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# CATALYSTS FOR UPGRADING COAL-DERIVED LIQUIDS

Quarterly Report, January 1—March 31, 1981

By
Billy L. Crynes

DIST 214
NTIS 25

April 15, 1981
Date Submitted

Work Performed Under Contract No. AC22-79ET14876

The Oklahoma State University
School of Chemical Engineering
Stillwater, Oklahoma

U. S. DEPARTMENT OF ENERGY

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Price: Printed Copy A03
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DOE/ET/14876-T3
Distribution Category UC-90d

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# (DE-14876-6)

## ABSTRACT

Run ZBF was conducted to determine the amount of sulfur and nitrogen removal from SRC-I/process solvent mixture in the absence of a hydrotreating catalyst (1 mm diameter, nonporous glass beads were used). Three temperatures of 350C, 375C, 400C and three space times; 0.5, 1.0, 2.0 hours were employed at pressures of 1500 to 1900 psig. Negligible nitrogen and sulfur removal resulted from this experiment. The hydrogen content of the coal liquid increased slightly over that of the feedstock (about 7.1 wt% vs 6.8 wt%). In similar studies using other coal liquids some sulfur removal (10-40%) was noted under "non-catalyzed" conditions.

Several commercial NiMo supported catalysts were analyzed for silica contents using atomic absorption. These results revealed that catalysts with large micropore size structures also contain high silica content (up to 22.5 weight percent).

Several short duration runs (12-110 hours) were conducted in the CLTU to gather data on catalyst coking mechanisms. These runs were conducted utilizing NiMo supported catalysts (Shell 324, HT 115, Amocat 1C). The catalysts activity decay rate was established in these experiments and the data will be utilized and assessed later. High radial temperature differences were observed across the catalyst beds during these runs. Both the hydrogenation performance of the catalysts and these temperature differences decayed with the same profile as time-on-oil increased during an experimental run. Typical temperature differences from previous experimental runs using lighter coal liquids and CoMo catalysts were observed to be only 3 to 5F.

Using the SRC material mixed with a process solvent or creosote oil (30 weight percent SRC) solid materials were observed to form and precipitate in the latter portions of the reactor bed. The reactor system was modified to prevent the accumulation of these "incompatible" solids which would result in premature termination of the experimental runs.

In the catalyst regeneration study (HDN-30, NiMo), a spent catalyst was regenerated and then used to hydrotreat a coal liquid consisting of 10% Synthoil II liquid mixed with raw anthracene oil This regenerated catalyst gave equal and somewhat superior performance with respect to heteroatom removal compared to that of the fresh catalyst. A second regeneration of this same catalyst loading has been conducted and the regenerated catalyst is being prepared for a third cycle. The spent catalyst lost approximately 33 % of its total surface area, yet regeneration recovered 97 percent of the fresh catalyst area.

## OBJECTIVE AND SCOPE OF WORK

The goal of this program is to investigate catalysts for upgrading liquids derived from coal-to-oil processes.

This research has the following technical objectives:

1. Investigate mechanisms responsible for rapid initial catalyst deactivation.
2. Study use of "throw away" catalysts and staged catalyst beds in hydroprocessing of coal liqiuds.

The investigation shall consist of the following tasks:

Task 1-a. Inexpensive "throw away" type catalyst for coal liquids upgrading shall be investigated for reactor guard chamber service

Task 1-b. Reactors packed with mixtures of catalyst types and zoned catalyst configurations shall be evaluated.

Task 2-a. Catalyst life tests shall be conducted using a standard Ni-Mo/alumina hydroprocessing catalyst in the existing catalyst life test unit.

Task 2-b. Changes in catalyst properties, including surface area, pore size distribution, pore volume, and coke and inorganics accumulation shall be measured as a function of coal-liquid contact time.

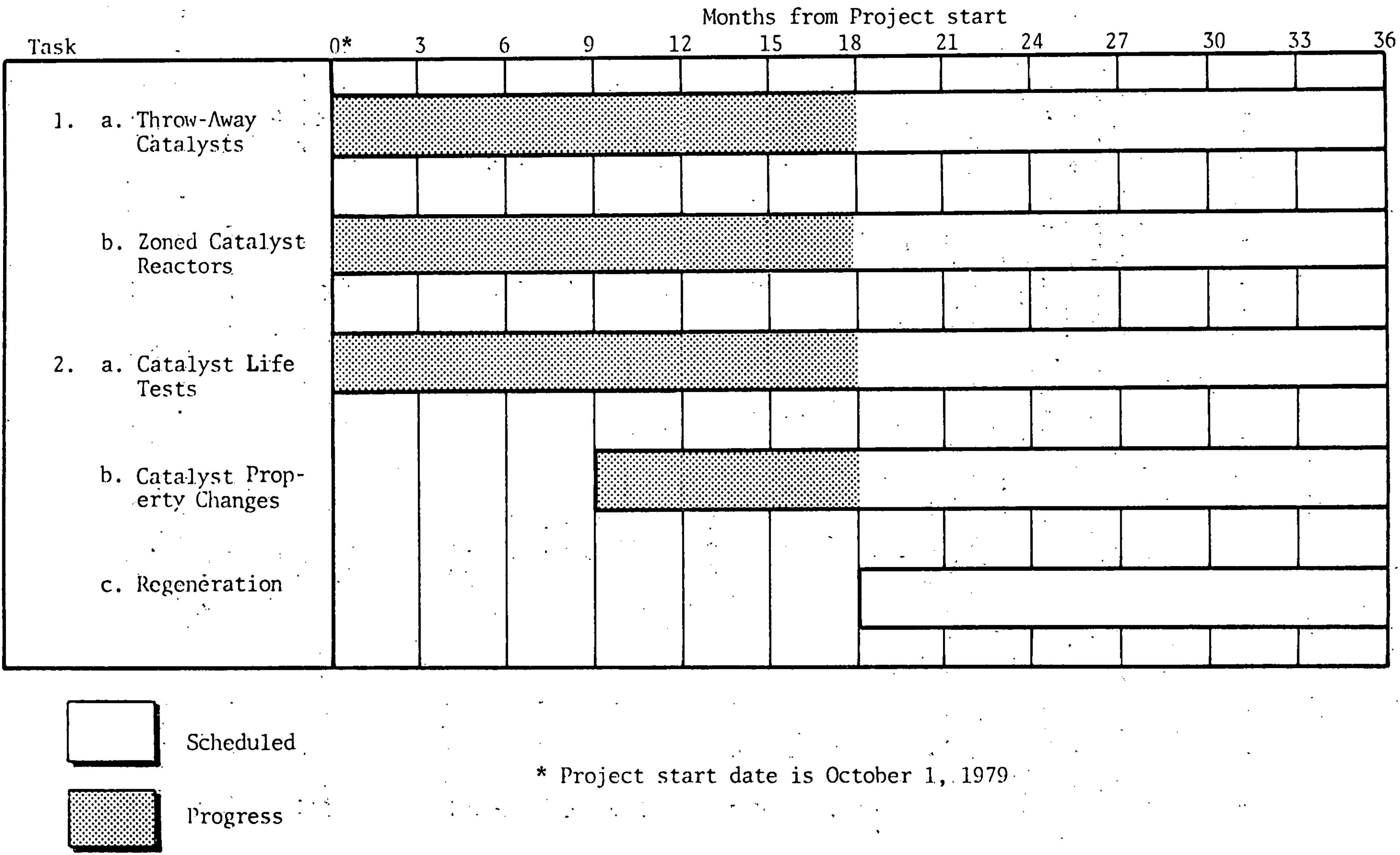
Task 2-c. The Ni-Mo/alumina catalyst tested in Task 2-a shall be regenerated by oxidation, and tested for activity recovery.

## SUMMARY OF PROGRESS TO DATE

The following chart summarizes the progress to date. The three tasks (1-a, 1-b, 2-a, and 2-b) show scheduled progress. Although not shown in the figure, some initial activity has begun in task 2-c.

As of March 31, 1981, 49% of the total budget has been expended ($88,690). This is an expected expenditure rate for the first six quarters of this project.

PROGRESS SUMMARY AS OF DECEMBER 31, 1980



* Project start date is October 1, 1979

## DESCRIPTION OF TECHNICAL PROGRESS

### Task 1 - Throw Away and Zoned Catalyst Systems (O. K. Bhan)

Experimental run ZBF was conducted with non-porous glass beads (1mm dia.), using a mixture of 30 wt% SRC-I in SRC-I process solvent. The properties of this feedstock are given in Table I. The run was terminated after 49 hours of continuous operation due to restriction in the reactor and the exit liquid lines. Erratic pressure control was observed after 45 hours of gas-liquid contact caused by liquid build up in the inlet and the exit gas lines. Details of this run follow in the next section.

Elemental analyses of the reactor plug material revealed a substance very similar to the SRC-I solid present in the feedstock. The restriction of the reactor was localized only to the bottom three inches of the reactor and the dip tube leading to the first sample bomb. This signifies precipitation and subsequent accumulation of a substance similar to SRC-I in the reactor bottom causing plugging to occur. Ash analysis of the plug material could not be carried out because of the very small quantity of this material available. The elemental analyses of the plug material and the SRC-I solid are given in Table I.

Some modifications are planned in the design of the EN-1 reactor to avoid plugging problems in future experimental runs. The gas inlet and exit system will be modified to avoid liquid seepage into the gas lines. This new system will be designed to operate at a pressure of 2000 psig and temperatures up to 500C (930F).

Attention was focused on establishing a fast method for pre-asphaltene and asphaltene determinations at our laboratory. The asphaltene determination method developed at Pittsburgh Energy Technology Center, employing ultrasonics and microfiltration will be employed at our laboratory, contrary to the Soxhlet method mentioned in the last report. The orders for this unit have been placed.

Commercial hydrotreating catalysts of similar metal loadings (3% NiO, 15% $MoO_3$) but varying pore diameters (50 - 260°A average pore diameter), both unimodal and bimodal have been acquired for use in future zonal catalyst bed studies.

### Run Series ZBF

The objective of this run was to determine the extent of hydrogenation, hydrodesulfurization and hydrodenitrogenation of a SRC-I plus solvent mixture in the absence of a hydrotreating catalyst. Three temperatures 350C, 375C, 400C and three space times; 0.5 hours, 1.0 hours, 2.0 hours were employed. The pressure was maintained constant at 1750 psig except for the last 12 hours of the run when the pressure was changed to 1900 and 1500 psig, respectively.

Sample analyses revealed negligible hydrodenitrogenation of the feed at all three temperatures and space times. Surprisingly, negligible sulfur removal was observed at all conditions. The hydrogen content of

## TABLE - I

## PROPERTIES OF FEEDSTOCK AND ELEMENTAL ANALYSIS OF SRC-I AND REACTOR PLUG MATERIAL

| | Feedstock[a] | SRC-I[b] | Reactor Plug Material[c] |
|---|---|---|---|
| Density @ 70 F, gm/mℓ | 1.114 | | |
| **Elemental composition, wt%** | | | |
| Carbon | 89.219 | 86.603 | 86.595 |
| Hydrogen | 6.761 | 5.847 | 5.764 |
| Nitrogen | 1.343 | 2.200 | 1.995 |
| Sulfur | 0.482 | 0.660 | 0.652 |
| Oxygen[d] | 2.098 | | |
| Ash | 0.097 | | |
| Normal Boiling Point[e] | | | |
| First Drop | 247 C (476F) | | |
| 5 Vol.% | 261 C (502F) | | |
| 10 | 267 C (513F) | | |
| 20 | 288 C (550F) | | |
| 30 | 309 C (589F) | | |
| 40 | 337 C (639F) | | |
| 50 | 370 C (698F) | | |
| 60 | 425 C (797F) | | |
| 70 | 479 C (894F) | | |

[a] Mixture of 30 wt% SRC-I and 70 wt% process solvent.
[b] Solid at room temperature.
[c] Reactor plug matter from dip tube at the reactor bottom.
[d] By difference.
[e] Determined from ASTM D-1160 at 10 mm Hg.

the feedstock increased slightly, the maximum increase was 0.457 wt% at 350C, 1750 psig and a space time of 1.0 hours. Negligible heteroatom removal at temperatures as high as 400C was surprising. In similar studies of other light coal liquids, some sulfur removal (10-40% removal) was noted under "non-catalyzed" conditions.

Table II presents the results of the analyses of this experimental run. The samples were analyzed in triplicates, and the standard deviations for sulfur ranged over 0.005 to 0.074, except for sample ZBF-9 which was unusually high at 0.171. Typical deviations for sulfur analyses were 0.042, nitrogen were 0.051 and hydrogen were 0.182.

## TABLE II

## RESULTS FROM RUN ZBF WITH GLASS-BEADS

## FEEDSTOCK: SRC-I/PROCESS SOLVENT

| Sample Number | Temp[a] (C/F) | Pressure (psig) | Space Time[b] (Volume Hrly) | Hydrogen (SCF/BBL) | Hours[c] on oil | wt%S[d] | wt%S[e] Removal | wt%N[d] | wt%N[e] Removal | wt%H[d] |
|---|---|---|---|---|---|---|---|---|---|---|
| Feed | | | | | | 0.482 | | 1.343 | | 6.761 |
| ZBF-1 | 350/662 | 1750 | 2.0 | 3500 | 6 | 0.477 | f | 1.232 | 8 | 6.592 |
| ZBF-2 | 350/662 | 1750 | 1.0 | 3500 | 10 | 0.441 | 8 | 1.170 | 12 | 6.097 |
| ZBF-3 | 350/662 | 1750 | 0.5 | 3500 | 15 | 0.489 | f | 1.313 | 2 | 7.071 |
| ZBF-4 | 375/707 | 1750 | 0.5 | 4000 | 20 | 0.537 | f | 1.332 | f | 7.072 |
| ZBF-5 | 375/707 | 1750 | 1.0 | 4000 | 26 | 0.527 | f | 1.286 | 4 | 7.218 |
| ZBF-6 | 375/707 | 1750 | 2.0 | 4000 | 31 | 0.436 | 9 | 1.372 | f | 6.945 |
| ZBF-7 | 400/752 | 1750 | 2.0 | 6000 | 37 | 0.480 | f | 1.322 | f | 7.070 |
| ZBF-8 | 400/752 | 1900 | 2.0 | 6000 | 42 | 0.467 | 3 | 1.335 | f | 6.750 |
| ZBF-9 | 400/752 | 1500 | 1.0 | 6000 | 47 | 0.394 | 18 | 1.344 | f | 6.725 |
| ZBF-10 | 400/752 | 1500 | 1.0 | 6000 | 49 | 0.445 | 7 | 1.334 | f | 7.030 |

a. Nominal reactor temperature.
b. This is a volume hourly space time (volume of catalyst/volume of oil per hour).
c. Total hours which the catalyst has been contacted with oil at reaction temperature.
d. Percent of sulfur, nitrogen or hydrogen in liquid product.
e. % Removal = 100 x (fraction in feed less fraction in product)/(fraction in feed).
f. Specifies neglegible removal.

## Task 2 - Catalyst Life Studies (H. J. Chang)

In the Catalyst Life Test Unit (CLTU), six experimental runs were made with 30 wt% SRC/process solvent as feedstock and three commercial NiMo supported catalysts. Four runs, LTF, LTG, LTV and LTU were made with Shell 324 catalyst, run LTH was made with Harshaw HT 115, and run LTI with Amoco's Amocat 1C catalyst. The properties of the catalysts and feedstock are shown in Tables III and XI respectively. Figures 1 and 2 show the pore size distributions of the three NiMo supported catalysts.

Several commerical NiMo supported catalysts were analyzed for silica contents using atomic absorption. The results along with average pore diameters are shown in Table IV. The table shows that large micropore size catalysts contain silica as high as 22.50 wt%. The interactions of the pore size, the silica content and coking of the catalysts are of interest in this study.

During this reporting quarter, all runs were made with 30 wt% SRC/process solvent. However, the use of this new feedstock showed no improvement in terms of solid formation and precipitation within the reactor with resultant plugging compared to the use of 30 wt% SRC/creosote oil in the previous experimental runs. We therefore modified the reactor exit and separation system to better tolerate solids formation from the reactor. This modification has proven to be effective as shown by Runs LTI and LTV which were shut down on schedule at 93 hours on oil and longer.

Temperature differences in the reactor radial direction were further investigated. These temperature differences decreased with time on oil and correlated well with hydrogenation activity of the catalysts as will be seen later.

### Run Series LTF, LTG, LTH, LTI, LTU and LTV

The run conditions, which are common to all these runs were:

| | |
|---|---|
| Reactor | CLTU II |
| Feedstock | 30 wt% SRC/process solvent (Table XI) |
| Temperature | 399 C (750F) |
| Pressure | 2000 psig |
| Hydrogen Flow | 10,000 SCF/Bbl |

The individual run conditions which were unique to each run were as follows:

| Run Series | Catalyst (Table III) | LVHST (Hrs) | Hours on oil | Plugging |
|---|---|---|---|---|
| LTF | Shell 324 | 2.26 | 12 | Yes |
| LTG | Shell 324 | 2.50 | 19 | Yes |
| LTV | Shell 324 | 2.16-2.43 | 97 | No |
| LTU | Shell 324 | 2.60-4.33 | 110 | No |
| LTH | HT 115 | 2.14 | 44 | Yes |
| LTI | Amocat 1C | 2.30-4.00 | 93 | No |

## TABLE III

## CATALYST PROPERTIES

| Catalyst Code | Shell 324 | HT 115 | Amocat 1C |
|---|---|---|---|
| Manufacturer | Shell | Harshaw | Amoco |
| Chemical Composition, wt% | | | |
| NiO | 3.4 (3.4)* | 3.6 (3.6) | 2.9 |
| $MoO_3$ | 19.3 (19.8) | 14.7 (16.4) | 15.8 |
| $SiO_2$ | 19.0 ** | 20.3 ** | 17.2** |
| Physical Properties | | | |
| Geometry | 1/16" extrudate | 1/16" extrudate | 1/16" extrudate |
| Reactor density, gm/ml | 0.79 | 0.63 | 0.63 |
| Surface area, $m^2$/gm | 146 (150) | (137) | |
| Pore volume, ml/gm | 0.42 (0.48) | 0.62 (0.74) | 0.61 |
| Most frequent Pore diameter, Å | 118 | 170 | 104 |
| Pore size distribution, % pore volume in pore diameter, Å | | | |
| 35-70 | 12 | 1 | 4 |
| 70-100 | 21 | 4 | 29 |
| 100-150 | 57 | 36 | 41 |
| 150-200 | 2 | 40 | 5 |
| 200-400 | 1 | 13 | 3 |
| 400-600 | 1 | 3 | 2 |
| >600 | 6 | 3 | 16 |
| Total | 100 | 100 | 100 |

*Values in the parentheses are vendor's data.

**Tentative results; interference in the atomic absorption analyses is possible. These are averages of three to four analyses.

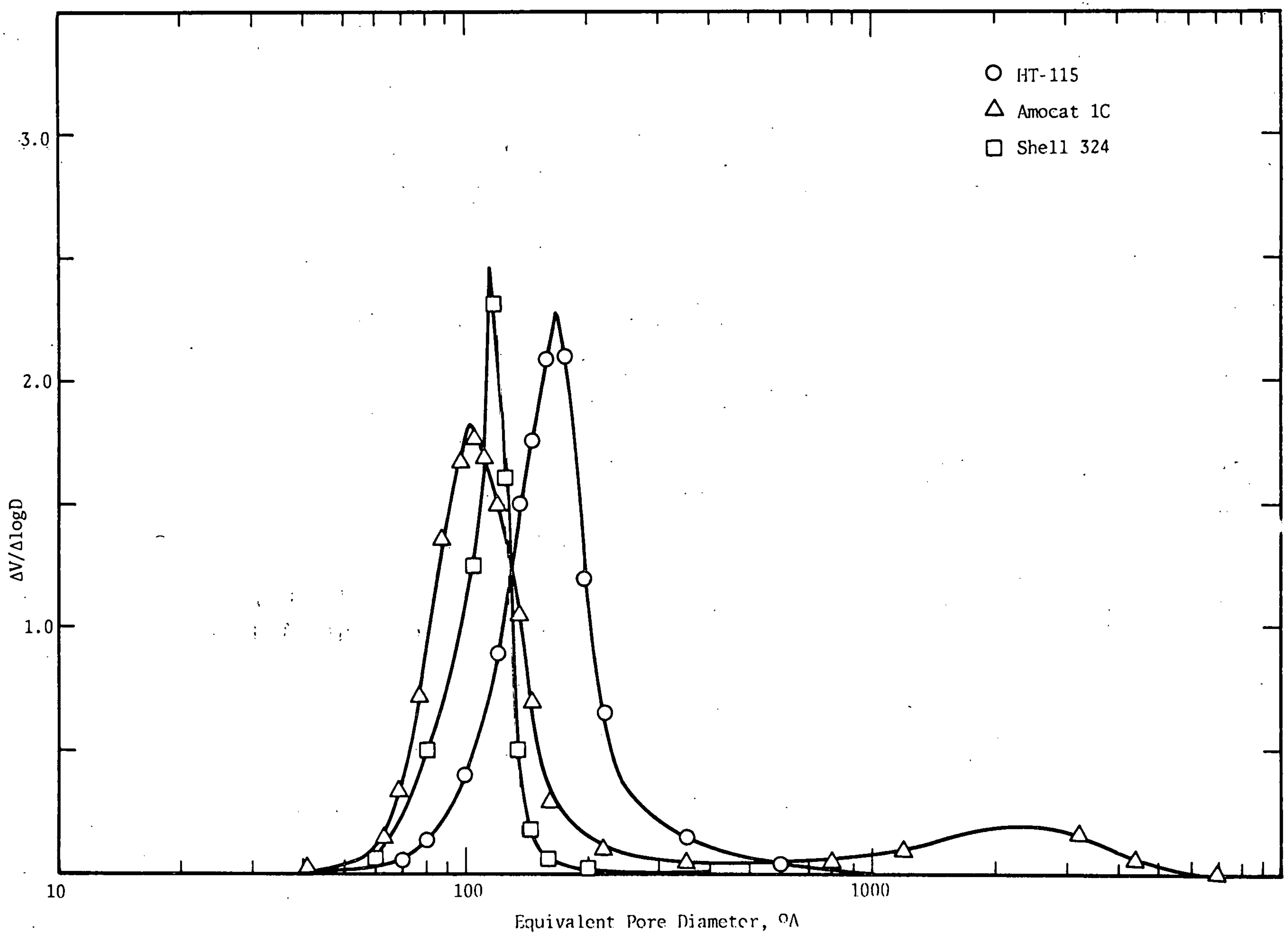


Figure 1. Pore Size Distribution

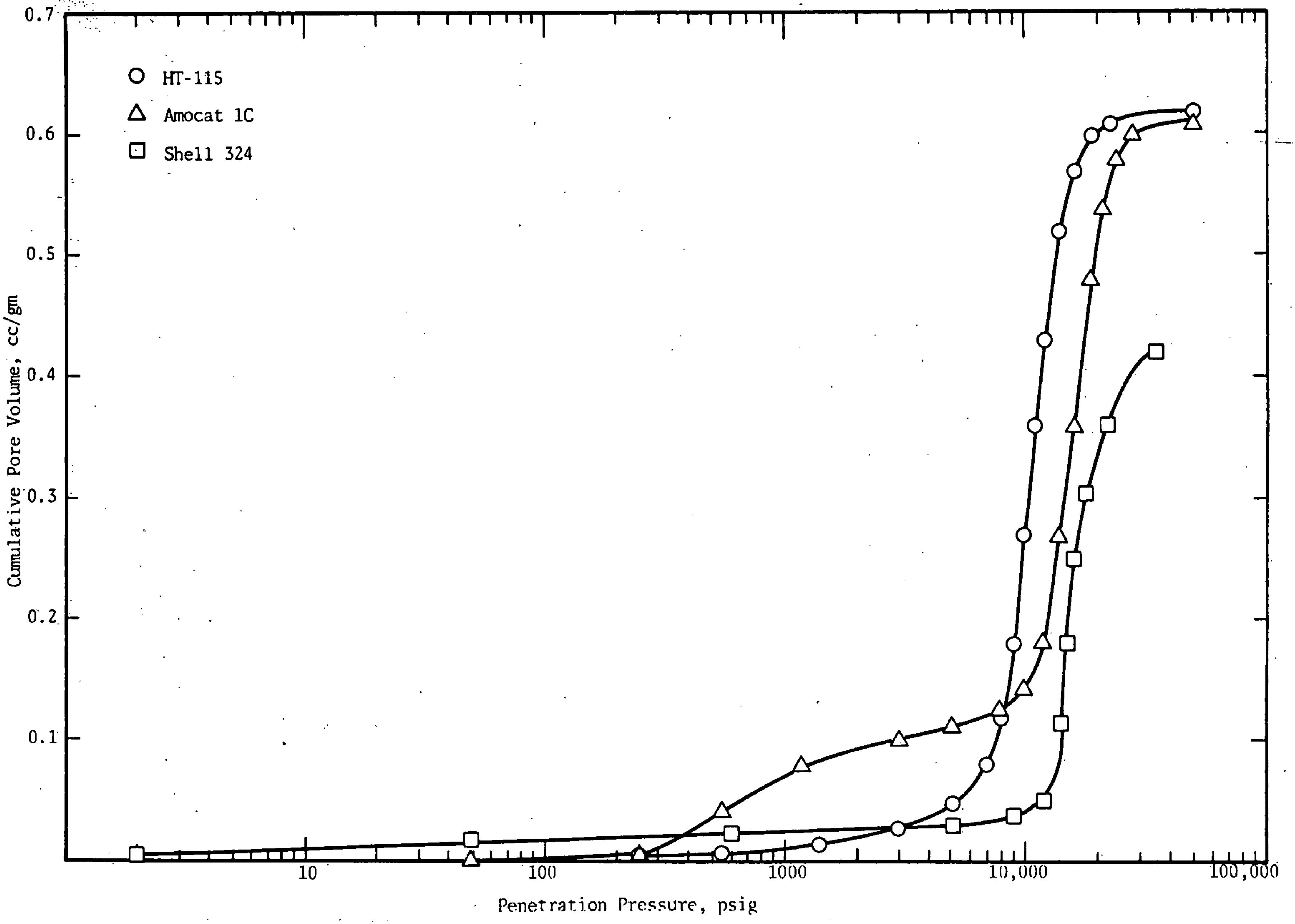


Figure 2. Cumulative Pore Volume vs. Pressure

## TABLE IV

## SILICA CONTENTS AND AVERAGE PORE SIZES OF COMMERCIAL NiMo SUPPORTED CATALYSTS

| Catalyst Code | Manufacturer | Average Micropore Diameter, °A | $SiO_2$** wt. % | Manufacturer's data |
|---|---|---|---|---|
| HT 115 | Harshaw | 170 | 20.3 | NA* |
| Shell 324 | Shell | 118 | 19.0 | NA |
| Amocat 1C | Amoco | 104 | 17.2 | NA |
| HDN-30 | American Cyanamid | 110 | 15.1 | NA |
| NM 504 | Katalco | 101 | 22.5 | 1.5 |
| Shell 214 | Shell | 59 | 5.1 | NA |
| KS 153S | Armark | 88 | 8.6 | 4.5 |
| NM 506 | Katalco | 71 | 2.1 | NA |
| NM 502 | Katalco | 88 | 1.1 | NA |
| H-oil | Armark | 94 | 0.47 | 0.46 |

*Not available.

**Tentative results; interference in the atomic absorption analyses is possible. These are averages of three to four analyses.

The purposes of Runs LTF, LTG, LTV and LTU were to obtain the data on the properties of the spent catalysts versus time on oil; whereas runs LTH and LTI were designed to compare the decaying characteristics of the catalysts Harshaw HT 115 and Amocat 1C with Shell 324. As shown in Figure 1, HT 115 is a monodisperse catalyst with a large and wide range micropore. Amocat 1C is a bidisperse catalyst with a narrow micropore distribution as that in Shell 324, which is a monodisperse catalyst.

The results from sample analyses are listed in Tables V to X. Sulfur data will be provided in a subsequent report. The variations in liquid volume hourly space time (LVHST) were caused by the malfunctioning of the oil pumping system. These frequent variations should be partially responsible for the deviations in the resulting data. For clarity, the nitrogen contents of the product oils are normalized to the LVHST of 2.50 according to the liquid hold up model proposed by Henry and Gilbert* for the pseudo-first order reaction:

$$\ln \frac{Co}{Ci} \quad \alpha \quad (\text{LVHST})^{2/3}$$

where Co: Concentration at reactor outlet
Ci: Concentration at reactor inlet
LVHST: Liquid volume hourly space time

The results are plotted in Figures 3-5.

Figure 3 shows HDN activities versus time on oil for Runs LTF, LTG and LTV. These runs were made essentially at the same conditions and were shut down at different times on oil. Run LTV was a rerun of LTU which was made during the testing of the newly modified system and was shut down and restarted several times. A new batch of feedstock was used in Runs LTV and LTI. This might have caused inconsistency between the results from Runs LTF, LTG and Run LTV. The data show that the catalyst decayed rapidly in the first 30 hours period then demonstrated a reduced decay rate. The same decaying pattern was observed when HT 115 and Amocat 1C catalysts were used as shown in Figures 4 and 5. When comparing the catalyst activity responses, one can see that the Shell 324 catalyst has higher initial activity than the other two catalysts. Note that Shell 324 has a bulk reactor density of 0.79 grams/ml which is higher than those of HT 115 and Amocat 1C, 0.63 grams/ml. There is no observable difference in initial activity if the comparison is made on a weight basis. However, a comparison of the decaying rate of these catalysts is difficult because of the short run periods and the data scattering.

In all these experimental runs, a thermocouple was located four inches down from the entrance of the 20 inch catalyst bed. The temperature difference (ΔT) across the catalyst bed center and outer reactor wall has been further investigated. Figures 6 and 7 show that ΔT's decrease with time on oil and closely follow the hydrogenation activities. The ΔT was 25F and higher initially, then decreased rapidly to around 10F at 30 hours on oil. This decay pattern is the same as the HDN activity as shown earlier. A ΔT of 20F, with no decrease with time on oil, was observed when EDS process oil was used as feedstock in Run LTB reported

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*Henry, H. C. and J. B. Gilbert, I&EC Process Des. Dev., <u>12</u>, 328 (1973).

## TABLE V

## RESULTS FROM RUN LTF WITH SHELL 324 CATALYST

FEEDSTOCK: 30 wt% SRC/PROCESS SOLVENT

| Sample Number | Temp[a] (F) | Pressure (psig) | Space Time[b] (Volume Hrly) | Hydrogen (SCF/BBL) | Hours[c] on oil | wt%S[d] | wt%S[e] Removal | wt%N[d] | wt%N[e] Removal | wt%H[d] |
|---|---|---|---|---|---|---|---|---|---|---|
| Feed | | | | | | 0.50 | | 1.40 | | 6.73 |
| LTF-1 | 750 | 2000 | 2.26 | 10,000 | 2 | - | - | - | - | - |
| LTF-2 | 750 | 2000 | 2.26 | 10,000 | 6 | <0.02 | >96 | 0.22 | 84 | 9.70 |
| LTF-3 | 750 | 2000 | 2.26 | 10,000 | 12 | 0.04 | 92 | 0.38 | 73 | 9.87 |

a. This was the temperature at the outer wall of the reactor. The temperature at the center of the catalyst bed was 10-25F higher.
b. This is a volume hourly space time (volume of catalyst/volume of oil per hour).
c. Total hours which the catalyst has been contacted with oil at reaction temperature.
d. Percent of sulfur, nitrogen or hydrogen in liquid product.
e. % Removal = 100 x (fraction in feed less fraction in product)/(fraction in feed).

## TABLE VI

## RESULTS FROM RUN LTG WITH SHELL 324 CATALYST

## FEEDSTOCK: 30 wt% SRC/PROCESS SOLVENT

| Sample Number | Temp[a] (F) | Pressure (psig) | Space Time[b] (Volume Hrly) | Hydrogen (SCF/BBL) | Hours[c] on oil | wt%S[d] | wt%S[e] Removal | wt%N[d] | wt%N[e] Removal | wt%H[d] |
|---|---|---|---|---|---|---|---|---|---|---|
| Feed | | | | | | 0.50 | | 1.40 | | 6.73 |
| LTG-1 | 750 | 2000 | 2.50 | 10,000 | 2 | - | | - | | - |
| LTG-2 | 750 | 2000 | 2.50 | 10,000 | 6 | <0.02 | >96 | 0.25 | 82 | 10.50 |
| LTG-3 | 750 | 2000 | 2.50 | 10,000 | 12 | 0.02 | 96 | 0.35 | 75 | 10.00 |
| LTG-4 | 750 | 2000 | 2.50 | 10,000 | 19 | 0.06 | 88 | 0.37 | 74 | 9.68 |

a. This was the temperature at the outer wall of the reactor. The temperature at the center of the catalyst bed was 10-25F higher.
b. This is a volume hourly space time (volume of catalyst/volume of oil per hour).
c. Total hours which the catalyst has been contacted with oil at reaction temperature.
d. Percent of sulfur, nitrogen or hydrogen in liquid product.
e. % Removal = 100 x (fraction in feed less fraction in product)/(fraction in feed).

## TABLE VII

## RESULTS FROM RUN LTH WITH HT-115 CATALYST

FEEDSTOCK: 30 wt% SRC/PROCESS SOLVENT

| Sample Number | Temp[a] (F) | Pressure (psig) | Space Time[b] (Volume Hrly) | Hydrogen (SCF/BBL) | Hours[c] on oil | wt%S[d] | wt%S[e] Removal | wt%N[d] | wt%N[e] Removal | wt%H[d] |
|---|---|---|---|---|---|---|---|---|---|---|
| Feed | | | | | | 0.50 | | 1.40 | | 6.73 |
| LTH-1 | 750 | 2000 | 2.14 | 10,000 | 2 | NA | | NA | | NA |
| LTH-2 | 750 | 2000 | 2.14 | 10,000 | 6 | NA | | 0.40 | 71 | 10.26 |
| LTH-3 | 750 | 2000 | 2.14 | 10,000 | 12 | NA | | 0.49 | 65 | 9.93 |
| LTH-4 | 750 | 2000 | 2.14 | 10,000 | 21 | NA | | 0.46 | 67 | 9.63 |
| LTH-5 | 750 | 2000 | 2.14 | 10,000 | 33 | NA | | 0.53 | 62 | 9.52 |
| LTH-6 | 750 | 2000 | 2.14 | 10,000 | 44 | NA | | 0.59 | 58 | 9.56 |

a. This was the temperature at the outer wall of the reactor. The temperature at the center of the catalyst bed was 10-25F higher.
b. This is a volume hourly space time (volume of catalyst/volume of oil per hour).
c. Total hours which the catalyst has been contacted with oil at reaction temperature.
d. Percent of sulfur, nitrogen or hydrogen in liquid product.
e. % Removal = 100 x (fraction in feed less fraction in product)/(fraction in feed).

# TABLE VIII

## RESULTS FROM RUN LTU WITH SHELL 324 CATALYST

FEEDSTOCK: 30 wt% SRC/PROCESS SOLVENT

| Sample Number | Temp[a] (F) | Pressure (psig) | Space Time[b] (Volume Hrly) | Hydrogen (SCF/BBL) | Hours[c] on oil | wt%S[d] | wt%S[e] Removal | wt%N[d] | wt%N[e] Removal | wt%H[d] |
|---|---|---|---|---|---|---|---|---|---|---|
| Feed | | | | | | 0.50 | | 1.40 | | 6.73 |
| LTU-1 | 750 | 2000 | 2.60 | 10,000 | 3 | NA | | NA | | NA |
| LTU-2 | 750 | 2000 | 2.60 | 10,000 | 7 | NA | | 0.23 | 84 | 10.53 |
| LTU-3 | 750 | 2000 | 2.60 | 10,000 | 11 | NA | | 0.19 | 86 | 10.62 |
| LTU-4 | 750 | 2000 | 2.60 | 10,000 | 14 | NA | | 0.24 | 83 | 10.40 |
| LTU-5 | 750 | 2000 | 2.90 | 10,000 | 21 | NA | | 0.23 | 84 | 10.22 |
| LTU-6 | 750 | 2000 | 2.90 | 10,000 | 27.5 | NA | | 0.24 | 83 | 9.81 |
| LTU-7 | 750 | 2000 | 2.90 | 10,000 | 34 | NA | | 0.33 | 76 | 10.16 |
| LTU-8 | 750 | 2000 | 4.00 | 10,000 | 46 | NA | | 0.39 | 72 | 9.64 |
| LTU-9 | 750 | 2000 | 3.43 | 10,000 | 50 | NA | | 0.39 | 72 | 9.75 |
| LTU-10 | 750 | 2000 | 3.43 | 10,000 | 62 | NA | | 0.40 | 71 | 9.83 |
| LTU-11 | 750 | 2000 | 4.33 | 10,000 | 74 | NA | | 0.29 | 79 | 9.87 |
| LTU-12 | 750 | 2000 | 3.55 | 10,000 | 86 | NA | | 0.36 | 74 | 9.83 |
| LTU-13 | 750 | 2000 | 3.08 | 10,000 | 97 | NA | | 0.48 | 66 | 9.69 |
| LTU-14 | 750 | 2000 | 2.50 | 10,000 | 110 | NA | | 0.48 | 66 | 9.11 |

a. This was the temperature at the outer wall of the reactor. The temperature at the center of the catalyst bed was 10-25F higher.

b. This is a volume hourly space time (volume of catalyst/volume of oil per hour).

c. Total hours which the catalyst has been contacted with oil at reaction temperature.

d. Percent of sulfur, nitrogen or hydrogen in liquid product.

e. % Removal = 100 x (fraction in feed less fraction in product)/(fraction in feed).

## TABLE IX

## RESULTS FROM RUN LTI IWTH AMOCAT 1C CATALYST

## FEEDSTOCK: 30 wt% SRC/PROCESS SOLVENT

| Sample Number | Temp[a] (F) | Pressure (psig) | Space Time[b] (Volume Hrly) | Hydrogen (SCF/BBL) | Hours[c] on oil | wt%S[d] | wt%S[e] Removal | wt%N[d] | wt%N[e] Removal | wt%H[d] |
|---|---|---|---|---|---|---|---|---|---|---|
| Feed | | | | | | 0.50 | | 1.40 | | 6.73 |
| LTI-1 | 750 | 2000 | 4.00 | 10,000 | 2 | NA | | NA | | NA |
| LTI-2 | 750 | 2000 | 4.00 | 10,000 | 6 | NA | | 0.32 | 77 | 10.52 |
| LTI-3 | 750 | 2000 | 4.00 | 10,000 | 12 | NA | | 0.40 | 71 | 10.25 |
| LTI-4 | 750 | 2000 | 2.30 | 10,000 | 21 | NA | | 0.64 | 54 | 9.94 |
| LTI-5 | 750 | 2000 | 2.60 | 10,000 | 33 | NA | | 0.59 | 58 | 9.97 |
| LTI-6 | 750 | 2000 | 2.60 | 10,000 | 45 | NA | | 0.55 | 61 | 9.73 |
| LTI-7 | 750 | 2000 | 2.50 | 10,000 | 57 | NA | | 0.59 | 58 | 9.62 |
| LTI-8 | 750 | 2000 | 2.50 | 10,000 | 69 | NA | | 0.60 | 57 | 9.67 |
| LTI-9 | 750 | 2000 | 2.40 | 10,000 | 81 | NA | | 0.65 | 53 | 9.72 |
| LTI-10 | 750 | 2000 | 2.50 | 10,000 | 93 | NA | | 0.56 | 60 | 9.69 |

a. This was the temperature at the outer wall of the reactor. The temperature at the center of the catalyst bed was 10-25F higher.
b. This is a volume hourly space time (volume of catalyst/volume of oil per hour).
c. Total hours which the catalyst has been contacted with oil at reaction temperature.
d. Percent of sulfur, nitrogen or hydrogen in liquid product.
e. % Removal = 100 x (fraction in feed less fraction in product)/(fraction in feed).

## TABLE X

## RESULTS FROM RUN LTV WITH SHELL 324 CATALYST

FEEDSTOCK: 30 wt% SRC/PROCESS SOLVENT

| Sample Number | Temp[a] (F) | Pressure (psig) | Space Time[b] (Volume Hrly) | Hydrogen (SCF/BBL) | Hours[c] on oil | wt%S[d] | wt%S[e] Removal | wt%N[d] | wt%N[e] Removal | wt%H[d] |
|---|---|---|---|---|---|---|---|---|---|---|
| Feed | | | | | | 0.50 | | 1.40 | | 6.73 |
| LTV-1 | 750 | 2000 | 2.50 | 10,000 | 2 | NA | | NA | | NA |
| LTV-2 | 750 | 2000 | 2.50 | 10,000 | 6 | NA | | 0.38 | 73 | 10.77 |
| LTV-3 | 750 | 2000 | 2.50 | 10,000 | 10 | NA | | 0.42 | 70 | 10.90 |
| LTV-4 | 750 | 2000 | 2.50 | 10,000 | 19 | NA | | 0.47 | 66 | 10.47 |
| LTV-5 | 750 | 2000 | 3.43 | 10,000 | 32 | NA | | 0.37 | 74 | 10.40 |
| LTV-6 | 750 | 2000 | 2.79 | 10,000 | 43 | NA | | 0.42 | 70 | 10.30 |
| LTV-7 | 750 | 2000 | 3.43 | 10,000 | 55 | NA | | 0.39 | 72 | 9.92 |
| LTV-8 | 750 | 2000 | 2.16 | 10,000 | 67 | NA | | 0.58 | 59 | 9.83 |
| LTV-9 | 750 | 2000 | 2.50 | 10,000 | 79 | NA | | 0.54 | 61 | 9.78 |
| LTV-10 | 750 | 2000 | 2.50 | 10,000 | 91 | NA | | 0.50 | 64 | 9.68 |
| LTV-11 | 750 | 2000 | 2.50 | 10,000 | 97 | NA | | 0.52 | 63 | 9.56 |

a. This was the temperature at the outer wall of the reactor. The temperature at the center of the catalyst bed was 10-25F higher.
b. This is a volume hourly space time (volume of catalyst/volume of oil per hour).
c. Total hours which the catalyst has been contacted with oil at reaction temperature.
d. Percent of sulfur, nitrogen or hydrogen in liquid product.
e. % Removal = 100 x (fraction in feed less fraction in product)/(fraction in feed).

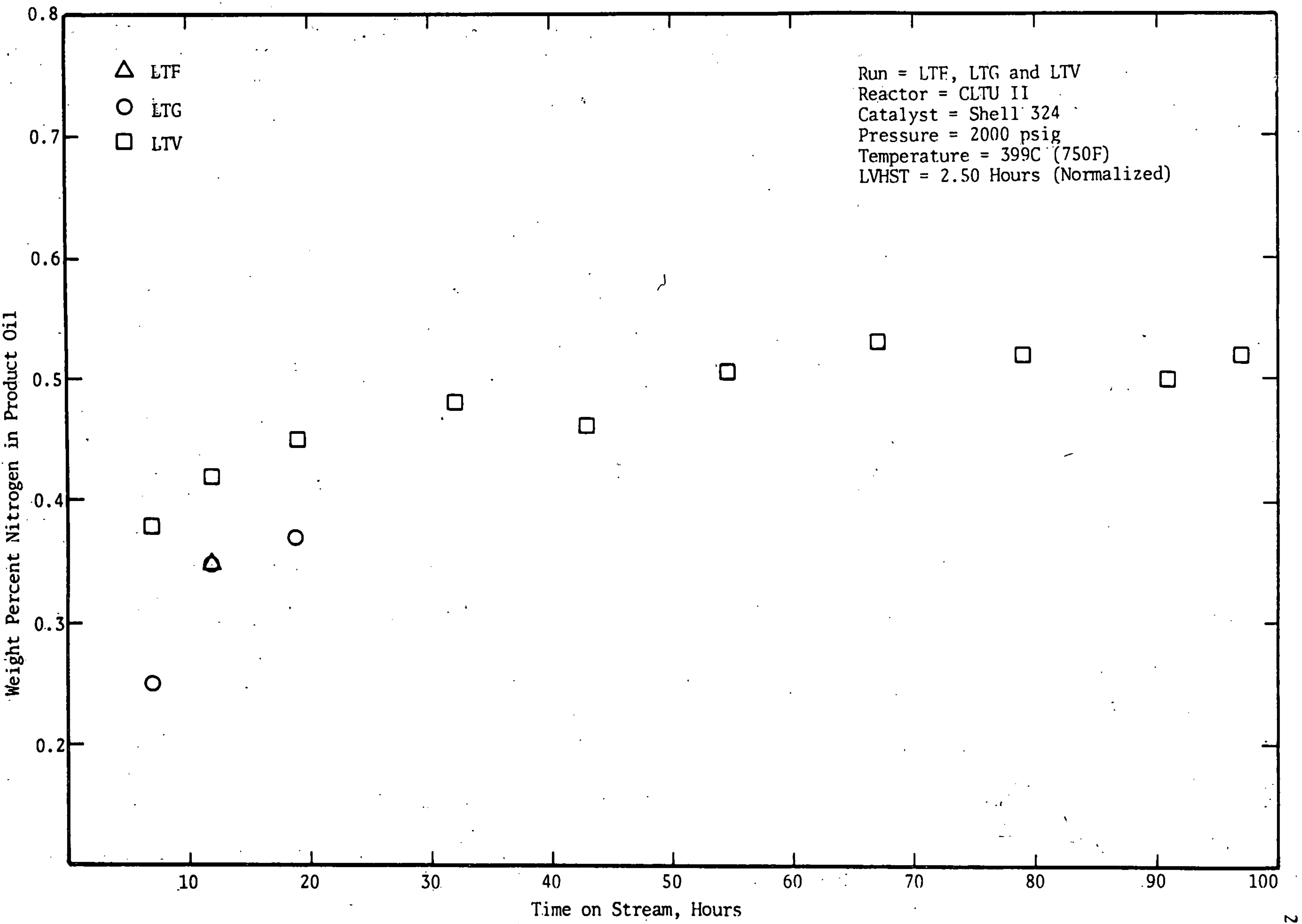

Figure 3. Hydrodenitrogenation Activity Response, Runs LTF, LTG and LTV

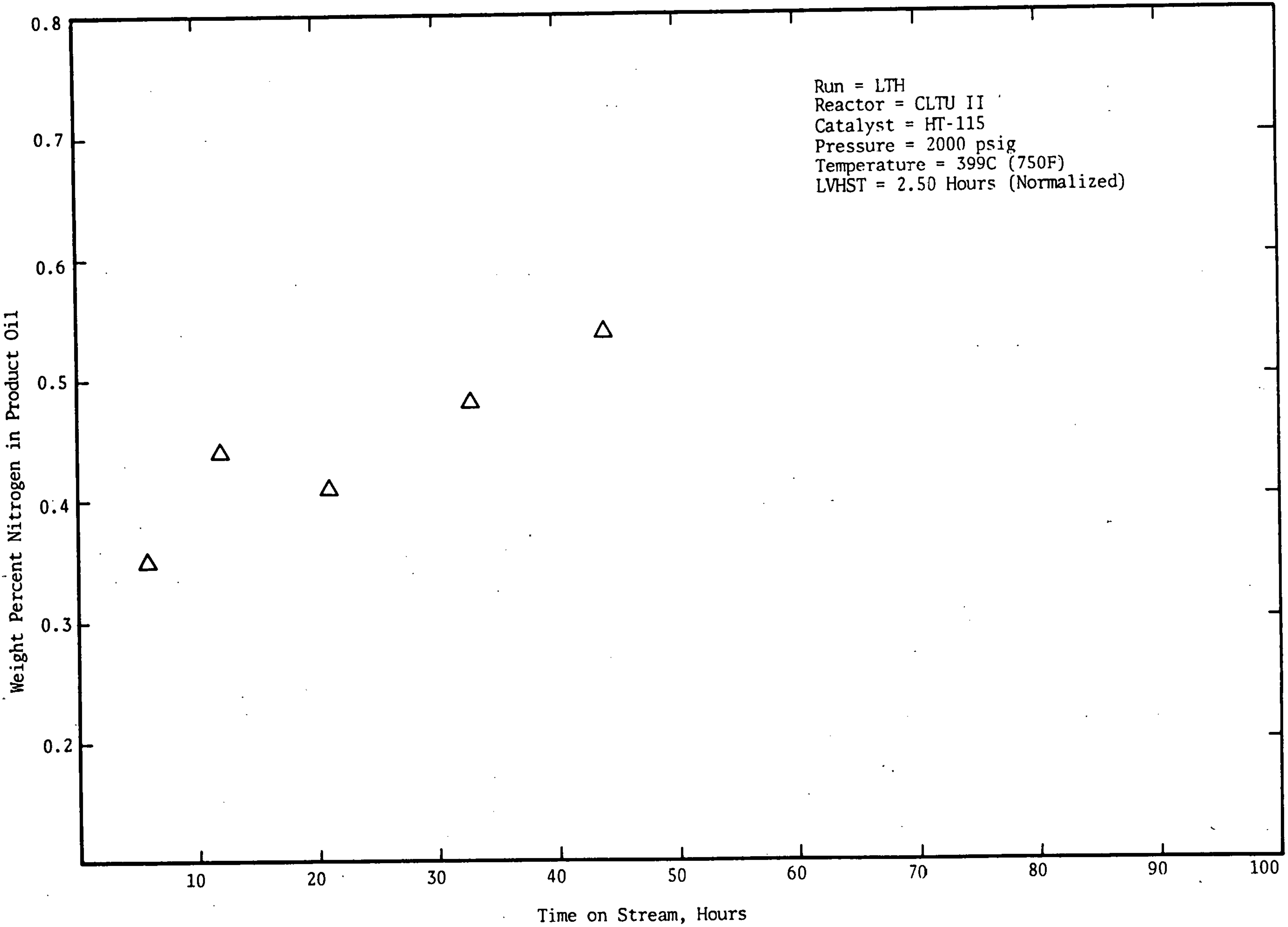

Figure 4. Hydrodenitrogenation Activity Response, Run LTH

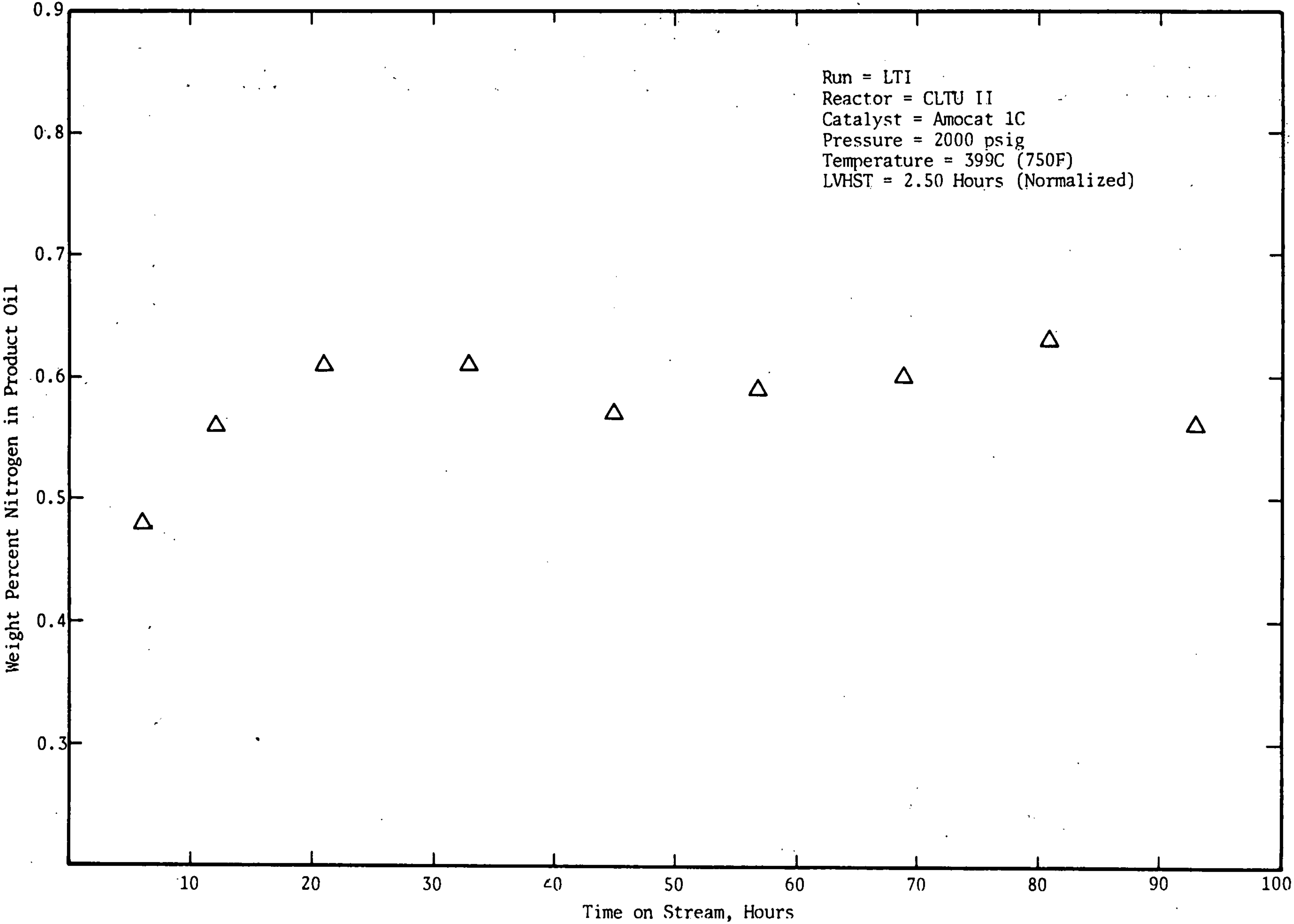

Figure 5. Hydrodenitrogenation Activity Response, Run LTI

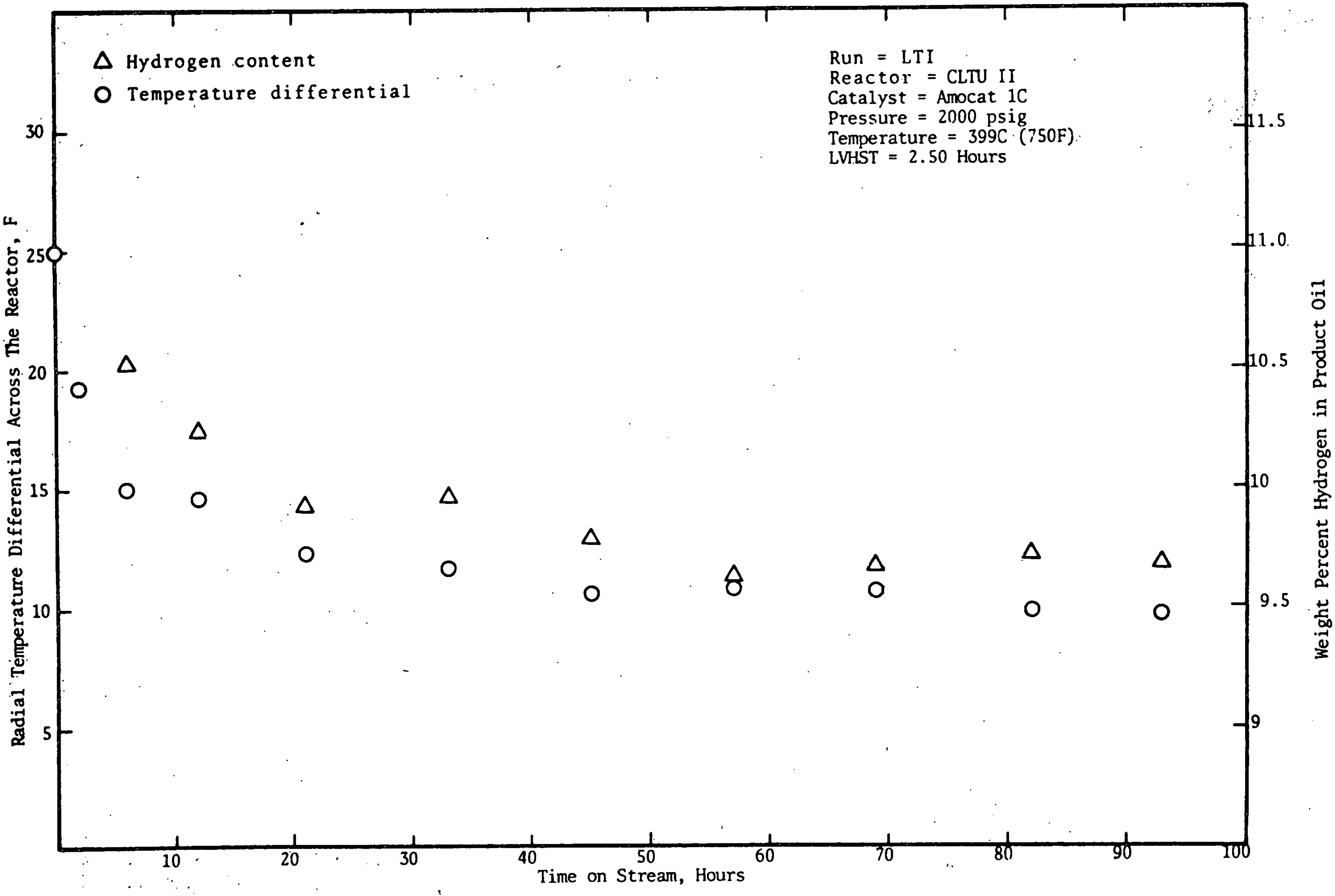

Figure 6. Temperature Differential and Hydrogen Content vs. Time on Stream, Run LTI

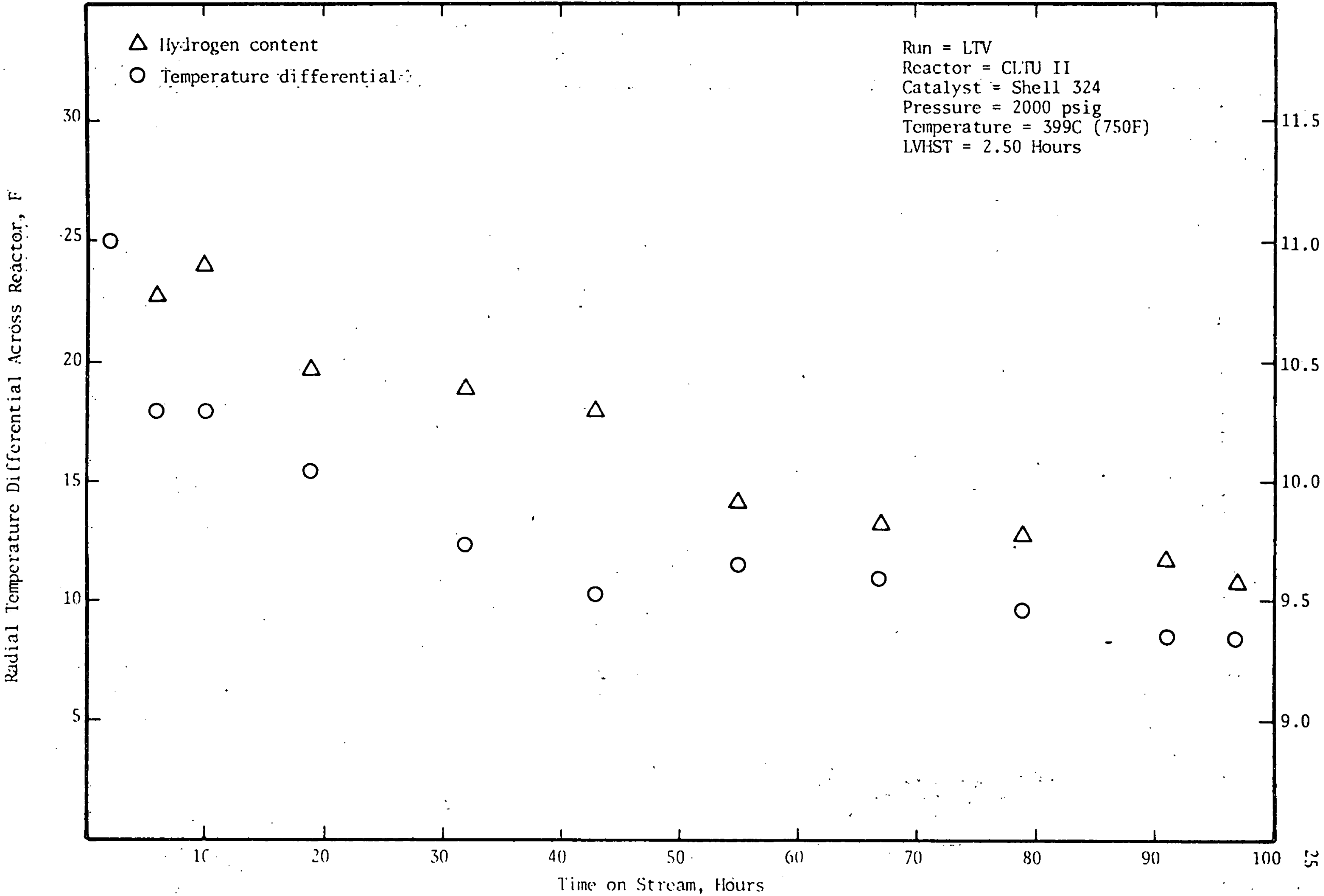

Figure 7. Temperature Differential and Hydrogen Content vs. Time on Stream for Run LTV

previously.* In Run LTB, essentially no deactivation was observed during the entire 261 hours on oil. In contrast, the typical ΔT observed in most previous runs using lighter feedstocks has been only 3 to 5F, however, less active catalysts were used.

## Results of Distillations

Selected samples were distillated for boiling point distributions, and the elemental compositions in both distillate and residual fractions were analyzed. The results are shown in Tables XI to XIII. Details for the Runs LTD, LTE and LTB which used 30 wt% SRC/creosote oil and EDS process oil as feedstocks were reported previously.* Not surprisingly, the residual fractions contain most of the refractory heteroatoms.

## Conclusions

1. The reactor exit and separation system was modified to overcome the plugging problems.
2. Six experimental runs were made during this reporting quarter. Two runs were made with the newly modified system and without serious plugging problem.
3. The commercial NiMo supported catalysts with large micropore diameters usually contain high percentage of silica (10-20%).
4. The use of process solvent oil instead of creosote oil as solvent in hydrotreating SRC offered no advantage in terms of reactor solids formation. However, process solvent was derived from a coal liquefaction process and will still be used in the future runs.
5. On a volume basis, Shell 324 catalyst has higher initial activity than HT 115 and Amocat 1C. However, Shell 324 has a higher bulk reactor compact density than the other catalysts.
6. The catalyst activities decayed rapidly in the first 30 hours on oil and than demonstrated a reduced decay rate.
7. The temperature differential across the reactor radius decreased with time on oil and correlated with the hydrotreating activity response pattern.

## Work Forecast

During the coming quarter, work will be done to get the oil flow rate better controlled. One or more experimental runs of 100 hours

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*Quarterly Report for the period October 1 - December 31, 1980, DE-14576-5.

and less will be made using Shell 324 NiMo supported catalyst and 30 wt% SRC/process solvent as feedstock. These runs will be part of a series investigation of short-term catalyst decaying mechanisms. The properties of the spent catalysts will be analyzed.

## TABLE XI

## PROPERTIES OF FEEDSTOCK AND PRODUCTS OF RUNS LTF AND LTG

| Sample | LTF,G Feed[a] | LTG-3 | LTF-3 |
|---|---|---|---|
| Catalyst |  | Shell 324 | Shell 324 |
| Temperature ,F |  | 750 | 800 |
| Pressure ,psig |  | 2000 | 2000 |
| Space time , LVHST |  | 2.50 | 2.26 |
| Time on oil , Hrs |  | 12 | 12 |
| Total liquid density @ 70F,gm/ml | 1.129 | 0.945 | 0.961 |
| Normal boiling point[b], F |  |  |  |
| IBP | - | 284 | 274 |
| 5 vol. % | 494 | - | - |
| 10 | 522 | 435 | 430 |
| 20 | - | 486 | 483 |
| 30 | - | 510 | 513 |
| 40 | 607 | 537 | 545 |
| 50 | - | 571 | 581 |
| 60 | 714 | 613 | 631 |
| 70 | 813 | 671 | 722 |
| 80 | - | 796 | - |
| 90 | - | - | - |
| End point | 850 | 850 | 850 |
| Recovery, wt% | 67 | 80 | 76 |
| Residue, wt% | 32 | 17 | 17 |
| Loss, wt% | 1 | 3 | 7 |
| Elemental composition, wt% |  |  |  |
| Total liquid |  |  |  |
| C | 87.25 | 86.68 | 87.96 |
| H | 6.73 | 10.00 | 9.87 |
| N | 1.40 | 0.35 | 0.38 |
| S | 0.50 | 0.02 | 0.04 |
| H/C atom | 0.93 | 1.38 | 1.35 |
| Ash | 0.097 | - | - |
| $850F^+$ |  |  |  |
| C | 87.91 | 89.85 | 89.70 |
| H | 5.41 | 7.62 | 7.10 |
| N | 2.27 | 1.08 | 1.16 |
| S | 0.65 | 0.10 | 0.14 |
| H/C atom | 0.74 | 1.02 | 0.95 |
| $850F^-$ |  |  |  |
| C | 87.92 | 88.56 | 86.01 |
| H | 7.51 | 10.41 | 10.12 |
| N | 0.88 | 0.08 | 0.15 |
| S | 0.31 | 0.00 | 0.00 |
| H/C atom | 1.03 | 1.41 | 1.41 |

a. A mixture of 30 wt% SRC-I in 70 wt% process solvent

b. Determined from ASTM D1160 at 20 mm Hg vacuum.

## TABLE XII

## PROPERTIES OF FEEDSTOCK AND PRODUCTS OF RUNS LTD AND LTE

| Sample | LTC,D,E Feed[a] | LTD-3 | LTE-3 |
|---|---|---|---|
| Catalyst | | Shell 324 | Shell 324 |
| Temperature, F | | 750 | 700 |
| Pressure, psig | | 2000 | 2000 |
| Space time, LVHST | | 1.90 | 1.90 |
| Time on oil, Hrs | | 12 | 12 |
| Total liquid density @ 70F, gm/ml | 1.129 | 0.965 | 1.010 |
| Normal boiling point[b], F | | | |
| IBP | 424 | 279 | - |
| 5 vol. % | 473 | - | - |
| 10 | 488 | 421 | 448 |
| 20 | 531 | 462 | 480 |
| 30 | 596 | 501 | 539 |
| 40 | 640 | 545 | 584 |
| 50 | - | 586 | 619 |
| 60 | 737 | 629 | 667 |
| 70 | 816 | 691 | 737 |
| 80 | - | 850 | |
| 90 | | | |
| End point | 850 | 850 | 850 |
| Recovery, wt% | 67 | 78 | 74 |
| Residue, wt% | 32 | 17 | 23 |
| Loss, wt% | 1 | 5 | 3 |
| Elemental composition, wt% | | | |
| Total liquid | | | |
| C | 90.70 | 88.03 | 89.65 |
| H | 6.02 | 9.67 | 8.71 |
| N | 1.25 | 0.30 | 0.60 |
| S | 0.54 | 0.04 | 0.08 |
| H/C atom | 0.80 | 1.32 | 1.17 |
| Ash | 0.073 | | |
| 850 F$^+$ | | | |
| C | 87.09 | 87.02 | 87.45 |
| H | 5.46 | 6.95 | 6.64 |
| N | 2.14 | 1.30 | 1.68 |
| S | 0.55 | | |
| H/C atom | 0.75 | 0.96 | 0.91 |
| 850 F$^-$ | | | |
| C | 90.54 | 89.48 | 89.96 |
| H | 6.34 | 10.42 | 9.50 |
| N | 0.86 | 0.07 | 0.24 |
| S | 0.52 | 0.00 | 0.00 |
| H/C atom | 0.84 | 1.40 | 1.27 |

a. A mixture of 30 wt% SRC-I in 70 wt% Creosote oil.
b. Determined from ASTM D1160 20 mm Hg vacuum.

## TABLE XIII

## PROPERTIES OF FEEDSTOCK AND PRODUCTS OF RUN LTB

| Sample number | LTB-Feed[a] | LTB-3 | LTB-20 | LTB-25 |
|---|---|---|---|---|
| Catalyst | | Shell 324 | Shell 324 | Shell 324 |
| Temperature, F | | 750 | 750 | 800 |
| Pressure, psig | | 2000 | 2000 | 2000 |
| Space time, LVHST | | 2.26 | 2.26 | 2.26 |
| Time on oil, Hrs. | | 12 | 201 | 261 |
| Total Liquid density @ 70F, gm/mℓ | 1.050 | 0.925 | 0.935 | 0.901 |
| Normal boiling point[b], F | | | | |
| IBP | 411 | 310 | 279 | 268 |
| 5 vol. % | 435 | - | 402 | 378 |
| 10 | 448 | 408 | 426 | 400 |
| 20 | 473 | 443 | 456 | 438 |
| 30 | 541 | 480 | 490 | 464 |
| 40 | 610 | 522 | 533 | 501 |
| 50 | 731 | 566 | 577 | 547 |
| 60 | 843 | 629 | 629 | 590 |
| 70 | - | 706 | 691 | 640 |
| 80 | - | 798 | 763 | 702 |
| 90 | - | - | 850 | 775 |
| End point | 850 | 850 | 850 | 850 |
| Recovery, wt% | 56 | 83 | 88 | 94 |
| Residue, wt% | 43 | 15 | 10 | 2 |
| Loss, wt% | 1 | 2 | 2 | 4 |
| Elemental composition, wt% | | | | |
| Total liquid | | | | |
| C | 88.21 | 88.71 | 89.28 | 89.26 |
| H | 7.66 | 11.36 | 11.18 | 11.26 |
| N | 0.72 | 0.14 | 0.10 | 0.00 |
| S | 0.70 | 0.00 | 0.00 | 0.00 |
| H/C atom | 1.04 | 1.54 | 1.50 | 1.51 |
| Ash | 0.086 | | | |
| 850 $F^+$ | | | | |
| C | 85.89 | 90.16 | 89.34 | 89.54 |
| H | 6.63 | 8.70 | 9.58 | 10.15 |
| N | 1.40 | 0.74 | 0.46 | 0.13 |
| S | 1.29 | 0.03 | 0.00 | 0.00 |
| H/C atom | 0.93 | 1.16 | 1.29 | 1.36 |
| 850 $F^-$ | | | | |
| C | 89.16 | 87.98 | 87.77 | 89.45 |
| H | 8.85 | 12.14 | 11.81 | 11.72 |
| N | 0.36 | 0.10 | 0.10 | 0.00 |
| S | 0.12 | 0.00 | 0.00 | 0.00 |
| H/C atom | 1.19 | 1.66 | 1.61 | 1.57 |

a. A mixture of 40 wt% EDS vacuum gas oil/EDS raw solvent.
b. Determined from ASTM D-1160 at 20 mm Hg vacuum.

## Task 2-c. Catalyst Regeneration (A. N. Tayrien)

In the past quarter, samples from run CRS (II) and CDS (I) were analyzed for sulfur and nitrogen. Also, the catalyst from run CRS (II) was regenerated by controlled oxidation and prepared for a third and final run to be completed later. Conditions for runs CRS and CDS were identical: 427C (800F), 1500 psig nominal pressure, 2.75 hours space time (liquid hourly volume basis). Run durations were 101 and 103 hours, respectively. The fresh and regenerated catalyst was HDN-30 (Ni-Mo-$Al_2O_3$)*. Feedstock consisted of 10 vol. % Synthoil II liquid with 90 vol. % raw anthracene oil. Elemental analysis of the feed is shown in Table XIV.

Nitrogen removal from the feed oil was found to be in the range of 53.8% to 91.3%, and 56.6% to 93.4% for runs CDS and CRS, respectively as shown in Table XVI and XVII. The catalyst was found to lose approximately 33% of its surface area through coking and inorganics deposition at the conclusion of each experimental run, Table XV (82 vs 122 $m^2/g$). Upon regeneration the catalyst regained essentially all of its surface area, (118 vs 122 $m^2/g$ or 96.7% recovery). Sulfur removal from the feedstock was found to be in the range of 75.3% to 83.9% for run CDS and 76.7% to 97.1% removal for run CRS.

The regenerated catalyst performed as well, if not better than the fresh catalyst with respect to sulfur and nitrogen removal, Figure 8. Only one more run is planned on this catalyst charge because of insufficient amount of catalyst remaining, from losses from run to run and with each regeneration.

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*Catalyst properties found in Quarterly Report for period April 1 - June 30, 1980, DE-14876-3.

## TABLE XIV

## FEED OIL PROPERTIES

## 10 VOL.% SYNTHOIL II PLUS 90 VOL.% RAW ANTHRACENE OIL

| ELEMENT | wt.% |
|---|---|
| Carbon | 90.81 |
| Hydrogen | 5.41 |
| Nitrogen | 1.26 |
| Sulfur | 0.96 |
| Ash | 0.20 |

## TABLE XV

## CATALYST SURFACE AREAS, HDN-30

## SURFACE AREA ($m^2/g$)

| Fresh | CDS Spent | CDS Regenerated | CRS Spent | CRS Regenerated |
|---|---|---|---|---|
| 122 (160)* | 82.4 | 121 | 82.4 | 118 |

*Vendor's data.

## TABLE XVI

## RESULTS FROM RUN CRS WITH HDN-30 CATALYST

FEEDSTOCK: 90 VOL.% RAW ANTHRACENE OIL PLUS 10 VOL.% SYNTHOIL II

| Sample Number | Temp[a] (F) | Pressure (psig) | Space Time[b] (Volume Hrly) | Hydrogen (SCF/BBL) | Hours[c] on oil | wt%S[d] | wt%S[e] Removal | wt%N[d] | wt%N[e] Removal | wt%H[d] |
|---|---|---|---|---|---|---|---|---|---|---|
| Feed | | | | | | .963 | | 1.26 | | NA |
| CRS-1 | 800 | 1500 | 2.75 | 6740 | 10 | .196 | 79.6 | .547 | 56.6 | NA |
| CRS-2 | 800 | 1500 | 2.75 | 6740 | 20 | .0341 | 96.5 | .120 | 90.5 | NA |
| CRS-3 | 800 | 1500 | 2.75 | 6740 | 30 | .0283 | 97.1 | .0995 | 92.1 | NA |
| CRS-4 | 800 | 1500 | 2.75 | 6740 | 40 | .0497 | 94.8 | .0827 | 93.4 | NA |
| CRS-5 | 800 | 1500 | 2.75 | 6740 | 50 | .0346 | 96.4 | .162 | 87.1 | NA |
| CRS-6 | 800 | 1500 | 2.75 | 6740 | 60 | .0524 | 94.5 | .193 | 84.7 | NA |
| CRS-7 | 800 | 1500 | 2.75 | 6740 | 70 | .0749 | 92.2 | .271 | 78.5 | NA |
| CRS-8 | 800 | 1500 | 2.75 | 6740 | 80 | .107 | 88.9 | .155 | 87.7 | NA |
| CRS-9 | 800 | 1500 | 2.75 | 6740 | 90 | .102 | 89.4 | .305 | 75.8 | NA |
| CRS-10 | 800 | 1500 | 2.75 | 6740 | 100 | .0791 | 91.8 | .415 | 67.1 | NA |
| CRS-11 | 800 | 1500 | 2.75 | 6740 | 101 | .224 | 76.7 | .390 | 69.0 | NA |

---

a. Nominal reactor temperature.
b. This is a volume hourly space time (volume of catalyst/volume of oil per hour).
c. Total hours which the catalyst has been contacted with oil at reaction temperature.
d. Percent of sulfur, nitrogen or hydrogen in liquid product.
e. % Removal = 100 x (fraction in feed less fraction in product)/(fraction in feed).

# TABLE XVII

## RESULTS FROM RUN CDS WITH HDN-30 CATALYST

FEEDSTOCK: 90 VOL.% RAW ANTHRACENE OIL PLUS 10 VOL.% SYNTHOIL II

| Sample Number | Temp[a] (F) | Pressure (psig) | Space Time[b] (Volume Hrly) | Hydrogen (SCF/BBL) | Hours[c] on oil | wt%S[d] | wt%S[e] Removal | wt%N[d] | wt%N[e] Removal | wt%H[d] |
|---|---|---|---|---|---|---|---|---|---|---|
| Feed | | | | | | .963 | | 1.26 | | NA |
| CDS-1 | 800 | 1500 | 2.75 | 6740 | 10 | .238 | 75.3 | .582 | 53.8 | NA |
| CDS-2 | 800 | 1500 | 2.75 | 6740 | 20 | NA | | .226 | 82.1 | NA |
| CDS-3 | 800 | 1500 | 2.75 | 6740 | 30 | NA | | .184 | 85.4 | NA |
| CDS-4 | 800 | 1500 | 2.75 | 6740 | 40 | .159 | 83.5 | .359 | 71.5 | NA |
| CDS-5 | 800 | 1500 | 2.75 | 6740 | 50 | NA | | .307 | 75.6 | NA |
| CDS-6 | 800 | 1500 | 2.75 | 6740 | 60 | NA | | .271 | 78.5 | NA |
| CDS-7 | 800 | 1500 | 2.75 | 6740 | 70 | .155 | 83.9 | .257 | 79.6 | NA |
| CDS-8 | 800 | 1500 | 2.75 | 6740 | 80 | NA | | .144 | 88.6 | NA |
| CDS-9 | 800 | 1500 | 2.75 | 6740 | 90 | NA | | .198 | 84.3 | NA |
| CDS-10 | 800 | 1500 | 2.75 | 6740 | 100 | NA | | .109 | 91.3 | NA |
| CDS-11 | 800 | 1500 | 2.75 | 6740 | 103 | NA | | .156 | 87.6 | NA |

a. Nominal reactor temperature.
b. This is a volume hourly space time (volume of catalyst/volume of oil per hour).
c. Total hours which the catalyst has been contacted with oil at reaction temperature.
d. Percent of sulfur, nitrogen or hydrogen in liquid product.
e. % Removal = 100 x (fraction in feed less fraction in product)/(fraction in feed).

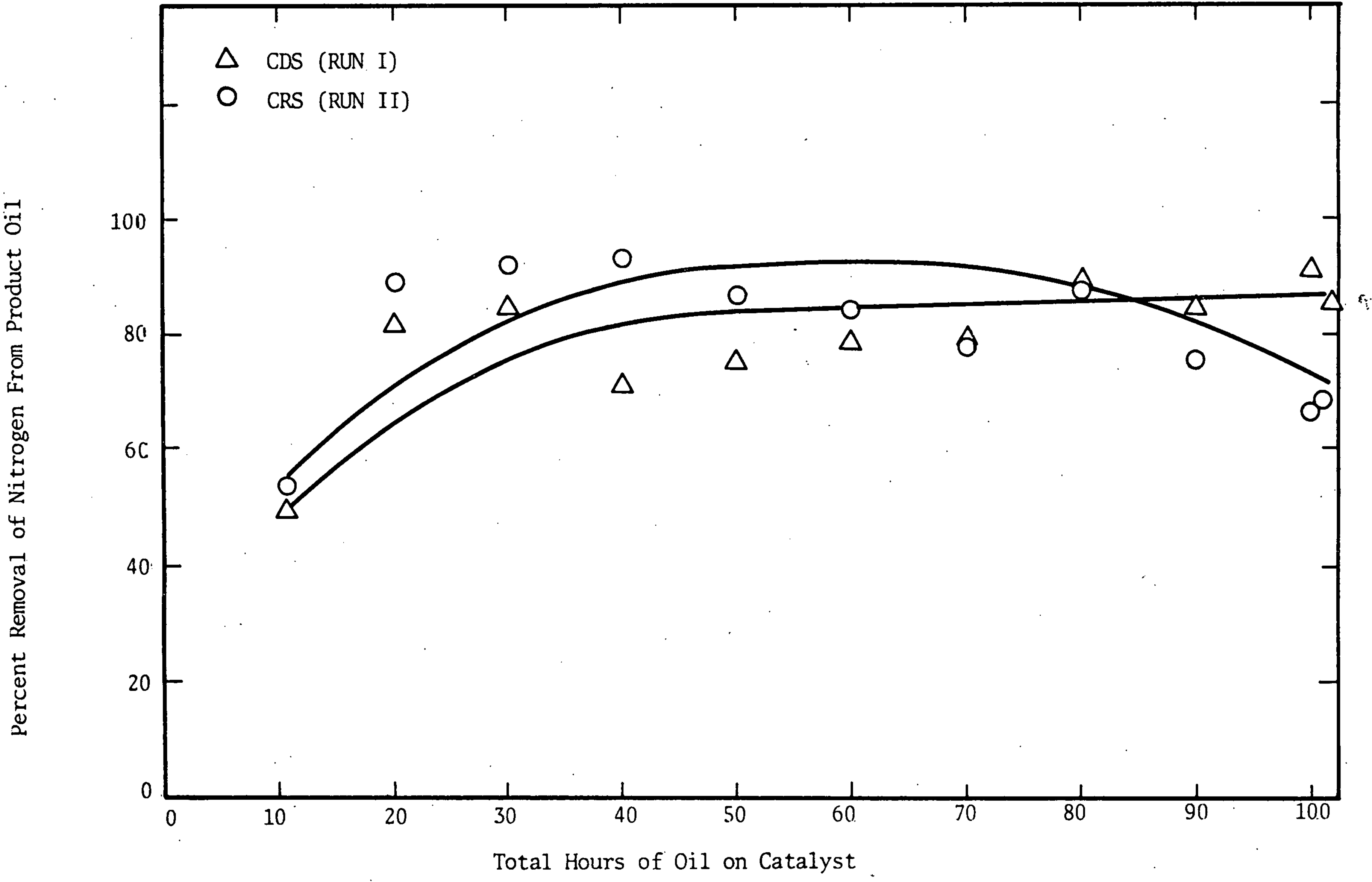

Figure 8. Nitrogen Content of Product Oil vs. Hours on Oil