydrogen consumption are calculated using the procedure described in the appendix.

During these experiments there was no significant evidence of catalyst deactivation or changes in catalyst behavior with time which is in marked contrast to the behavior of similar catalysts in H-Coal experiments. Extended experiments designed to detect such changes might provide interesting information that could help in understanding the nature of the catalyst deactivation process which occurs with coal. However, when the reaction temperature is increased from 750°F to 810°F many statistically significant changes are seen in the heteroatom removal and yield of distillate products as well as in the atom ratios of hydrogen to carbon in some of the distillation fractions. These changes are described next.

With all three catalysts, an increase in the reaction temperature resulted in an increase in the amount of nitrogen and sulfur being removed, and, except for Amocat 1C, the oxygen removal also increased. The oxygen result for Amocat 1C would be very interesting if it were real, but it is more likely due to experimental error. At 750°F the oxygen removal for Amocat 1C was very high compared with the other two catalysts and this tends to support the idea about experimental error.

At both temperatures, the amount of nitrogen being removed was quite comparable for Amocat 1C and Shell 324, while Amocat 1C removed somewhat more sulfur. Shell 324 removed the most oxygen at the higher temperature, but as noted before, Amocat 1C removed more oxygen at the lower temperature. American Cyanamid 1442B showed the poorest removal of all three heteroatoms at the lower temperature where its removal of nitrogen and oxygen were approximately equal to the amount obtained in the uncatalyzed experiment using only the Amocat alumina support. At the higher temperature, 1442B also had the worst nitrogen removal although it produced sulfur and oxygen removals comparable to Shell 324 and Amocat 1C respectively. For heteroatom removal, therefore American Cyanamid 1442B showed the worst performance while Amocat 1C was the best at the lower temperature and at least as good as Shell 324 at the higher temperature. The average heteroatom data are listed in Table IV and the individual data are plotted in Figures 1 through 3.

All three of the catalysts yielded less resid and correspondingly more atmospheric distillate when the reaction temperature was increased. The amount of vacuum distillate being formed was not greatly effected by temperature with any of the catalysts; Amocat 1C and American Cyanamid 1442B produced approximately equal amounts at about 54% while Shell 324 yielded less at 50%. At both temperatures, Amocat 1C produced less resid. At the lower temperature, 1442B gave the most resid while at the higher temperature 1442B and Shell 324 gave approximately equal amounts. At the higher temperature, Shell 324 gave the most atmospheric distillate of the three catalysts by a small margin. Thus Amocat 1C gave the best performance in producing distillate products and American Cyanamid 1442B gave the worst. These data are listed in Table IV and plotted in Figures 4 through 6.

In terms of the atom ratio of hydrogen to carbon, Amocat 1C and Shell 324 gave very similar results. At both temperatures, starting with a feed H/C ratio of 0.98, they both yielded a product with an H/C of about 1.1 while American Cyanamid 1442B gave an H/C of approximately 1.04. With both Shell 324 and Amocat 1C, an increase in temperature caused the H/C ratios of the vacuum distillate and resid to decrease. This may be in part due to the increase in nitrogen removal at the higher temperature as nitrogen removal is thought to require a large amount of hydrogen. With American Cyanamid 1442B the H/C ratio of the distillation fractions and thus the product is not changed by an increase in the reaction temperature and this may correspond with 1442B's poor nitrogen removal which even at the high temperature was less than that obtained with the other two catalysts at the lower temperature. In the uncatalyzed reaction at 750°F, the H/C of the product and the feed were equal and the H/C ratios of the distillation fractions were correspondingly low. These data may be indicating that nitrogen elimination becomes increasingly difficult as the H/C ratio drops. The data are plotted in Figures 7 through 9 and listed in Table IV.

# TABLE IV

## AVERAGE CATALYST PERFORMANCE WITH SRCI

| | 750°F Reaction Temp. | | | | 810°F Reaction Temp. | | |
|---|---|---|---|---|---|---|---|
| Property | Amocat 1C | Shell 324 | Am.Cy. 1442B | Support | Amocat 1C | Shell 324 | Am. Cy. 1442B |
| % N Removed | 45.7 | 43.9 | 13.8 | 17.0 | 53.8 | 53.7 | 42.8 |
| % S Removed | 78.3 | 68.9 | 64.1 | 49.4 | 93.0 | 58.9 | 85.9 |
| % O Removed | 73.2 | 64.9 | 55.1 | 53.5 | 72.8 | 86.5 | 74.3 |
| % Atm. Dist. | 28.5 | 28.8 | 23.6 | 24.3 | 33.0 | 34.7 | 32.0 |
| % Vac. Dist. | 55.3 | 51.0 | 53.3 | 56.6 | 54.0 | 49.9 | 53.8 |
| % Resid | 13.2 | 17.9 | 21.1 | 16.9 | 10.8 | 13.0 | 12.5 |
| H/C Atm.Dist. | 1.28 | 1.32 | 1.20 | 1.16 | 1.27 | 1.28 | 1.22 |
| H/C Vac.Dist. | 1.08 | 1.08 | 1.03 | 0.96 | 1.03 | 1.04 | 1.02 |
| H/C Resid | 0.87 | 0.87 | 0.83 | 0.77 | 0.82 | 0.81 | 0.82 |
| H/C Product | 1.11 | 1.12 | 1.03 | 0.98 | 1.09 | 1.10 | 1.04 |

FIGURE 1
AMOCAT 1C

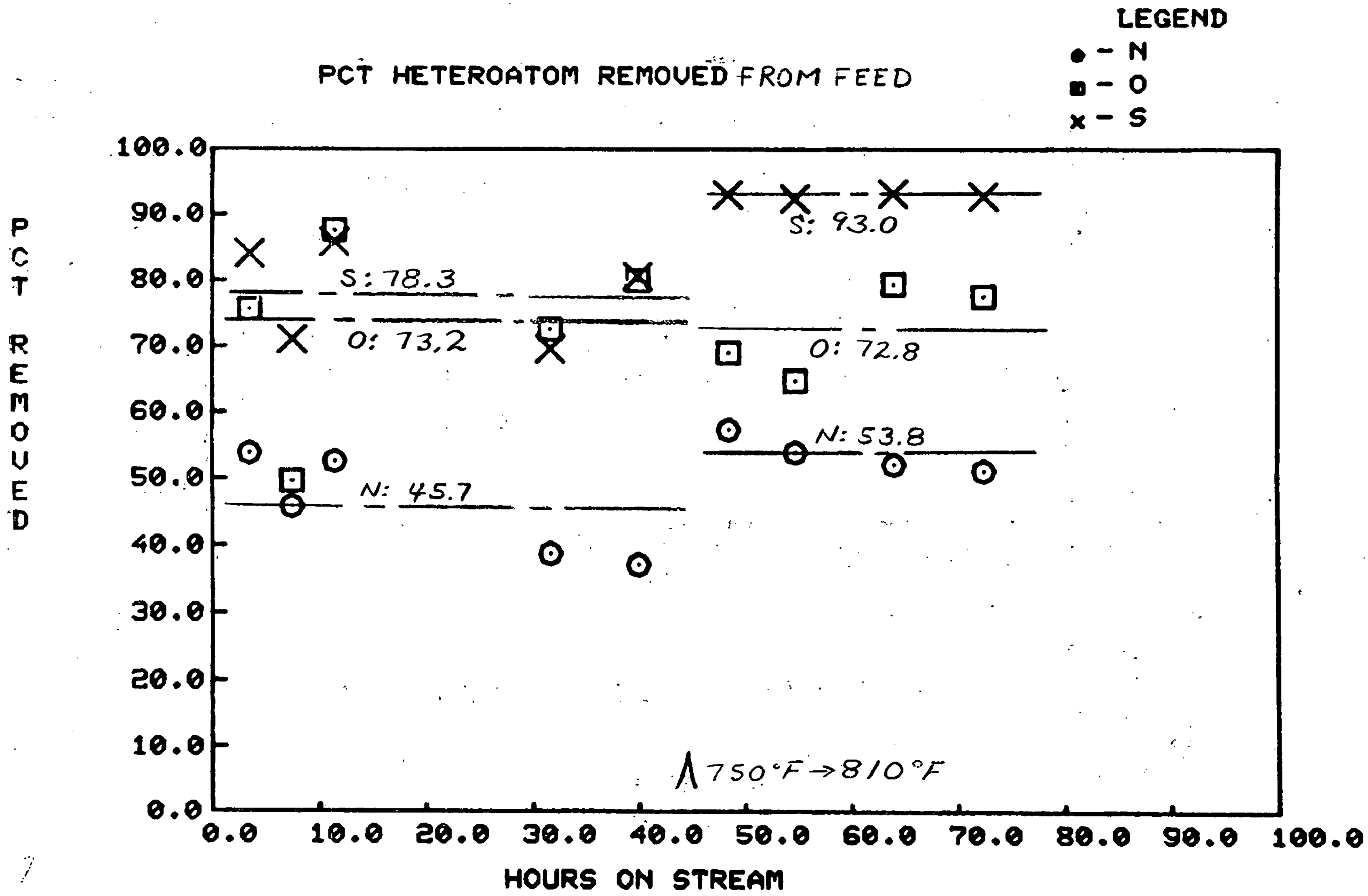
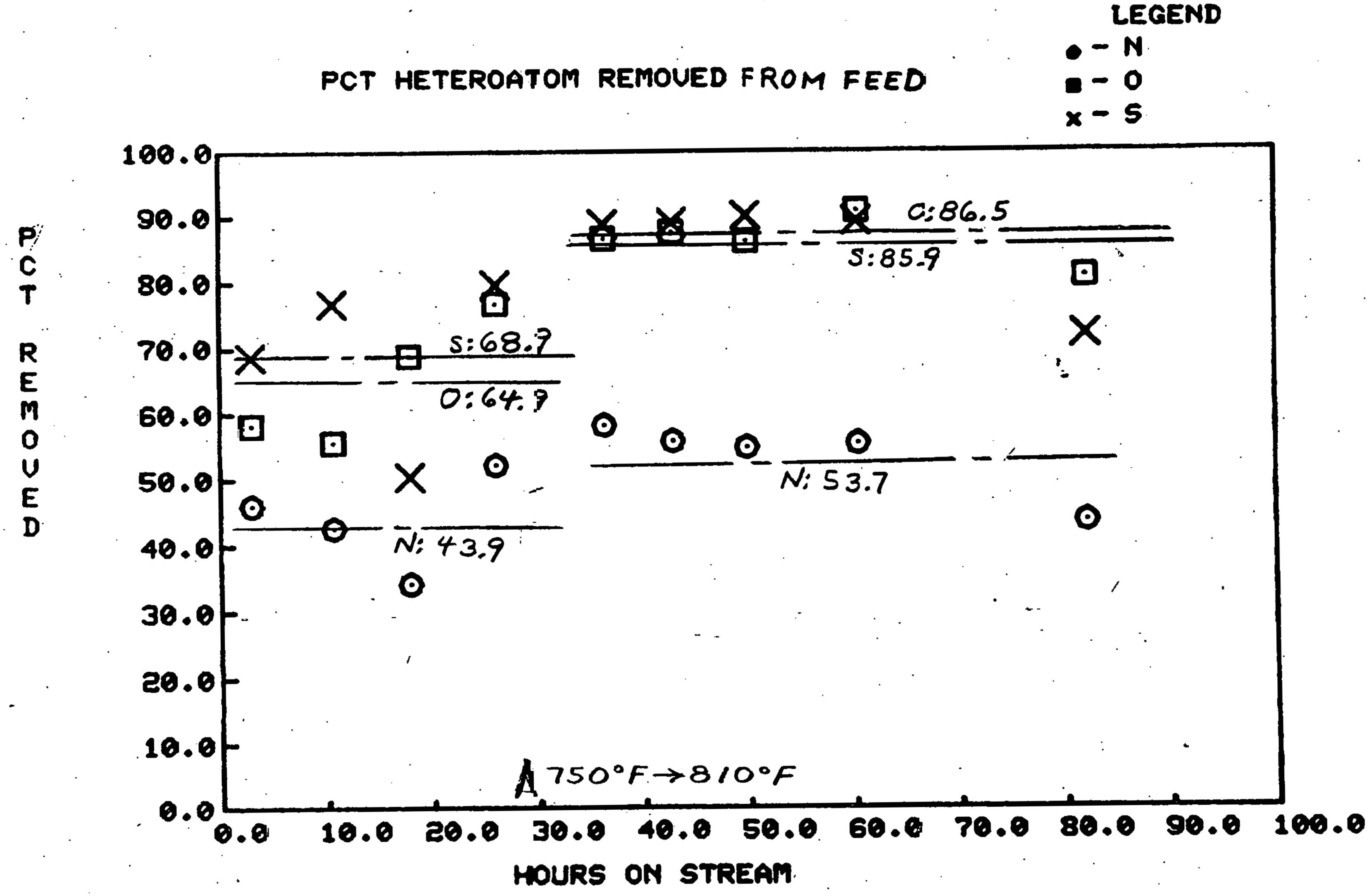


FIGURE 2
SHELL 324



OCT 1,1980

FIGURE 3

AM. CY. 1442 B

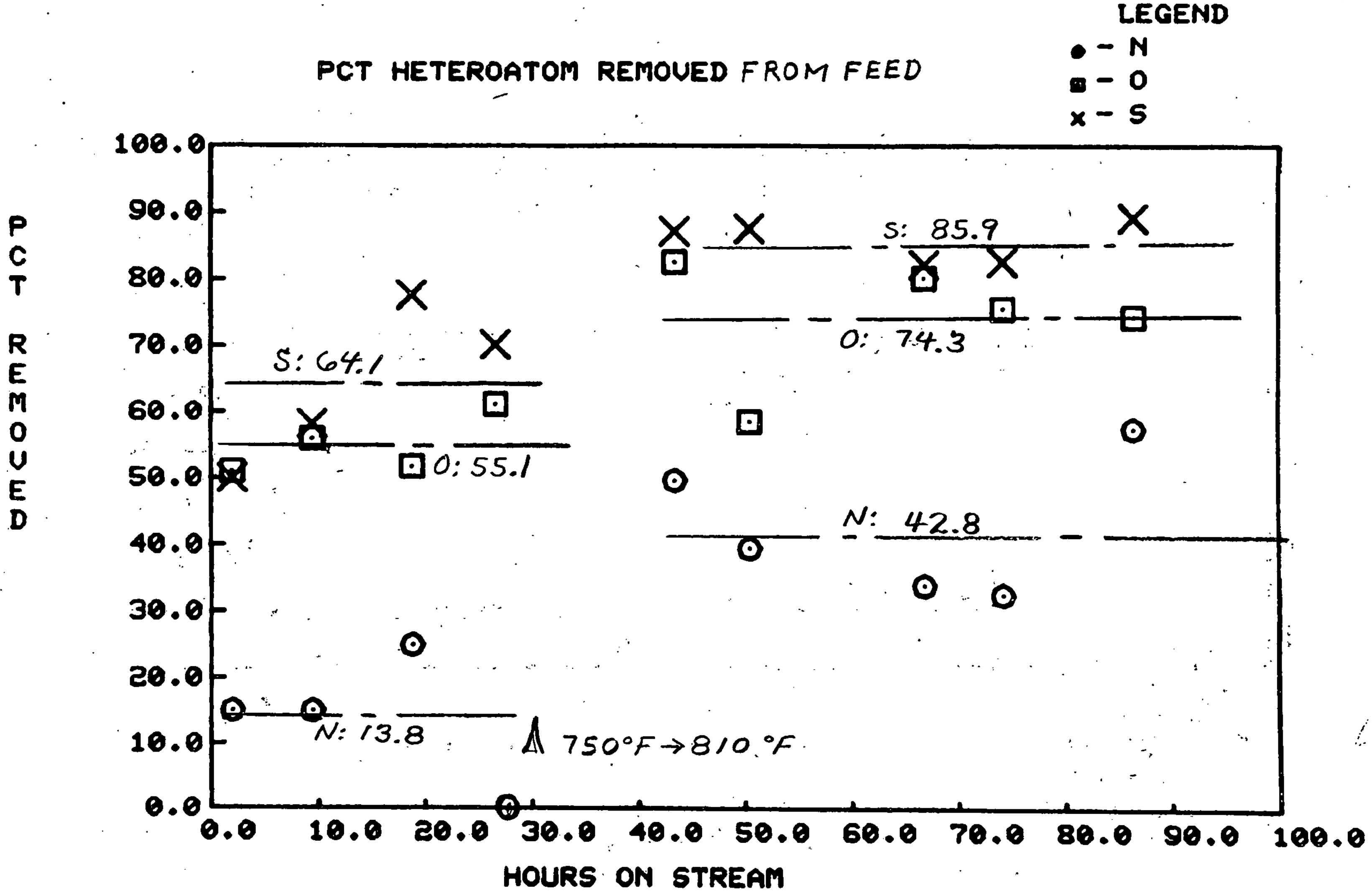


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FIGURE 4

AMOCAT 1C

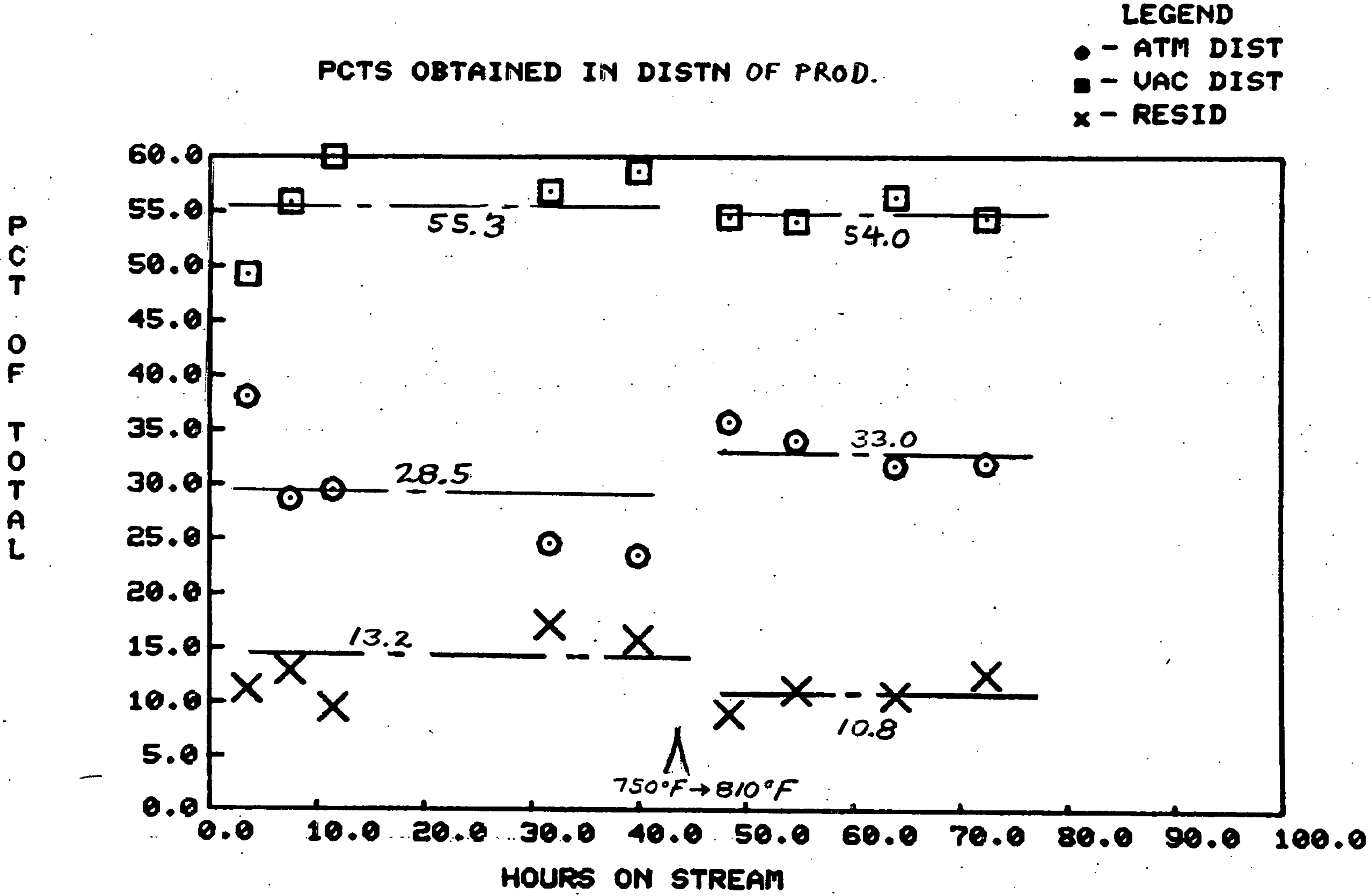
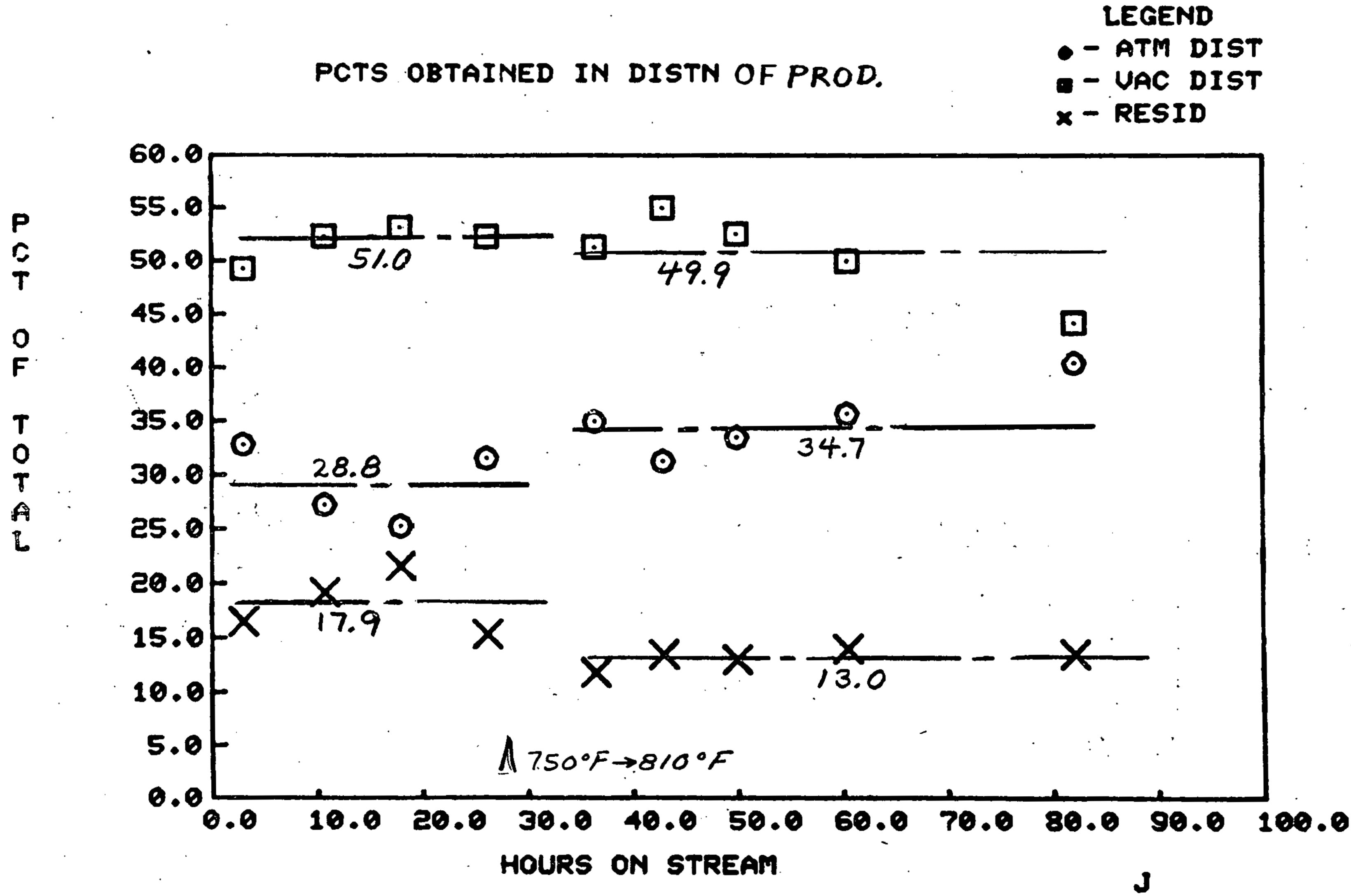


FIGURE 5
SHELL 324



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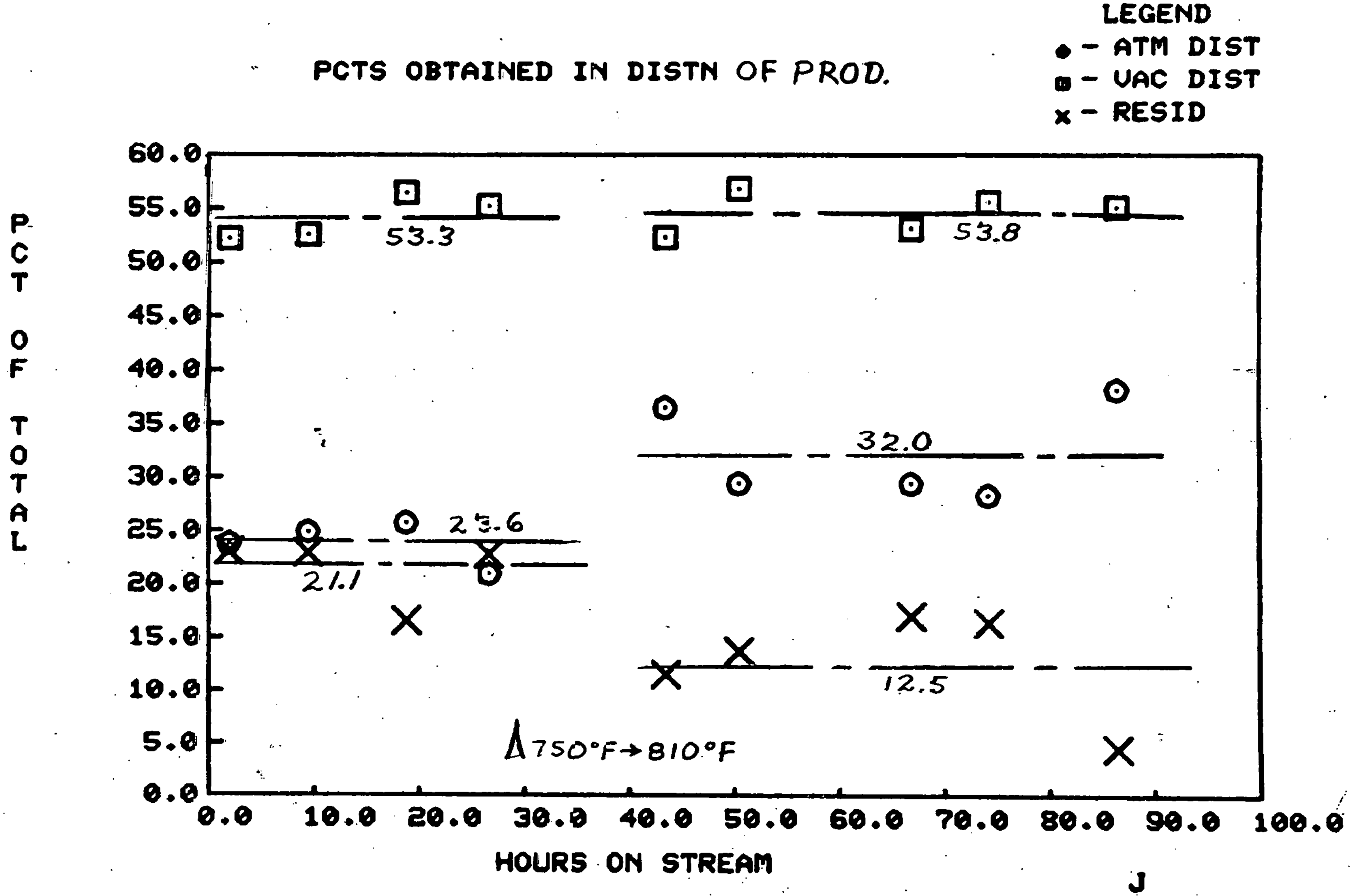
OCT 6, 1980

FIGURE 6
AM.CY. 1442B

PCTS OBTAINED IN DISTN OF PROD.



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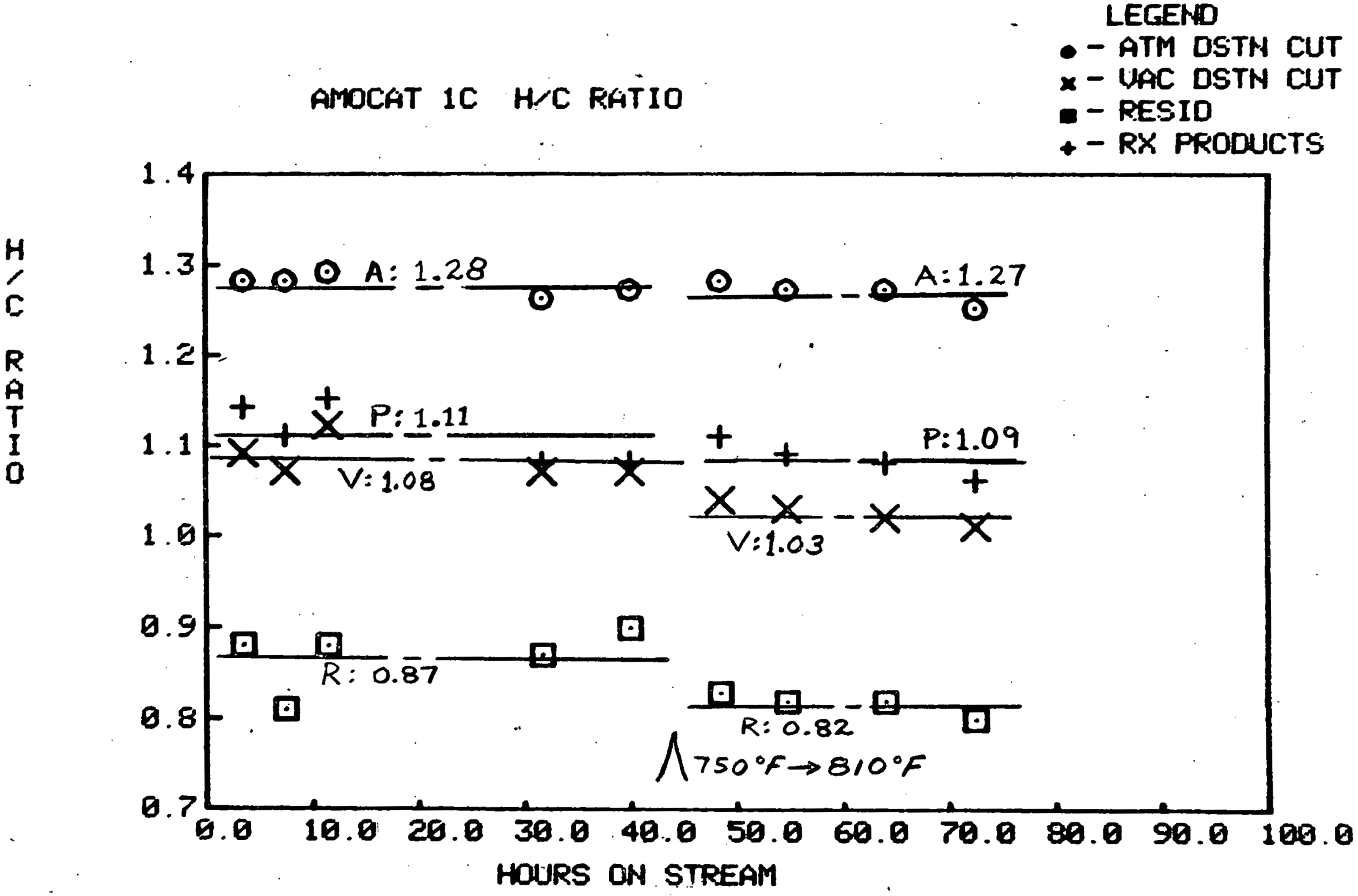
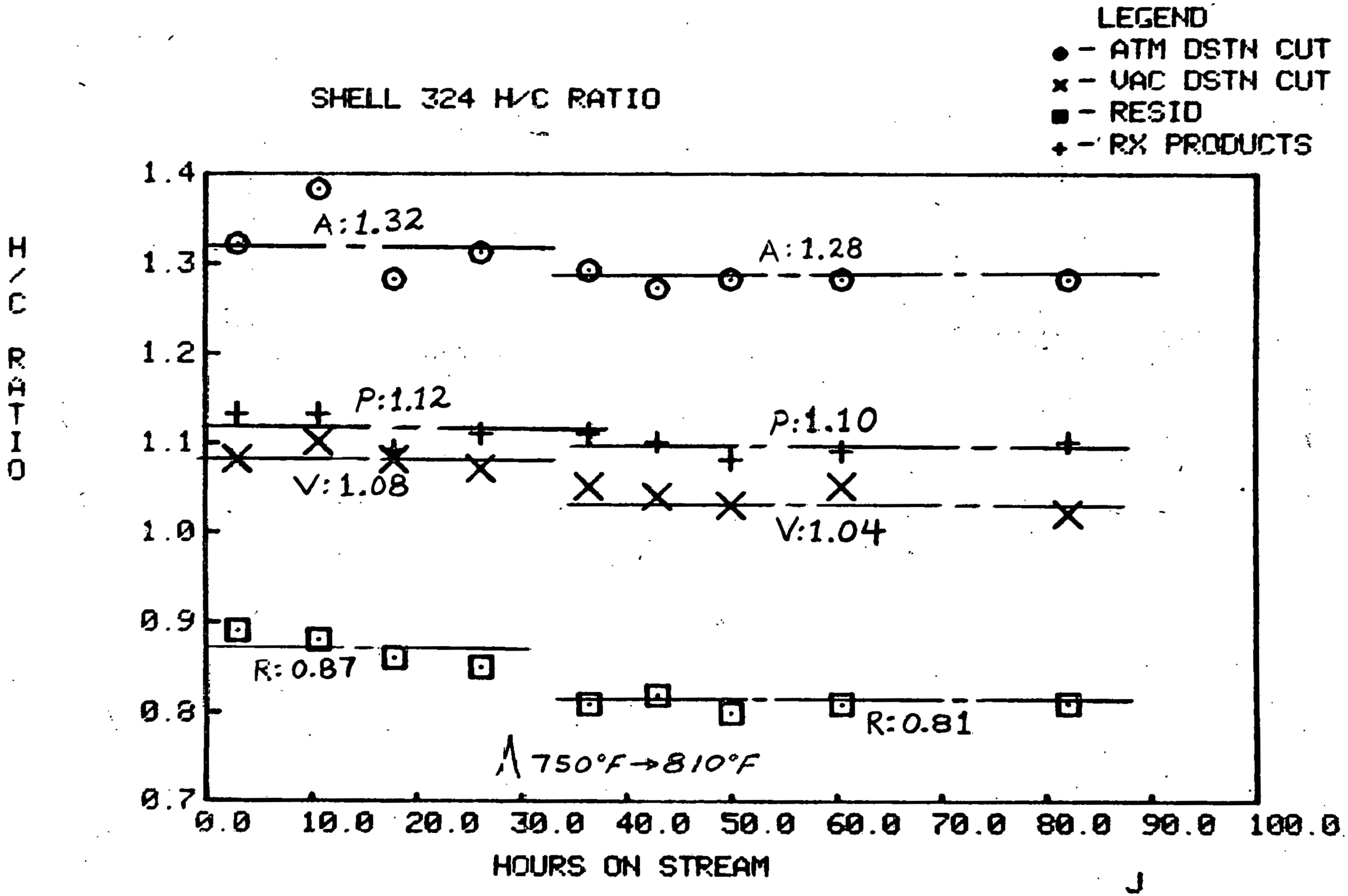
OCT 6, 1980

FIGURE 7



OCT 9,1980

FIGURE 8



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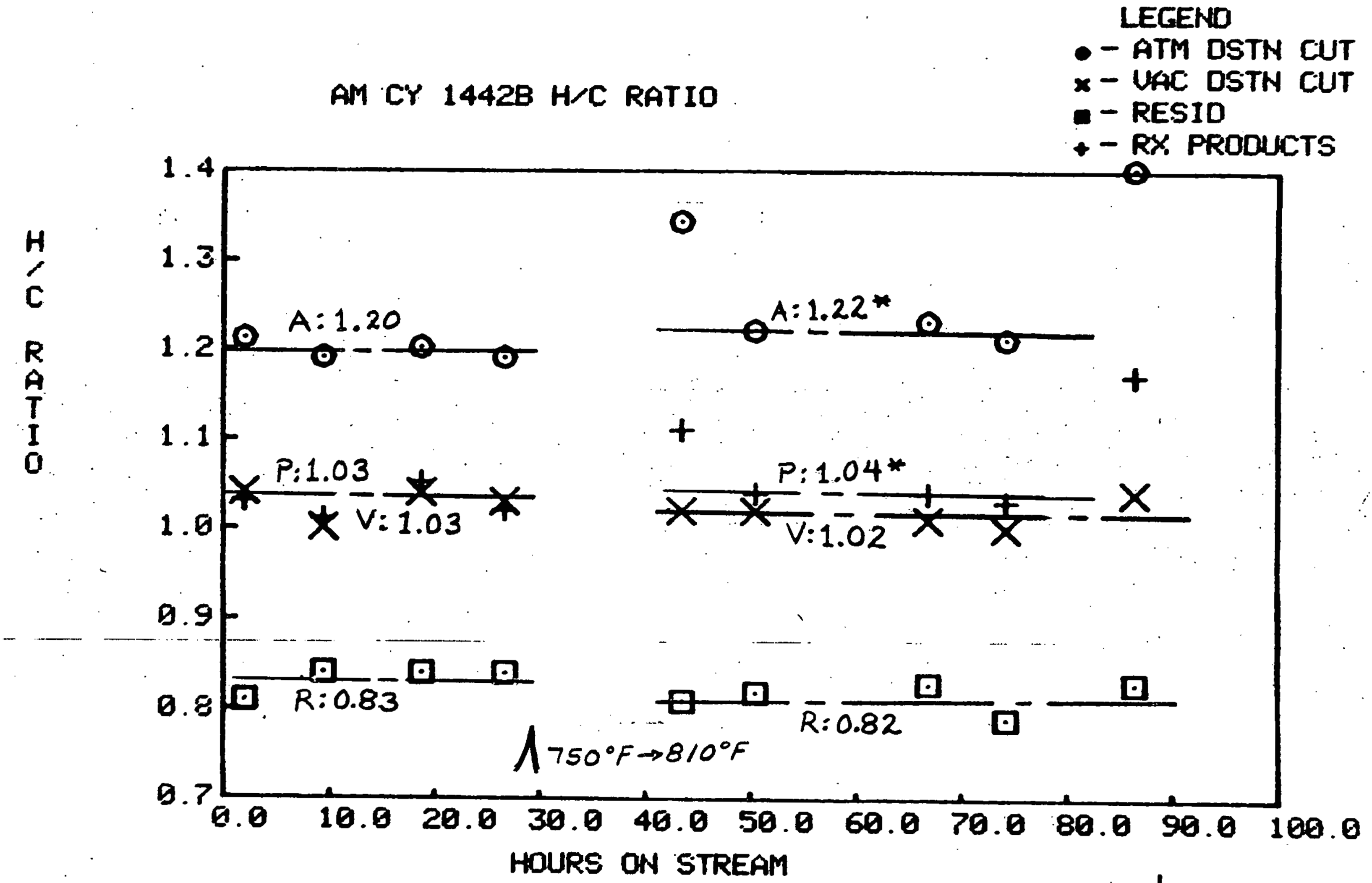
OCT 9,1980

FIGURE 9



* THE AVERAGES FOR THE PRODUCT AND VACUUM DISTILLATION CUT DO NOT INCLUDE THE HIGH RESULTS AT 43.5 AND 86.6 HOURS ON STREAM.

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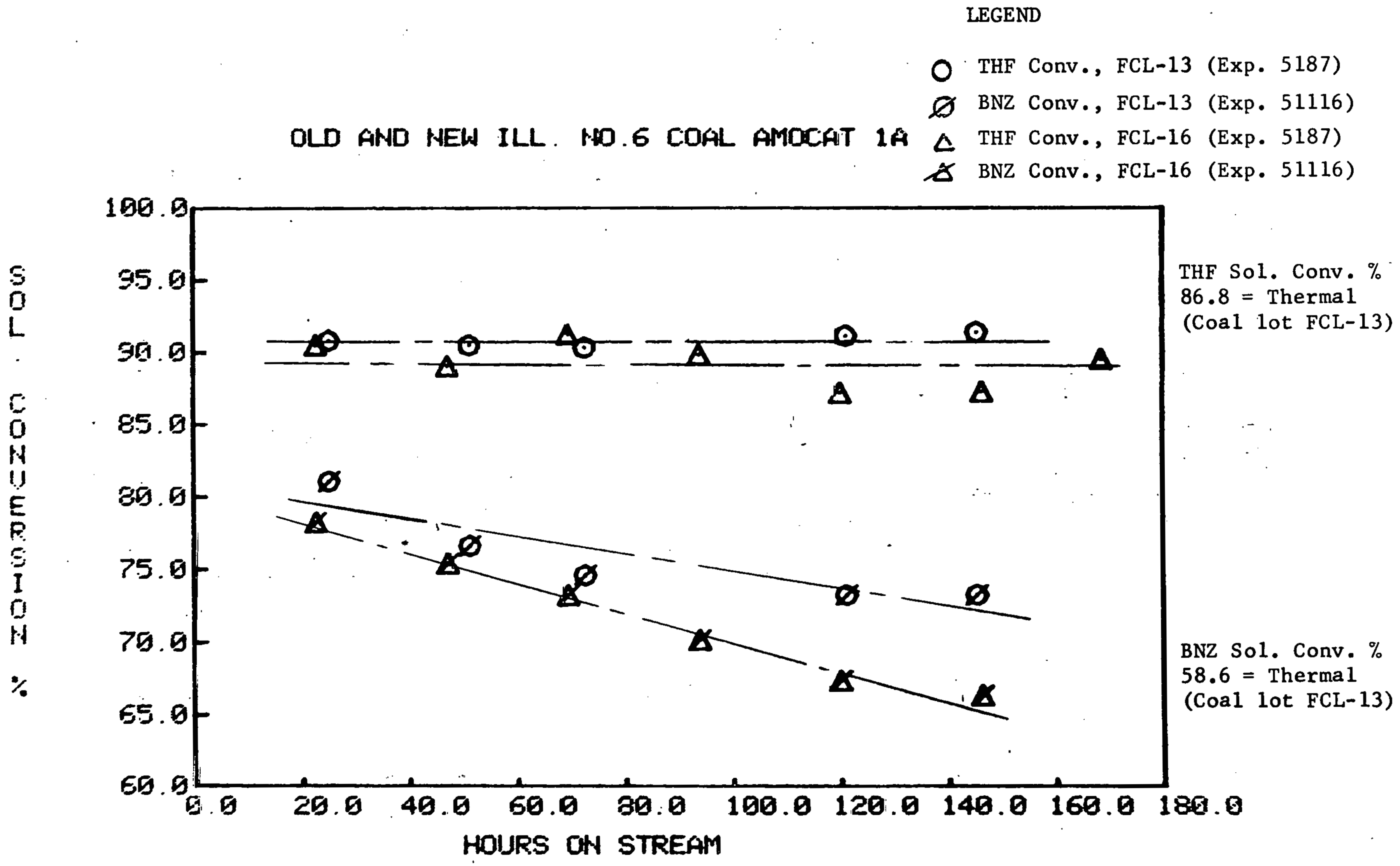
OCT 9, 1980

FIGURE 10

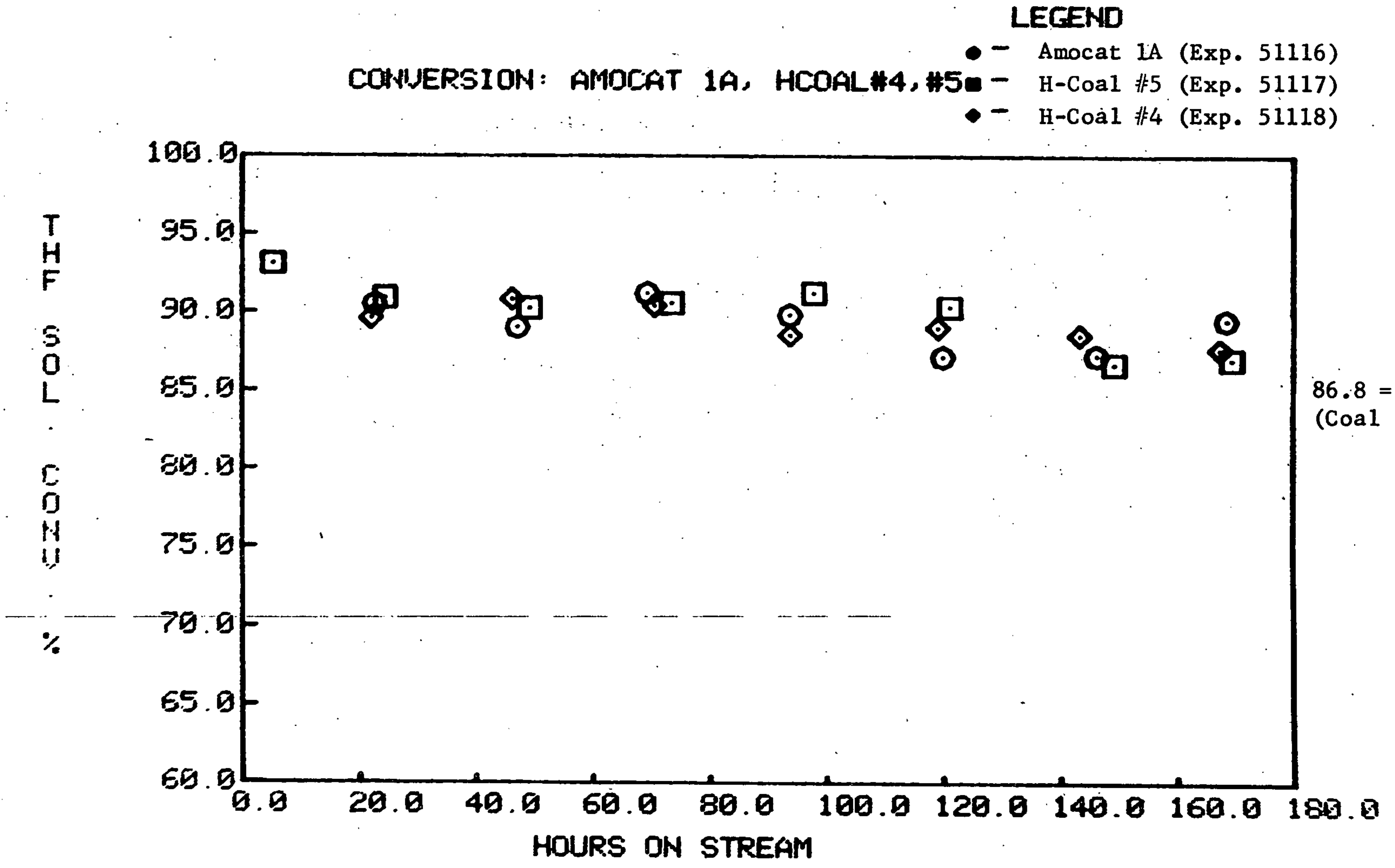


THF Sol. Conv. %
86.8 = Thermal
(Coal lot FCL-13)

BNZ Sol. Conv. %
58.6 = Thermal
(Coal lot FCL-13)

Old lot of Illinois No. 6 Coal - Lot. No. FCL-13
New lot of Illinois No. 6 Coal - Lot. No. FCL-16

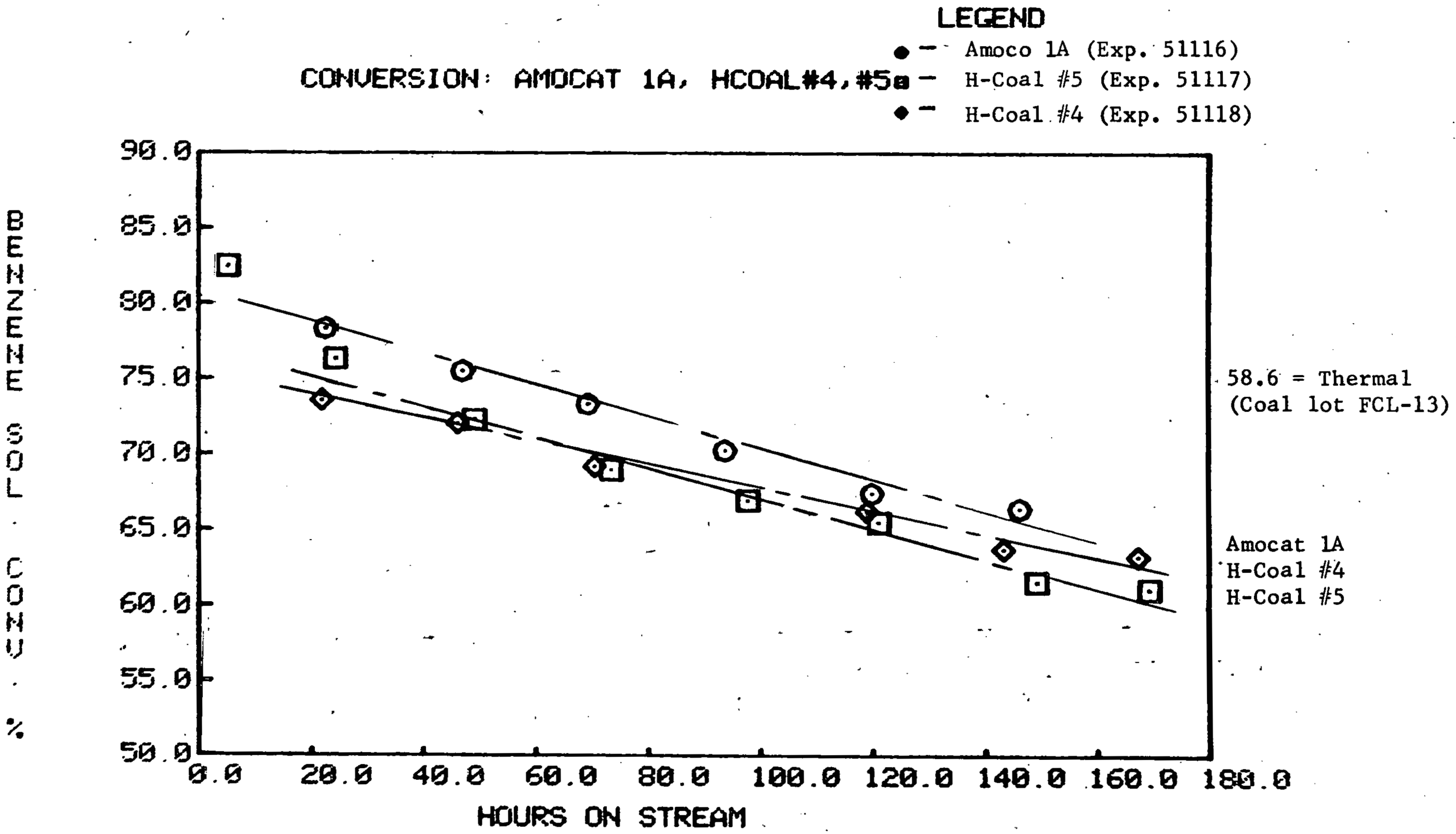
FIGURE 11



86.8 = Thermal
(Coal lot FCL-13)

Coal: Illinois No. 6, lot FCL-16

FIGURE 12



58.6 = Thermal
(Coal lot FCL-13)

Amocat 1A
H-Coal #4
H-Coal #5

Coal: Illinois No. 6, lot FCL-16

## New Batch of Illinois No. 6 Coal

A new batch of Illinois No. 6 coal (FCL-16) was started. Its composition and the composition of the previous batch are listed in Table V.

TABLE V

COMPOSITIONS OF OLD AND NEW BATCHES OF ILLINOIS NO. 6 COAL

| Component | Old (FCL-13) | New (FCL-16) |
|---|---|---|
| Moisture | 2.58 | 3.64 |
| Oxide Ash | 12.31 | 10.81 |
| N | 1.31 | 1.31 |
| H | 4.41 | 4.37 |
| O, Direct | 10.71 | 10.56 |
| C | 66.42 | 67.42 |
| S | 2.94 | 2.61 |

Note: Hydrogen and oxygen for coal only, excluding contribution from water.

Except for the new batch containing slightly more water and slightly less ash, the elemental compositions of the two coals are very close. To determine how closely the liquefaction characteristics of the new coal batch match the old, the first experiment was made using lot 2392-147 of the Amocat 1A catalyst. The percentage conversion to THF and benzene soluble products are shown in Figure 10. Although both coals yield about the same amount of THF soluble products, the benzene conversion was slightly lower for the new coal especially in the second half of the experiment.

The next two experiments, 51117 and 51118, used HRI's H-Coal No. 5 and No. 4 catalysts in that order. The THF and benzene conversion data from these experiments are compared with the Amocat 1A results of experiment 51116 in Figures 11 and 12. The THF conversions obtained with the three catalysts are very similar. The benzene conversions, however, are higher with Amocat 1A. It also appears that the H-Coal No. 5 catalyst may be deactivating a little faster than the other two after about three days of use. The elemental analyses and D-1160 distillation data are incomplete at this time.

The next experiment, number 51119, was to evaluate a new samarium stabilized CoMo alumina catalyst with Wyodak coal. This catalyst has shown excellent resistance to deactivation caused by water at high temperature in the batch screening reactor. The run was terminated after only 71 hours when the reactor rupture disk failed and the temperature controller also failed. This temperature controller must be adjusted specially to control the natural tendency of the reactor temperature to cycle because of the long lag times that the thick heater and reactor walls cause, and another controller was not immediately available. When the reactor was opened, it was found to be full of coke which probably resulted when the temperature controller failed and large temperature deviations occurred. This coke had to be chipped out of the reactor, and in the process the catalyst basket was destroyed so that no used could be obtained. The rupture disk material of construction has been changed from stainless steel to Hastelloy which has better high temperature and corrosion resisting properties, and it is hoped that this will eliminate the rupture disk failure problem.

The catalyst evaluation was immediately repeated without problems as experiment No. 51120. The THF and benzene soluble conversion data are shown in Figure 13. The valves for the stabilized catalyst are seen to consistently fall below the results obtained with the standard Amocat 1A CoMo catalyst. It can also be seen that the difference between THF and benzene conversions is considerably less than the results obtained with Amocat 1A. It is currently thought the difference between the batch experimental results and the continuous flow aging results could either be due to: (a) the samarium being poorly dispersed and when the catalyst is ground up for the batch test, the dispersion is improved, or (b) the activity of the sulfided and unsulfided catalysts is different. The state of dispersion of the samarium on the catalyst is presently being investigated.

The last experiment run during the quarter for which data are available is 51121 which used 1/32 inch diameter catalyst pellets and NiMo on bimodal alumina so that it was a small diameter Amocat 1C. The THF and benzene soluble conversions are shown in Figure 14 where the data for the standard Amocat 1C (1/16 inch dia., exp. 5190) are included for comparison. It can readily be seen that for the THF and benzene conversions at least, there is no difference between the two catalysts. This would seem to indicate that diffusional resistances play a minor role in determining the reaction rate with Amocat type catalysts. Further conclusions are best put off until more data become available.

FIGURE 13A

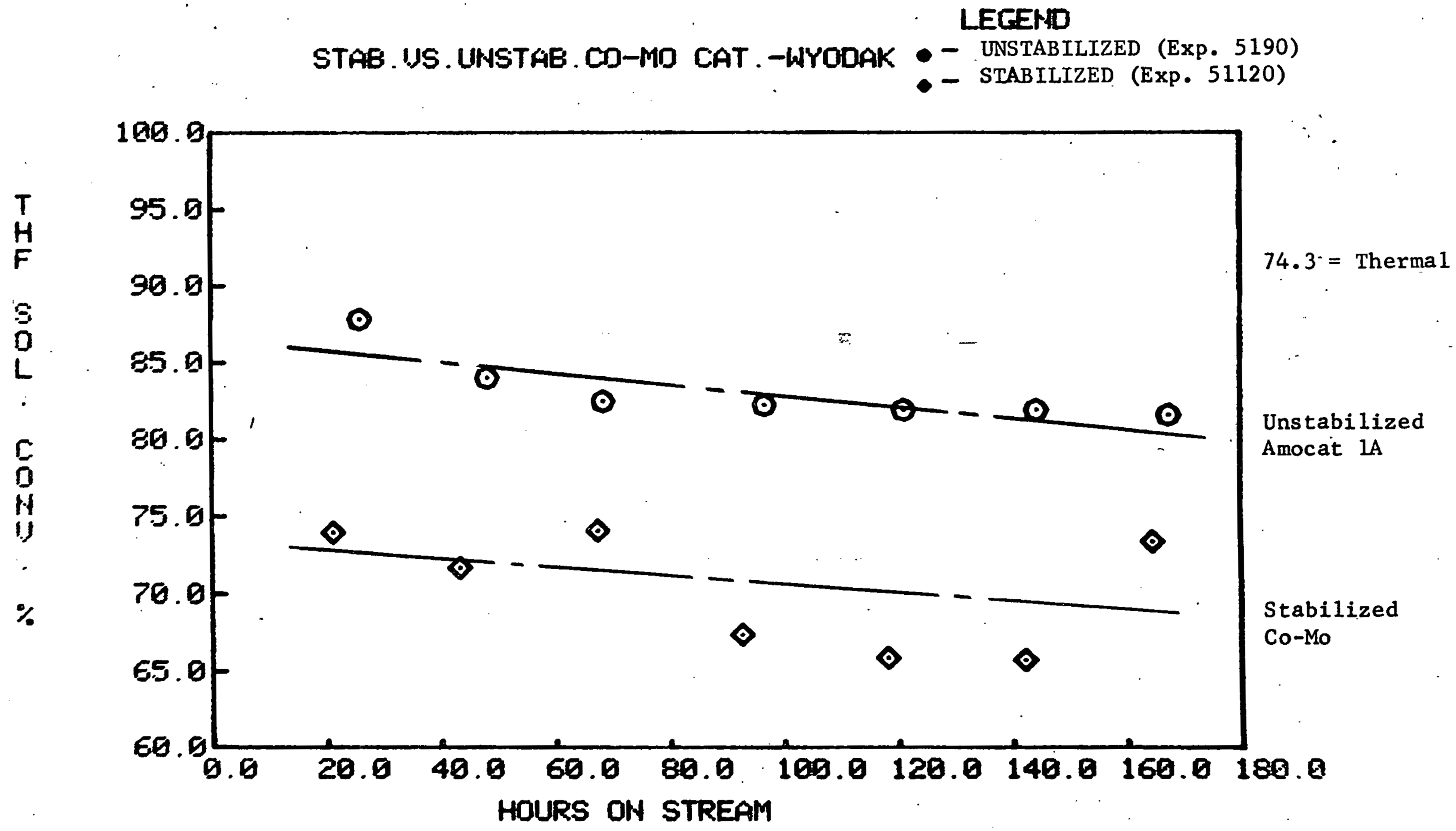

STAB.VS.UNSTAB.CO-MO CAT.-WYODAK
LEGEND
● – UNSTABILIZED (Exp. 5190)
◆ – STABILIZED (Exp. 51120)
THF SOL. CONV. %
100.0
95.0
90.0
85.0
80.0
75.0
70.0
65.0
60.0
0.0
20.0
40.0
60.0
80.0
100.0
120.0
140.0
160.0
180.0
HOURS ON STREAM
74.3 = Thermal
Unstabilized Amocat 1A
Stabilized Co-Mo

FIGURE 13B

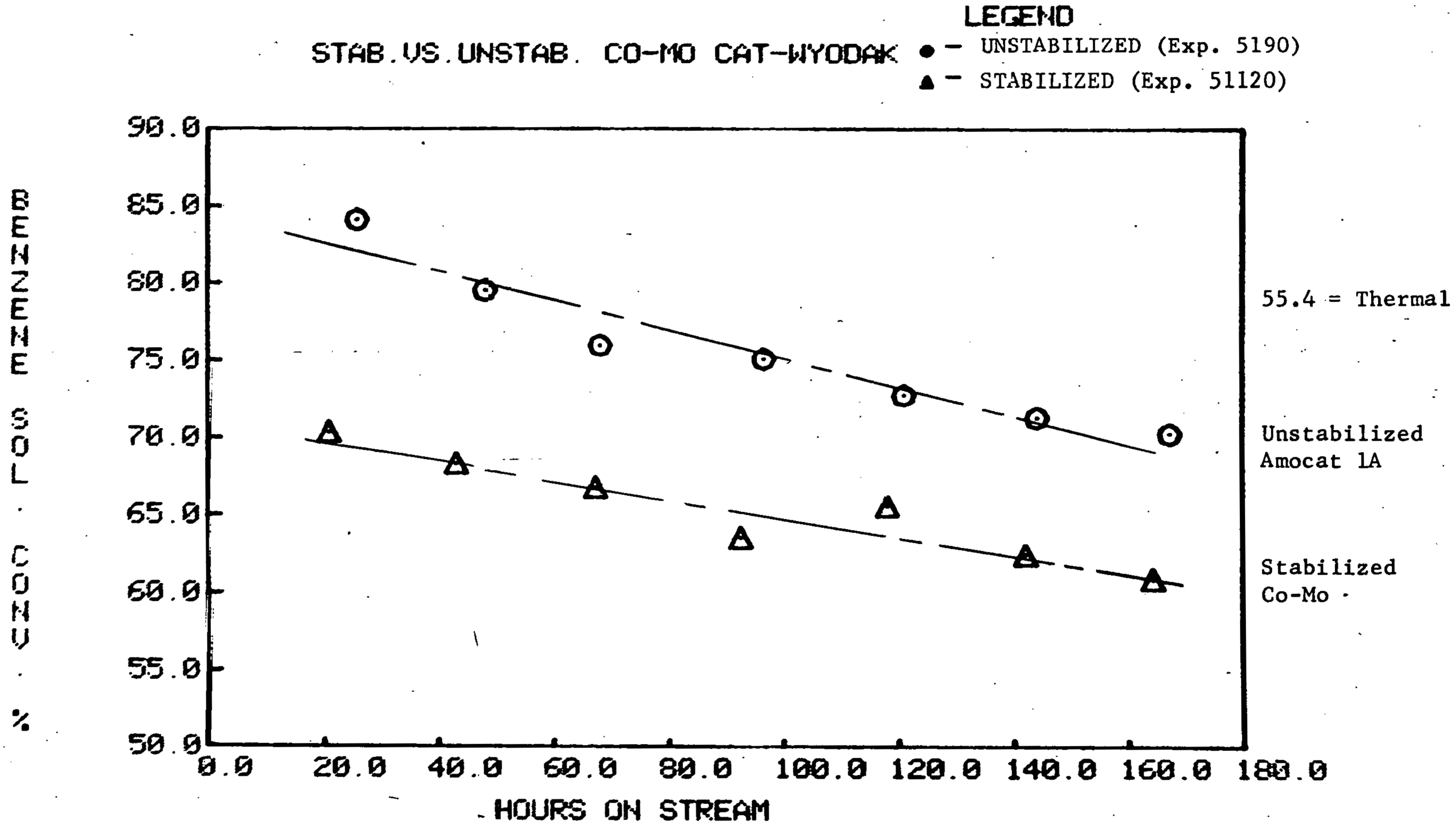

STAB.VS.UNSTAB. CO-MO CAT-WYODAK
LEGEND
● – UNSTABILIZED (Exp. 5190)
▲ – STABILIZED (Exp. 51120)
BENZENE SOL. CONV. %
90.0
85.0
80.0
75.0
70.0
65.0
60.0
55.0
50.0
0.0
20.0
40.0
60.0
80.0
100.0
120.0
140.0
160.0
180.0
HOURS ON STREAM
55.4 = Thermal
Unstabilized
Amocat 1A
Stabilized
Co-Mo

FIGURE 14A

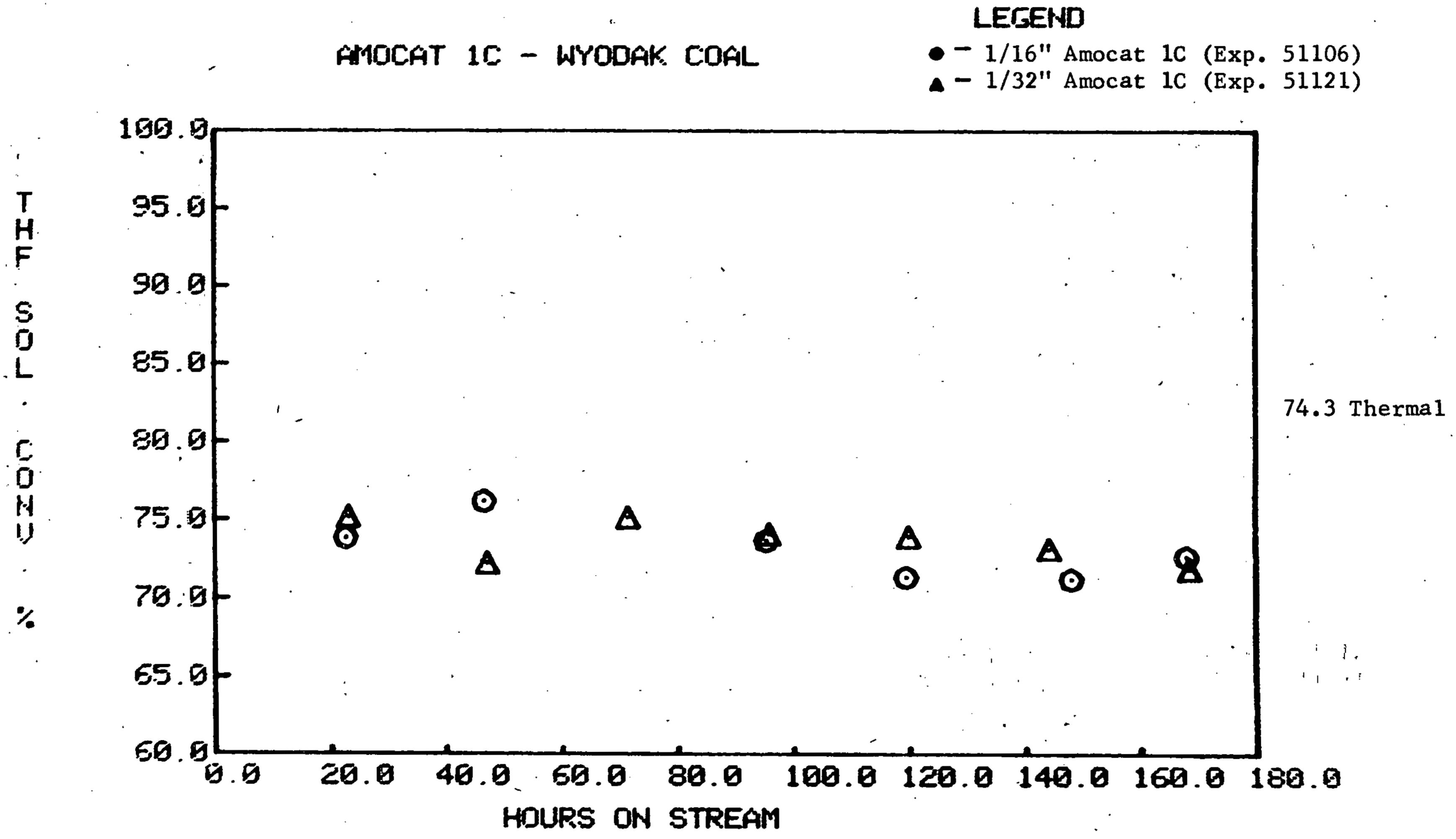

AMOCAT 1C - WYODAK COAL
LEGEND
● – 1/16" Amocat 1C (Exp. 51106)
▲ – 1/32" Amocat 1C (Exp. 51121)
THF SOL. CONV. %
100.0
95.0
90.0
85.0
80.0
75.0
70.0
65.0
60.0
0.0
20.0
40.0
60.0
80.0
100.0
120.0
140.0
160.0
180.0
HOURS ON STREAM
74.3 Thermal

FIGURE 14B

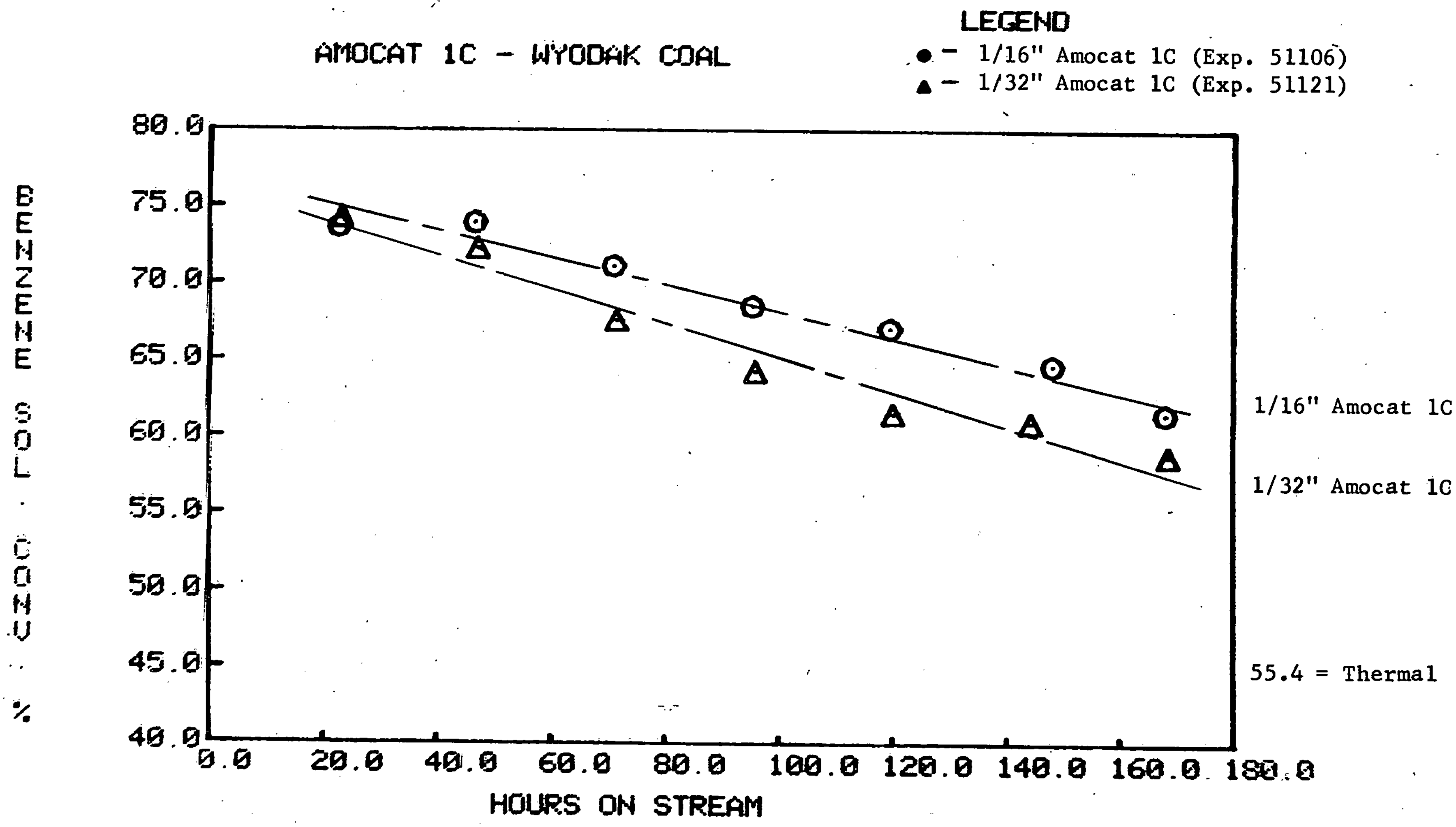
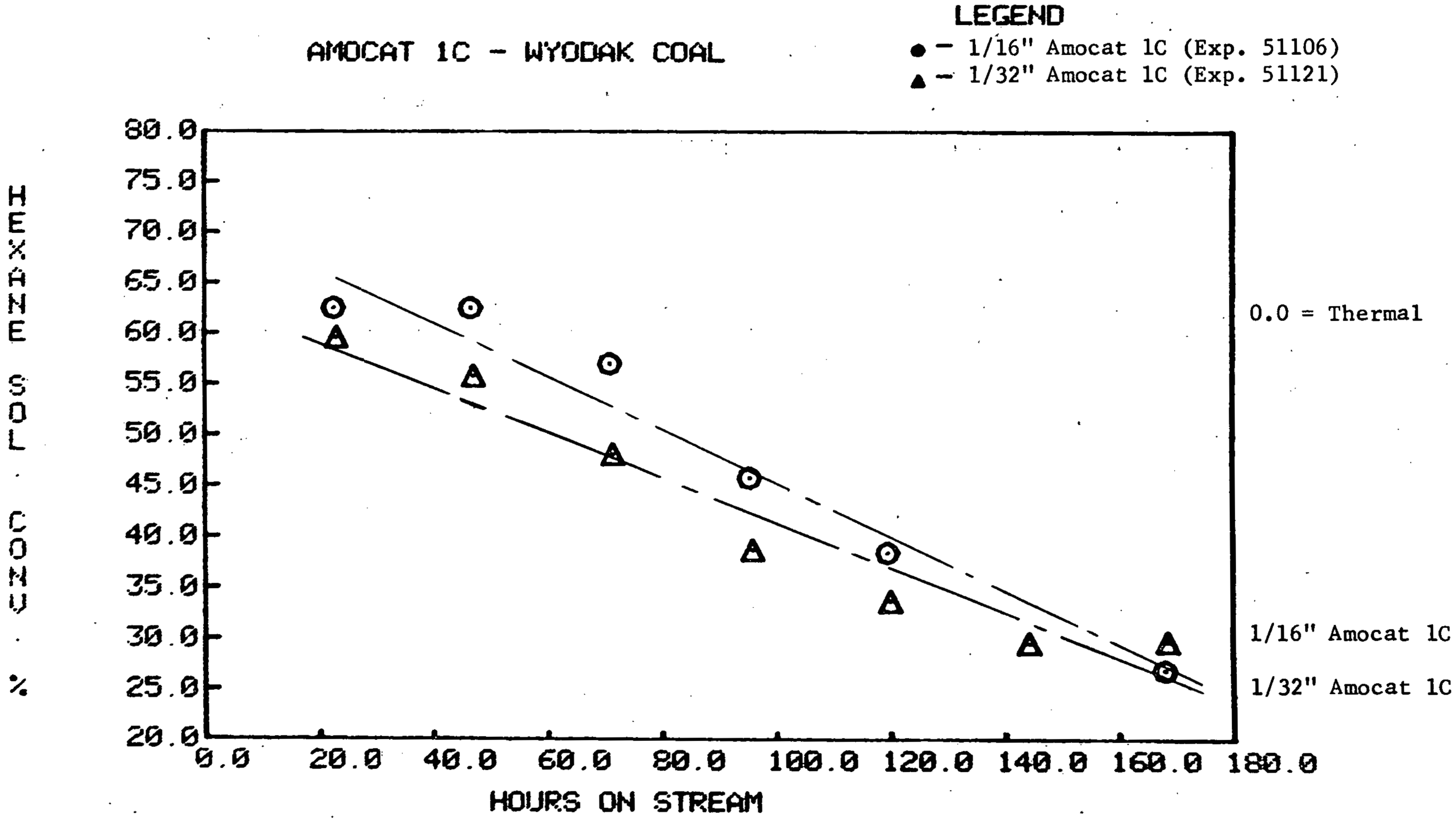

AMOCAT 1C - WYODAK COAL
LEGEND
● - 1/16" Amocat 1C (Exp. 51106)
▲ - 1/32" Amocat 1C (Exp. 51121)
BENZENE SOL. CONV. %
80.0
75.0
70.0
65.0
60.0
55.0
50.0
45.0
40.0
0.0
20.0
40.0
60.0
80.0
100.0
120.0
140.0
160.0
180.0
HOURS ON STREAM
1/16" Amocat 1C
1/32" Amocat 1C
55.4 = Thermal

FIGURE 14C


AMOCAT 1C - WYODAK COAL
LEGEND
● – 1/16" Amocat 1C (Exp. 51106)
▲ – 1/32" Amocat 1C (Exp. 51121)
HEXANE SOL. CONV. %
80.0
75.0
70.0
65.0
60.0
55.0
50.0
45.0
40.0
35.0
30.0
25.0
20.0
0.0
20.0
40.0
60.0
80.0
100.0
120.0
140.0
160.0
180.0
HOURS ON STREAM
0.0 = Thermal
1/16" Amocat 1C
1/32" Amocat 1C

## TASK 4. DEVELOPMENT SUPPORT STUDIES--SYNTHETIC COAL

Deliverability of an improved catalyst for the H-Coal process is a primary objective of the program. To achieve this goal the catalyst development program will be supplemented with work aimed at answering fundamental questions. Significant advances in catalyst technology frequently require a blend of fundamental and applied work; the catalyst development programs in the petroleum industry have successfully used this approach on numerous occasions.

The mechanism studies by Curran et al have been tremendously valuable in understanding hydrogen donor reactions involved in non-catalytic coal liquefaction. However, the presence of a catalyst in the liquefaction medium adds a new dimension to the picture. Although certain theories have been advanced on the function of the liquefaction catalyst, there is an obvious need to more clearly define its role.

Some significant strides in coal liquefaction can be accomplished in a fundamental study using synthetic coal mixtures. Two types of synthetic coals will be used--one representing Eastern coal and the other Western. Differences in sulfur and oxygen content will reflect the two types of coal. It should be pointed out that the specific compounds which comprise the synthetic coals are not as large as those present in coal; however, they should adequately represent units of functionality found in coal. This reasoning is based on the excellent work by Whitehurst, et al, at Mobil Oil. The specific catalyst functions that we believe are important in coal liquefaction include:

1. hydrogenation,
2. cracking,
3. hydrogenolysis to remove sulfur, nitrogen, and oxygen,
4. isomerization.

The first three listed catalytic functions are the most important, and these will be examined by an appropriate mixture of model compounds in a hydrogen donor solvent.

## EXPERIMENTAL

### Feed and Test Conditions

Initially a twelve-component mixture, containing compounds with units of functionality found in coal was used to separately analyze the catalytic functions of hydrogenation, hydrocracking, hydrodesulfurization, hydrodenitrogenation, and hydrodeoxygenation. The synthetic feed blend was simplified to a six-component mixture. The composition of the synthetic coal mixtures are as follows:

| Compounds | Eastern Synthetic<br>Wt.% | Western Synthetic<br>Wt.% |
|---|---|---|
| Oxygen Containing: | | |
| p-cresol | 11.0 | 25.0 |
| dibenzofuran | 10.0 | 5.0 |
| Nitrogen Containing: | | |
| indole | 2.0 | 1.5 |
| quinoline | 1.0 | 1.4 |
| Sulfur Containing: | | |
| dibenzothiophene | 4.0 | 1.2 |
| Hydrocarbons: | | |
| anthracene | 1.0 | 0.9 |
| Solvent: | | |
| Panasol AN-3 (trimethylnaphthalene) | 71.0 | 65.0 |
| H/C | 0.81 | 0.97 |

The Eastern synthetic feed blend contains 3.1% sulfur, 1.0% nitrogen, and 8.1% oxygen. The western blend contains 0.9% sulfur, 1.0% nitrogen, and 11.2% oxygen. Anthracene was the most difficult component to dissolve in the Panasol solvent and 1.0 wt% was the maximum concentration that could be obtained at room temperature. Since some of the components of the synthetic feed are light sensitive it is essential that the feed and product be stored in shielded containers.

Final debugging of the development support unit was completed during scoping studies with Amocat 1A catalyst, which were employed to develop suitable operating conditions for actual runs on the unit. In these studies it was discovered that a catalyst charge of 10 grams led to almost complete reactant conversion, a phenomenon which would make precise analytical work rather difficult. When the catalyst loading was cut to 5 grams, however, the conversion percentages were more moderate, and, yet, all six model compounds did react significantly. The final test consisted of the following:

| | |
|---|---|
| Reactor Pressure | 2000 psig |
| Reactor Temperature | 700°F or 800°F |
| Hydrogen Feed Rate | 4.90 SCF/hr |
| Liquid Hourly Space Velocity | 9.5 $hr^{-1}$ |
| Liquid Feed Rate | 47.5 g/hr (48 cc/hr) |
| Catalyst Charge | 5.0 grams |
| Mixing Speed | 1800 RPM |

A run, by definition, consisted of continuous operation at one temperature for approximately 20 hours with all other run parameters steady at the values listed above. Two runs were made with each of the four catalysts of interest (HDS-1442A, Amocat 1A, Amocat 1B and Amocat 1C), one at 700°F followed by another at 800°F. A four-hour sample was taken about five hours into the run and then again during the last four hours of the run.

This approach overcame the shortcomings of our previous model compound studies under the EPRI contract, viz. the test conditions were not nearly as severe as commercial H-Coal operating conditions; Amocat series of catalysts was not available at that time; and the large number (12) of model compounds used in the synthetic coal feed as well as the complexity of the components themselves, made following the various reaction pathways difficult.

In addition to the runs mentioned above, two additional thermal runs were completed as well as a run with Amocat 1A and the Panasol solvent alone. The catalytic runs made with the Eastern synthetic coal feed are listed in Table 4-1.

Results

Samples from the runs listed in Table 4-1 were analyzed by gas chromatography as well as for total C, H, S, N, O, and aromatic content. Only reactant disappearance is measured in our kinetic analysis because the background trimethylnaphthalene peaks in the Panasol solvent obscures the gas chromatographic peaks of the lower-boiling products but not those of the higher boiling reactants.

Percentage conversions for the runs with Amocat 1A and HDS-1442A catalyst are shown in Table 4-2. Measurable conversions were obtained with all the reactants except dibenzofuran at 700°F. Conversions for all reactants except quinoline were higher with HDS-1442A catalyst than with Amocat 1A at the two temperature levels used in our experiments. At 800°F the difference in percentage conversion is small and such small activity differences would not be observed with a more complicated multicomponent feed. Extrapolating these results to 825°F and assuming an Arrhenius temperature dependency all percentage conversions except dibenzofuran would then be greater with Amocat 1A than HDS-1442A. The results at 700°F point out the danger in drawing conclusions with model compound data at conditions other than actual process conditions. Response to process variables, particularly temperature and hydrogen partial pressure, can drastically alter comparisons made at non-realistic operating conditions.

Additionally, it should be pointed out that the overall surface area of HDS-1442A is quite high ( 300 $m^2/g$) with a 50 to 60Å average pore diameter while the synthetic mixture of compounds has a molecular diameter of 5Å to 10Å compared to 50-150Å for the preasphaltenes in real coal. Thus, the small pore HDS-1442A can utilize all of its pores with a synthetic mixture while it could not do so for real coal. Conversely, the lower surface area, larger pore diameter Amocat 1A is apparently "less effective" with synthetic mixtures because of lower surface area ( $150 m^2/g$).

The conversion of 2-methylnaphthalene, a key component of the Panasol donor solvent, is especially significant. In our previous studies at 600°F no conversion of the Panasol solvent was evident. A run with Amocat 1A and the Panasol solvent alone was recently completed in an attempt to distinquish between reactions products formed from the synthetic coal feed reactants and the solvent alone.

Samples from the runs listed in Table 4-1 have been submitted for the following analytical tests in addition to the standard gas chromatography analyses:

Component Analyses

-Sulfur Specific Gas Chromatography
-Nitrogen Specific Gas Chromatography
-IR Spectroscopy for p-Cresol and Dibenzofuran
-UV Spectroscopy for Anthracene
-Mass Spectrometry in Conjunction with Component GC Analysis

Total Analyses

-XRF Sulfur
-Kjeldahl Nitrogen
-High Accuracy C and H
-Direct Oxygen
-Basic Nitrogen

No further runs are planned until the data analyses of this series is completed with the exception of a single run with Amocat 1A and the Western synthetic coal feed.

Future runs include Eastern synthetic coal feed runs with the used Amocat 1A from PDU 10 to establish a base case for our regeneration studies. We will try to ascertain the extent each catalytic function has deactivated and which functions can most easily be regenerated and which are the most difficult. During this quarter we also complete the anlytical work-up of the earlier runs.

TABLE 4-1

## EASTERN SYNTHETIC COAL FEED RUNS

| RUN NUMBER | CATALYST | TEMPERATURE | LENGTH OF RUN | SAMPLING TIMES* (HOURS INTO RUN) |
|---|---|---|---|---|
| 47-001 | AMOCAT 1A | 700°F | 18 HOURS | 2 AND 14 |
| 47-003 | AMOCAT 1A | 800°F | 18 HOURS | 2 AND 14 |
| 47-004 | HDS-1442A | 700°F | 19.5 HOURS | 3.5 AND 15.5 |
| 47-005 | HDS-1442A | 800°F | 22 HOURS | 6 AND 18 |
| 47-006 | AMOCAT 1B | 700°F | 20 HOURS | 6 AND 18 |
| 47-007 | AMOCAT 1B | 800°F | 23.5 HOURS | 7.5 AND 19.5 |
| 47-008 | AMOCAT 1C | 700°F | 19.5 HOURS | 3.5 AND 15.5 |
| 47-009 | AMOCAT 1C | 800°F | 22.5 HOURS | 6.5 AND 18.5 |

*ALL SAMPLING PERIODS WERE FOUR HOURS LONG.

TABLE 4-2

## REACTANT CONVERSION DATA FOR EASTERN SYNTHETIC COAL FEED CATALYTIC RUNS

| | Run Conditions | | | |
|---|---|---|---|---|
| | 700°F | | 800°F | |
| Component | AMOCAT 1A Catalyst | HDS-1442A Catalyst | AMOCAT 1A Catalyst | HDS-1442A Catalyst |
| p-Cresol | 56.3 | 80.0 | 92.6 | 96.3 |
| Dibenzofuran | 0.0 | 0.0 | 9.5 | 22.1 |
| Dibenzothiophene | 38.3 | 65.1 | 84.8 | 89.9 |
| Indole | 62.8 | 78.6 | 86.0 | 90.3 |
| Quinoline | 86.0 | 70.8 | -- | 94.8 |
| Anthracene | 92.9 | 96.3 | 95.9 | 98.1 |
| 2-Methylnaphthalene | 11.8 | 31.2 | 39.6 | 41.0 |

## TASK 5. APPLICATION OF NEW CATALYSTS--H-COAL

Most of the effort by the participants in the H-Coal project is directed at process development and reactor improvement. However, it is important to note that catalyst performance has a strong impact on product quality, operating strategy (catalyst replacement, reactor conditions) and economics.

The objective of Task 5 includes the following:

1. Provide technical support on H-Coal tests run at HRI.
2. Correlate performance between H-Coal and Amoco test units.
3. Provide large scale samples of liquefaction catalysts for evaluation in H-Coal PDU or upgrading processes.
4. Coordinate activities with other DOE facilities.

During this report period the large 500 lb. batch of our CoMo formulation was tested by Hydrocarbon Research, Inc. in their large 3 T/D pilot plant. This was the longest (46 days) and smoothest of all the PDU runs and the first successful run with Wyodak coal. Preliminary data indicate that conversion of 90 wt. was achieved at 830°F. Hydrogen consumption was also reduced with the Amocat catalyst. Preasphaltene yields were lowered resulting in less bottoms and reduced reactor liquid viscosity. Naphtha and distillate yields were significantly increased. Based on the results of PDU-10 Amocat 1A was qualified for use in the 600 T/D H-Coal pilot plant in Catlettsburg, Kentucky. During the last quarter of 1980 W. R. Grace will begin production of a 40,000 batch of Amocat 1A for the Catlettsburg pilot plant. Samples from this batch will be tested in the continuous aging unit before delivery to the H-Coal pilot plant.

During this period W. R. Grace, our subcontractor, produced a 25 lb. batch of 1/32 in. NiMo Amocat 1C for use in SRC I ebullated bed upgrading studies. A 5 lb. sample of 1/8 in. NiMo was produced for our study of the effect of extrudate size on initial activity and deactivation rates.

Two samples of catalyst from Hydrocarbon Research, Inc. were tested in both our batch screening and continuous aging units. Results from these experiments are reported in earlier sections in this Quarterly report. Neither of the catalysts was as active as Amocat 1A.

During this period a new analytical technique was developed to measure the presence of metal crystallites on used catalyst samples. It was found that the presence of metal crystallites on used catalyst samples correlated strongly with poor performance. It appears that proper presulfiding and pretreatment of the catalyst before it is exposed to the coal slurry feed is essential to ensure good liquefaction and heteroatom removal activity. We plan to screen all our used catalyst samples for the presence of metal crystallites.

During this period X-Ray microprobe and an electron microscope were used to study the deposition of coke and metals on H-Coal catalysts during the course of a run. The technique will also be used to prescreen fresh catalysts to determine if the metal components are uniformly impregnated across the catalyst cross-section.

Used catalyst samples from PDU 10 will be acquired for our regeneration studies. Since these catalysts have a slight amount of residual radioactivity from the Sandia tagging experiments we are proceeding to obtain radioisotope clearance through Amoco's normal channels. Batch screening and development support unit tests will be used to measure the effectiveness of the various regeneration techniques.

During this quarter work continued on developing techniques to measure the viscosity of the resid portion of the coal liquid product. Viscosity is an important process parameter in the operation of an evullated bed, such as in a H-Coal reactor. Hydrocarbon Research, Inc. found significant viscosity reduction of the resid portion in their experiments with Amocat 1A catalyst. Using coal liquid products from our continuous aging unit runs we measured relative viscosity differences between products obtained with Amocat 1A and HDS-1442A that were similar to those measured by HRI. The viscosity difference increased throughout our runs because of catalyst deactivation whereas the difference was constant in the HRI steady-state ebullated bed runs. We will continue to monitor the viscosity of the resid portion of our continuous aging unit coal liquid product.

# APPENDIX A

## SRC EXPERIMENTAL DATA

### Calculation of Heteroatom Removal and Hydrogen Consumption

The rate of product leaving the reactor is not as accurately known as the feed rate (which is determined from a continuous record of the weight of the feed tank vs. time), and a calculated product rate is therefore used to minimize the effect of experimental error. Also the hydrogen consumption is not found directly from the hydrogen flow rate data because differencing the hydrogen flow entering the leaving the reactor can not be done accurately in the existing system. The calculation of the hydrogen consumption requires making some assumptions concerning the amount of hydrogen taken up by the heteroatoms and other compounds leaving the liquid phase; these assumptions are: (1) the nitrogen, oxygen, and sulfur are removed as ammonia, water and hydrogen sulfide, and (2) no hydrocarbons are liberated and no CO or $CO_2$ is formed.

This leaves five unknown quantities to be calculated in each experiment: the amounts of nitrogen, oxygen, and sulfur being removed from the liquid phase, the amount of hydrogen consumed, and the liquid product rate. These could be calculated from the five atom mass balances listed in Table A-I, but because carbon is a major component and has a much greater experimental error associated with its concentration compared to the other components, this procedure is not desirable. The overall mass balance can be used in place of the carbon balance and the resulting equations, which are shown in Table A-II, will only involve the concentrations of the minor components (i.e. the nitrogen, hydrogen, oxygen, and sulfur).

A second problem involves the fractions of each cut which are obtained in the ASTM distillation of the product. In general the sum of the fractions usually comes to about 0.96 or 0.97 because of small but unavoidable losses. It is assumed that these losses reduce the amount of distillate collected and the fractions of these two distillate fractions are corrected by increasing them by the same proportion to make the total sum of fractions equal to 1.0 before the heteroatom calculations are made. Finally, the percentages of heteroatom removal are obtained by dividing the rates of heteroatom removal by the heteroatom feed rates.

## TABLE A-I

## MASS BALANCE EQUATIONS

Nitrogen Balance

$$F_{IN}\ X0_1 = F_{OUT}\ (Q\ F_1\ X1_1 + Q\ F_2\ X2_1 + F_3\ X3_1) + G_1$$

Hydrogen Balance

$$F_{IN}\ X0_2 = F_{OUT}\ (Q\ F_1\ X1_2 + Q\ F_2\ X2_2 + F_3\ X3_2) - H_{IN} + G_1H_1 + G_2H_2 + G_3H_3$$

Oxygen Balance

$$F_{IN}\ X0_3 = F_{OUT}\ (Q\ F_1\ X1_3 + Q\ F_2\ X2_3 + F_3\ X3_3) + G_2$$

Sulfur Balance

$$F_{IN}\ X0_4 = F_{OUT}\ (Q\ F_1\ X1_4 + Q\ F_2\ X2_4 + F_3\ X3_4) + G_3$$

Carbon Balance

$$F_{IN}\ X0_5 = F_{OUT}\ (Q\ F_1\ X1_5 + Q\ F_2\ X2_5 + F_3\ X3_5)$$

Overall Mass Balance

$$F_{IN} = F_{OUT} - H_{IN} + G_1R_1 + G_2R_2 + G_3R_3$$

$F_{IN}$: Liquid Feed Rate

$F_{OUT}$: Liquid Product Rate

$F_i$: Fraction of Total as Distillation Cut i

$H_{IN}$: Rate of Hydrogen Consumption

$XJ_k$: Fraction of Element k in Distillation Cut J

$XO_k$: Fraction of Element k in Feed

$G_i$: Rate of gasification of element i

$H_i$: Grams of Hydrogen Per Gram of element i

$R_i$: Total Mass of compound gasified per gram of element i

Q: Normalization factor defined by the equation $Q\ F_1 + Q\ F_2 + F_3 = 1.0$

## TABLE A-II

## EQUATIONS USED TO CALCULATE THE RATES OF HETEROATOM REMOVAL AND HYDROGEN CONSUMPTION

$$F_{OUT} = F_{IN} \quad \frac{(1 - XO_1 - XO_2 - XO_2 - XO_4)}{(1 - S_1 - S_2 - S_3 - S_4)}$$

Nitrogen: $G_1 = (F_{IN}\ X\ O_1 - F_{OUT}\ S_1)$

Oxygen: $G_2 = (F_{IN}\ X\ O_2 - F_{OUT}\ S_2)$

Sulfur: $G_3 = (F_{IN}\ X\ O_3 - F_{OUT}\ S_3)$

Where: $S_i = Q\ F_1\ X\ 1_i + Q\ F_2\ X\ 2_i + F_3\ X\ 3_i$

$Q = (1. - F_3)/(F_1 + F_2)$

## TABLE A-III

## PROPERTIES OF FRESH COAL LIQUEFACTION CATALYSTS

| | Metals, Wt% | | | Digisorb (Desorption) | | | Hg Porosimetry | |
|---|---|---|---|---|---|---|---|---|
| Catalyst | Co | Ni | Mo | Surf Area ($m^2/g$) | Pore Vol (cc/g) | AvgPoreDia (A) | Pore Vol. (cc/g) | Remarks |
| 2392-147 | 2.3 | 0.0 | 10.9 | 177 | 0.71 | 112 | 0.731 | 500 lb. Batch of Amocat 1A |
| 3651-131 | 0.0 | 2.4 | 10.6 | ---* | --- | --- | --- | 1/32" Dia Amocat 1C |
| 3651-136 | --- | 2.7 | 9.5 | --- | --- | --- | --- | H-Coal No. 5 Catalyst |
| 3651-142 | --- | 2.6 | 10.2 | --- | --- | --- | --- | H-Coal No. 4 Catalyst |
| 3651-143 | 2.4 | 0.0 | 11.1 | --- | --- | --- | 0.551 | Sm Stabilized Catalyst, Sm = 2.9 wt% |
| PROPERTIES OF FRESH SRC CATALYSTS | | | | | | | | |
| 3651-83 | 0.0 | 0.0 | 0.0 | 214 | 0.840 | 106 | 0.744 | Bimodal Amocat Support |
| 3651-1182 | 2.3 | .04 | 10.0 | 311 | 0.572 | 48 | 0.668 | American Cyanamid 1442B |
| 3651-1183 | 0.0 | 2.75 | 12.1 | 190 | 0.553 | 75 | 0.240 | Shell 324 |

*Analysis is outstanding

# TABLE A-IV

## SUMMARY OF EXPERIMENTS CONDUCTED IN CONTINUOUS AGING UNIT DURING QUARTER

| Experiment No. | Test Period | Catalyst | Remarks |
|---|---|---|---|
| 51115 | 6/30-7/2<br>(39 hours) | Bimodal Support<br>(3651-83) | 33% SRC & 67% Creosote Oil. Determine uncatalyzed reaction products to help evaluate performance of catalysts in hydrogenating SRC. |
| 51116 | 7/24-7/30<br>(167 hrs.) | Amocat 1A<br>(2392-147) | Establish a base case for the new batch of Ill. No. 6 coal (FCL-16). |
| 51117 | 8/1-8/8<br>(169 hrs.) | H-Coal #5<br>(3651-136) | Evaluate performance of HRI's H-Coal No. 5 catalyst with Ill. No. 6 coal. |
| 51118 | 8/13-8/19<br>(167 hrs.) | H-Coal #4<br>(3651-142) | Evaluate performance of HRI's H-Coal No. 4 catalyst with Ill. No. 6 coal. |
| 51119 | 8/22-8/25<br>(95 hrs.) | Sm Stabilized CoMo/Alumina<br>(3651-143) | Samarium stabilized CoMo on alumina catalyst with Wyodak coal. Rupture disk blew out and then reactor temperature controller failed stopping the experiment early. |
| 51120 | 9/4-9/11<br>(164 hrs.) | Sm Stabilized CoMo/Alumina<br>(3651-143) | Repeat of Exp. No. 51119 to evaluate the samarium stabilized catalyst. |
| 51121 | 9/22-9/29<br>(168 hrs.) | 1/32" Dia. Amocat 1C NiMo/Alumina<br>(3651-131) | Small diameter Amocat 1C with Wyodak coal to determine effect of pellet size on initial activity and deactivation rate. |