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MASTER

CATALYSTS FOR UPGRADING COAL-DERIVED LIQUIDS

Quarterly Report for the Period
July 1 - September 30, 1980

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DISCLAIMER

CATALYSTS FOR UP-GRADING COAL DERIVED LIQUIDS
(DE-14876-4)

ABSTRACT

Data on the HDN-30 and the Ketjenfine-124 catalysts not previously reported are given. These data show pore properties and reveal that the Ketjenfine catalyst has a most frequent pore diameter at about 50 angstroms and that of the HDN-30 catalyst at about 80 angstroms. A comparative figure revealed that no difference existed in nitrogen removal for over 120 hours of catalyst-oil contact for these two catalysts and for a reactor bed consisting of a 50 volume percent mixture of each.

The Catalyst Life Test Unit was modified to improve the feed control. Two high pressure feed tanks were installed which allow improved feed-pump performance while operating with preheated, heavy feedstocks. Analytical methods were developed for the scanning electron microscope and atomic absorption to assess more detailed analysis of catalysts properties and metals content of the oils.

One experimental run was conducted using the HDN-30($Ni-Mo-Al_2O_3$) catalyst and a feedstock consisting of 10% (vol) Synthoil II and 90% Raw Anthracene Oil. This experiment was conducted at nominal conditions of 1500 psig, 427 C and with a liquid volume hourly space time of 2.74 hours. The run duration was 103 hours of liquid-catalyst contact. Only partial results were available; all will be given in the subsequent quarterly report. Sulfur removal was noted to be 75-83%.

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 liquids.

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.

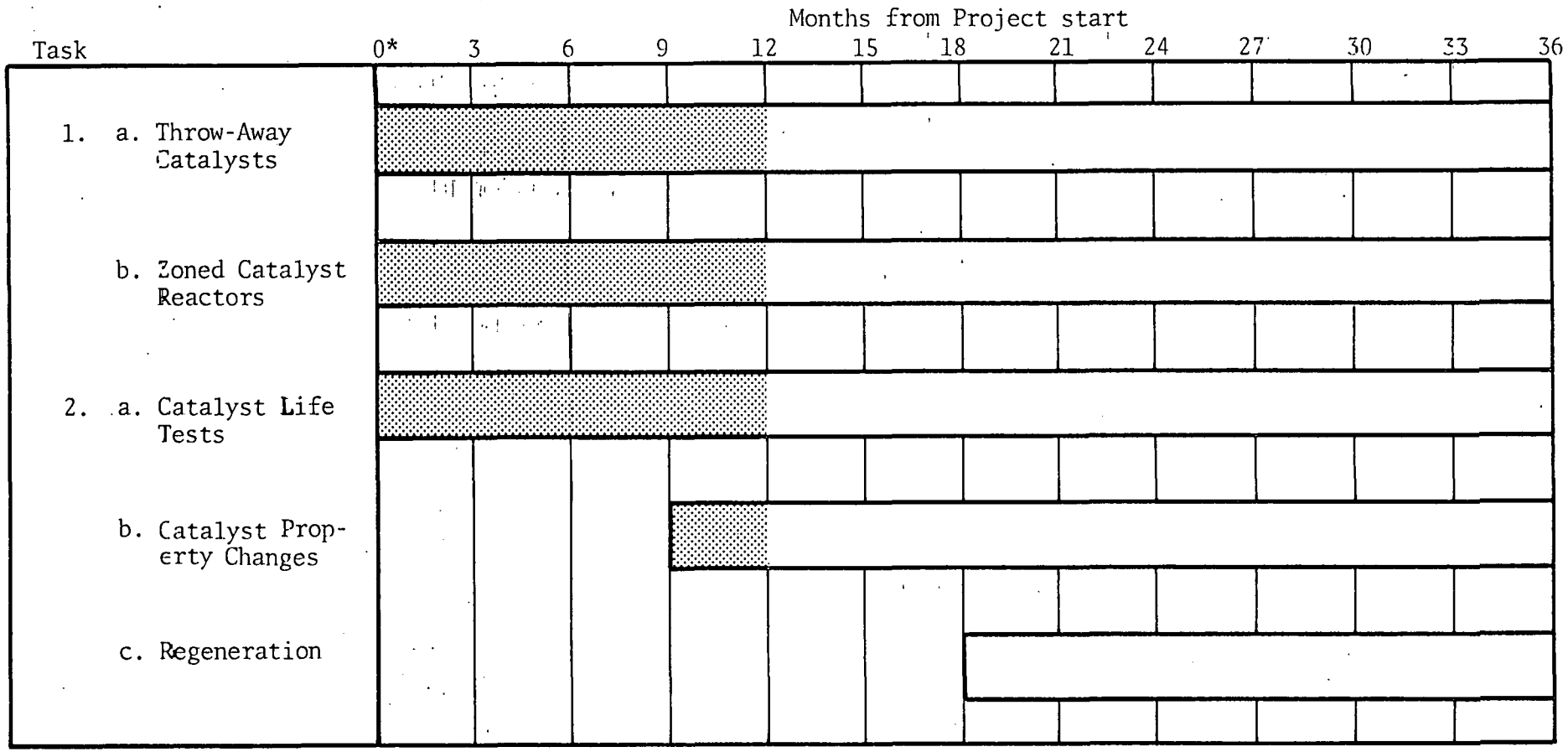
Task 2-b. Changes in catalyst properties, including surface area, pore size distribution, pore volume, and coke and inorganics accumulation shall be measured as a function of coal-liquid contact time.

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 figures, some initial activity has begun in task 2-c.

As of September 30, 1980, 28% of the total budget has been expended ($50,085). This is an expected expenditure rate for the first three quarters of this project.



* Project start date is October 1, 1979

DESCRIPTION OF TECHNICAL PROGRESS

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

Additional data and report (thesis) were prepared on the five runs presented last quarter under this task.

As indicated in the last quarterly report* five experimental runs were conducted in the newly constructed trickle-bed reactor. Two catalysts, HDN-30(Ni-Mo-Al_2O_3) and Ketjenfine-124 (Co-Mo-Al_2O_3), were used separately and in combination as zonal-catalyst beds. Pore structure properties of these two catalyst (not previously reported) are shown in Figures 1 and 2.

Our investigation revealed that the zonal bed combination of Co-Mo-Al_2O_3 and Ni-Mo-Al_2O_3 offered no advantage for hydrodenitrogenation and hydrodesulfurization of Pamco Process Solvent** oil over the single catalyst beds for the following operating conditions:

Temperature	815F (435C)
Pressure	1500 psig
Space Time (vol. Hrly.)	1.02, 2.05, 2.56
Hydrogen Flow	6730 SCF/Bbl

Figure 3 presents a comparison of the weight percent nitrogen in the product oil for the experimental runs ZBB, ZBC, ZBD.

Ni-Mo-Al_2O_3, Co-Mo-Al_2O_3 and their zonal-bed combination indicated significant loss in the activity for nitrogen removal. The catalyst activity is lost during the first 90 hours of oil-catalyst contact. The catalyst deactivation is due largely to carbonaceous deposits (note that the Pamco oil is ash-less).

The EN-1 reactor is presently being improved. Orders for a new temperature controller and recorder have been placed and the present heating system for the reactor is to be modified in the future.

* "Quarterly Report" for the period April 1-June 30, 1980. DE-14876-3

** Table for properties of feedstock present in "Quarterly Report" for the period April 1-June 30, 1980. DE-14876-3

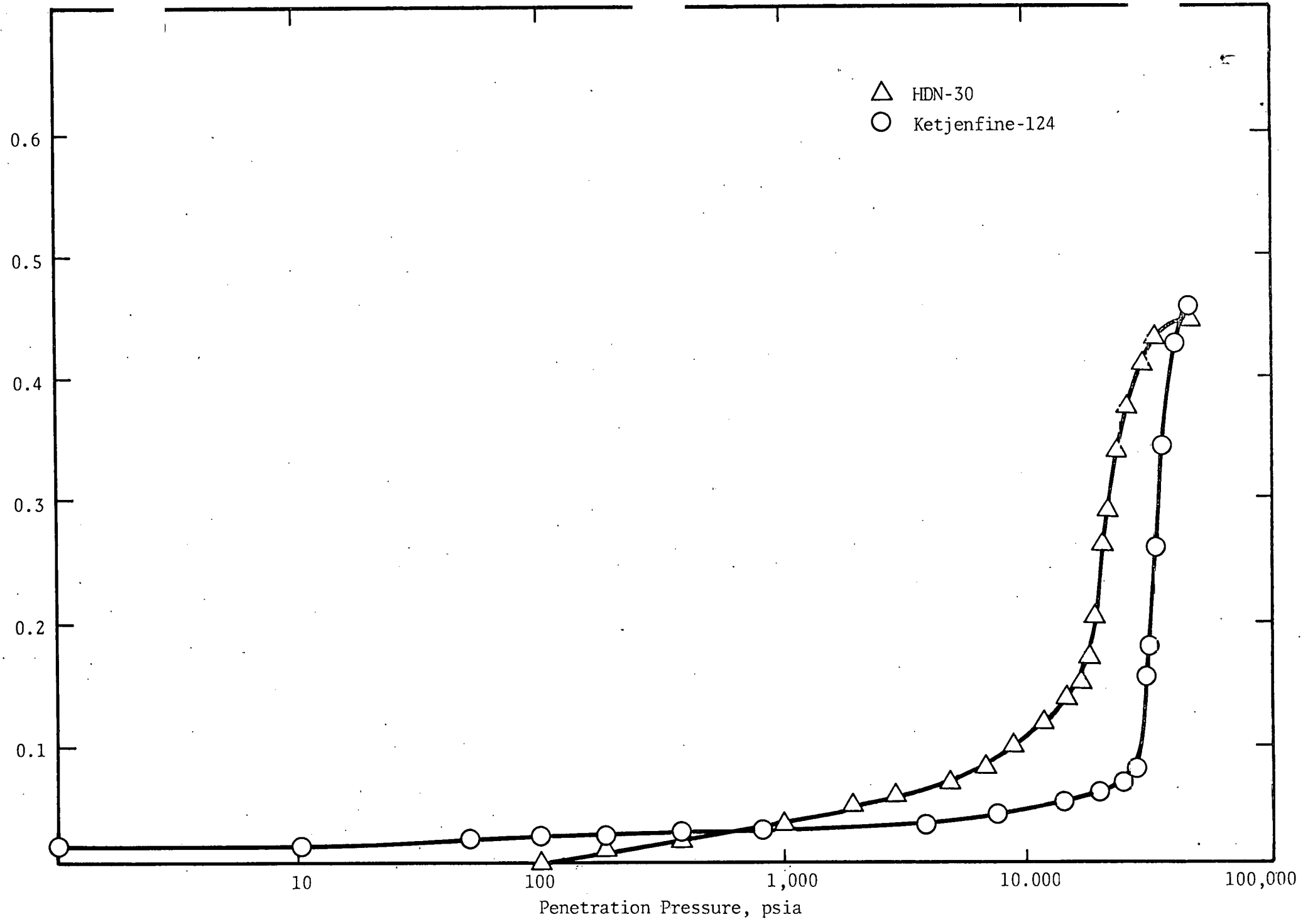


Figure 1. Dependence of Catalyst Pore Volume on Hg Penetration Pressure

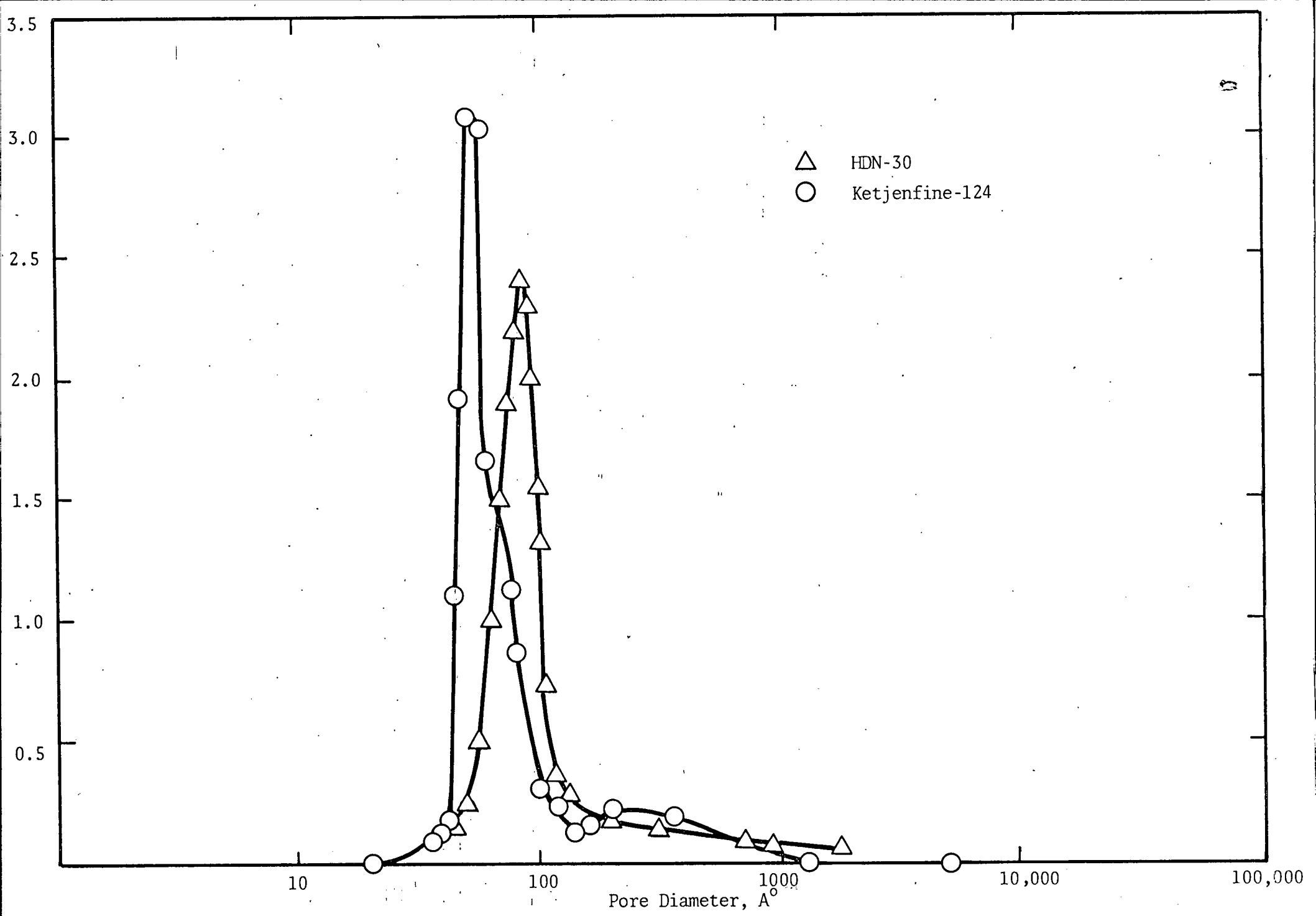


Figure 2. Pore Size Distribution of HDN-30 and Ketjenfine-124 Catalysts

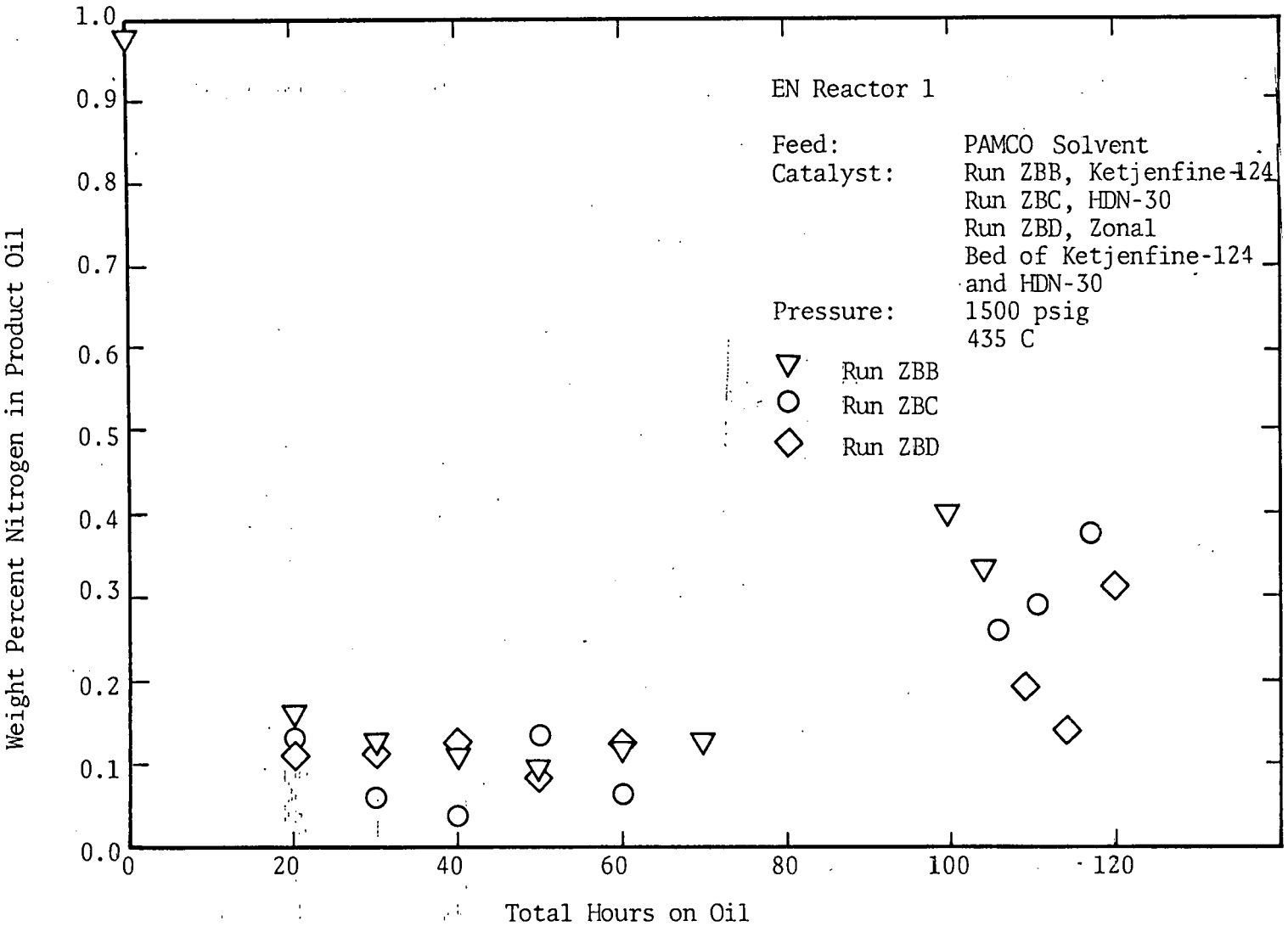


Figure 3. Hydrodenitrogenation Activity Response, Runs ZBB, ZBC and ZBD.

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

In the Catalyst Life Test Unit (CLTU), a major improvement has been made on the oil feed system by installation of two high pressure feed tanks. This new feed system will solve the problem of vapor lock in the metering pump heads when processing preheated, heavy feeds. More stable feed rates are expected with these modifications.

Considerable time was given to preparation and familiarization of analytical methods for catalysts characterization. The use of Scanning Electron Microscopy (SEM) to assess catalyst surfaces and atomic absorption to analyze bulk compositions of catalyst and metals contents in the oils will be used. Preliminary analyses have been made using these instruments.

During the coming quarter, one or more experimental runs of 200 ∿ 300 hours and less will be made using the Shell-324 NiMo/Al catalyst and EDS oil as feedstock. These runs will be part of a series investigation of short-term catalyst decaying mechanisms, and the results will be used as the reference to determine the durations of the succeeding runs.

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

One experimental run (CDS) was conducted in Reactor EN-1. This experiment was designed to obtain data on catalyst deactivation, with follow-up runs to be conducted using the regenerated catalyst from this run. The catalyst, HDN-30(Ni-Mo-Al_2O_3)*, was employed with a feedstock consisting of 10% Vol. Synthoil II and 90% Vol. Raw Anthracene Oil. This experiment was conducted at 1500 psig nominal pressure, 427°C (800°F); and subsequent runs will attempt to duplicate these conditions. Space time was 2.74 hours, liquid volume hourly basis. Run duration was 103 hours of liquid-catalyst contact.

Partial analyses of the feedstock and product oils have been completed and full results will be presented in the next quarterly. Under these experimental conditions, sulfur removal was 75-83%. The catalyst revealed little or no deactivation for sulfur removal during the run.

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