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FOSSIL ENERGY

CATALYSTS FOR UPGRADING COAL-DERIVED LIQUIDS

Quarterly Report for April 1—June 30, 1980

By
Billy L. Crynes

July 15, 1980
Date Submitted

Work Performed Under Contract No. AC01-79ET14876

The Oklahoma State University
School of Chemical Engineering
Stillwater, Oklahoma

U. S. DEPARTMENT OF ENERGY

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PREPARED FOR THE UNITED STATES
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CATALYSTS FOR UP-GRADING COAL DERIVED LIQUIDS
(DE-14876-3)

ABSTRACT

Five experimental runs were conducted in the newly constructed trickle-bed reactor. The experiments were designed to obtain data on zoned catalyst beds. This new reactor system demonstrated satisfactory performance in temperature, pressure and flow control. High desulfurization and denitrogenation were achieved on both catalysts tested at conditions of 815F, 1500 psig. These catalysts were a CoMo/Al and NiMo/Al. Zoned bed of 50-50 volume percent of the two catalysts tested revealed no advantages with respect to desulfurization, denitrogenation and activity decay. The level of nitrogen removal was initially high, but activity decay was significant over the operational interval of 100 hours.

Two experimental runs were completed in the Catalyst Life Test Unit (CLTU) utilizing a liquid containing 50% Synthoil and 50% Raw Anthracene Oil. This fluid has a 0.54 weight percent sulfur and a 1.21 weight percent nitrogen. The catalyst used in this study was a Ni-Mo-Al_2O_3 (Shell 324). The objective of the experiments was to demonstrate the effect of diluting the catalyst bed with a small size inert particle to improve gas-liquid contact and reduce channeling. No difference could be distinguished between the use of particle sizes in the range of 0.25-1.00 mm diameter. One run was terminated prematurely because the small particles plugged the catalyst support screens. Precipitous catalyst activity decay was noted for both nitrogen and sulfur removal.

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 catalysts 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.

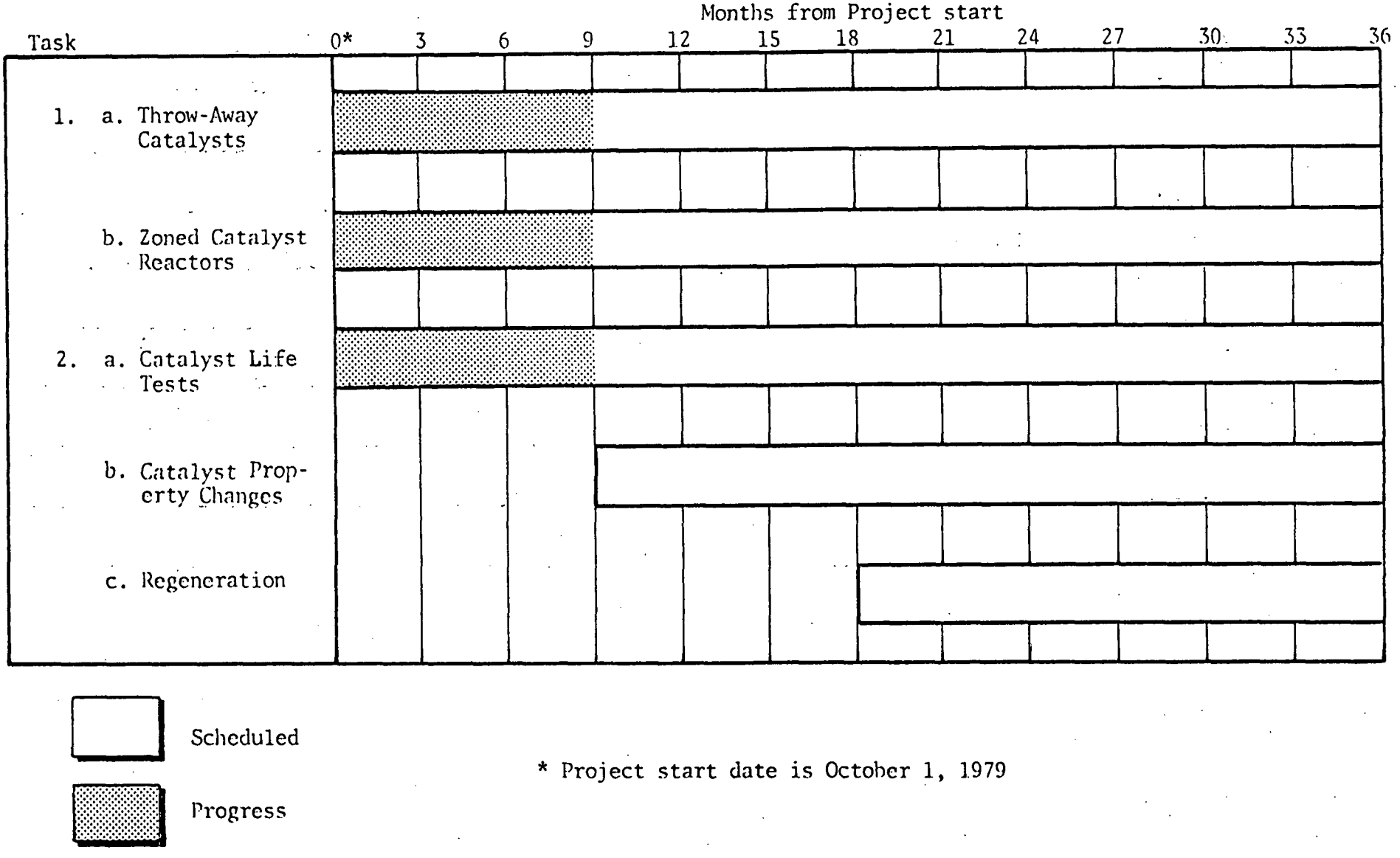
Task 2-c. The Ni-Mo/alumina catalyst tested in Task 2-a shall be regenerated by oxidation, and tested for activity recovery.

SUMMARY OF PROGRESS TO DATE

The following chart summarizes the progress to date. The three tasks (1-A, 1-B and 2-A) show scheduled progress. Although not shown in the figures, some initial activity has begun in task 2-C.

As of June 30, 1980, 15% of the total budget has been expended ($27,309). This is an expected expenditure rate for the first three quarters of this project.

PROGRESS SUMMARY AS OF JUNE 30, 1980



* Project start date is October 1, 1979

DESCRIPTION OF TECHNICAL PROGRESS

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

Five experimental runs were conducted in the newly constructed trickle-bed reactor. The experiments were designed to obtain data on zoned catalyst beds. Two catalysts, HDN-30 (Ni-Mo/Al) and Ketjenfine-124 (Co-Mo/Al), were used separately and in combination as zone beds. A Pamco coal-derived liquid was the feedstock for all the runs (Table I). All experiments were conducted at 1500 psig nominal pressure, the temperature was maintained at 324C (615F) for the first experimental run, subsequent runs were conducted at 435C (815F). Space times from 0.5 to 2.5 hours, volume basis, were employed.

Under the most severe conditions employed, much of the sulfur and nitrogen in the feedstock was removed (70-96+% removal). The catalysts showed some deactivation for nitrogen removal after 100 hours of operation. No loss in sulfur removal activity was observed during the duration of the runs. No advantage was shown in using mixed or zoned beds of the two catalysts relative to single catalyst beds. Details follow.

Run Series ZBA

The objective of this run was to test the newly constructed trickle bed reactor, obtain operational experience and establish reference conditions. Unfortunately a malfunctioning temperature indicator resulted in an undesirably low reaction temperature.

The run conditions were as follows:

Run Series	ZBA
Reactor	EN-1
Catalyst	HDN-30 (Table II)
Feedstock	Pamco Process Solvent (Table I)
Temperature	324C (615F)
Pressure	1500 psig ± 20
Space Time (Volume Hourly)	0.512, 2.048, 1.024 hrs.
Hydrogen flow	6730, 5510, 2525, 3122, 4426 SCF/Bbl

The results from sample analyses are listed in Table III. The ASTM D1160 results are presented in Table VIII. The run duration was 96 hours, and the shut down was scheduled. Excellent temperature control was achieved, primarily due to the lower temperature employed, no hot spots were encountered. Negligible pressure fluctuations were

TABLE I

PROPERTIES OF FEEDSTOCK

Pamco Process Solvent

Composition	Wt%
Carbon	89.08
Hydrogen	7.11
Nitrogen	0.97
Sulfur	0.43
Oxygen	2.41*
Ash	Nil

Boiling Point Data**	
Initial	159C (318F)
10 Vol. %	166C (331F)
20 %	170C (338F)
30 %	181C (358F)
40 %	192C (378F)
50 %	213C (415F)
60 %	230C (446F)
70 %	249C (480F)
80 %	265C (509F)

* By difference

** Determined at 50 mm Hg vacuum

TABLE II

CATALYST PROPERTIES

Catalyst Code	Ketjenfine-124	HDN-30
Manufacturer	Akzo Chemical	American Cynamid
Chemical Composition*, wt%		
MoO_3	11.8	20.5
NiO	--	5.0
CoO	3.93	--
Na_2O	0.09	0.03
SiO_2	1.22	--
SO_4	1.60	0.30
Al_2O_3	81.36**	74.17**
Physical Properties (1/16" extrudes)		
surface area m^2/gm	251	160
pore volume cc/gm	0.52	0.44
Most frequent pore diameter (Å)	84	110

* Vendor's data

**By difference

TABLE III

RESULTS FROM REACTOR EN-1 WITH HDN-30 CATALYST
FEEDSTOCK: PAMCO PROCESS SOLVENT

Sample Number	Temp[a] (°F)	Pressure (psig)	Space Time[b] (Volume hrly)	Hydrogen (SCF/BBL)	Hours[c] on oil	%S[d]	%S[e] Removal	%N[d]	%N[e] Removal	%H[d]
Feed						0.438		0.977		7.110
ZBA-2	615	1500	1.024	6730	15	0.255	43	0.593	37	9.076
ZBA-4	615	1500	1.024	5510	35	0.278	54	0.793	19	8.497
ZBA-6	615	1500	1.024	4592	40	0.235	47	0.829	15	7.950
ZBA-7	615	1500	1.024	5510	43	0.251	44	0.819	16	7.944
ZBA-10	615	1500	2.048	5510	55	0.251	44	0.827	15	7.718
ZBA-13	615	1500	2.048	6730	65	0.257	42	0.857	12	7.360
ZBA-15	615	1500	2.048	6730	70	0.207	54	0.845	14	7.491
ZBA-17	615	1500	0.512	2525	78	0.371	17	0.867	11	7.431
ZBA-18	615	1500	0.512	2525	80	0.309	31	0.925	5	7.340
ZBA-19	615	1500	1.024	3122	84	0.261	37	0.779	20	7.345
ZBA-24	615	1500	1.024	4426	96	0.286	36	0.890	9	8.551

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 conditions.
d. Percent of sulfur, nitrogen, or hydrogen in liquid product.
e. % Removal = 100 (fraction in feed less fraction in product) / (fraction in feed)

encountered throughout the run. Only about one half of the sulfur and 15 to 20% of the nitrogen was removed at these conditions.

Run Series ZBB

This run was conducted to obtain data on nitrogen and sulfur removal by a cobalt-molybdenum catalyst. This run was to serve as reference for further zonal catalyst bed studies.

The run conditions were as follows:

Run Series	ZBB
Reactor	EN-1
Catalyst	Ketjenfine-124 (Table II)
Feedstock	Pamco Process Solvent (Table I)
Temperature	435C (815F)
Pressure	1500 psig ± 20
Space Time (Volume hourly)	2.048, 1.024 hr.
Hydrogen flow	6730 SCF/Bbl

The run was conducted for a period of 104 hours, and the shut down was scheduled. Excellent pressure and gas flow control was achieved; hot spots were encountered throughout the duration of the run.

The samples were analyzed for nitrogen, sulfur and hydrogen, and the results are presented in Table IV. ASTM D1160 results are presented in Table VIII. Rapid nitrogen deactivation was encountered after 90 hours of catalyst-oil contact, slight sulfur deactivation was noted. Maximum nitrogen removal was rather high, 90% at this temperature and pressure, and especially for this CoMo/Al catalyst. Sulfur removal was over 95%, which would be expected.

Run Series ZBC

This run was conducted to obtain data on removal of sulfur and nitrogen by the nickel-molybdenum catalyst. The experiment was also meant to serve as reference for further zonal catalyst bed studies.

The run conditions were as follows:

Run Series	ZBC
Reactor	EN-1
Catalyst	HDN-30 (Table II)
Feedstock	Pamco Process Solvent (Table I)

TABLE IV

RESULTS FROM REACTOR EN-1 WITH KETJENFINE-124 CATALYST
FEEDSTOCK: PAMCO PROCESS SOLVENT

Sample Number	Temp[a] (°F)	Pressure (psig)	Space Time[b] (Volume hrly)	Hydrogen (SCF/BBL)	Hours[c] on oil	%S[d]	%S[e] Removal	%N[d]	%N[e] Removal	%H[d]
Feed						0.438		0.977		7.110
ZBB-2	815	1500	2.048	6730	20	0.048	90	0.161	84	10.439
ZBB-3	815	1500	2.048	6730	30	0.020	96	0.125	87	10.048
ZBB-4	815	1500	2.048	6730	40	0.020	96	0.111	88	9.366
ZBB-5	815	1500	2.048	6730	50	0.032	92	0.090	91	9.986
ZBB-6	815	1500	2.048	6730	60	0.041	91	0.116	88	10.027
ZBB-7	815	1500	2.048	6730	70	0.020	96	0.125	87	9.174
ZBB-8	815	1500	1.024	6730	78	0.050	88	0.320	67	10.155
ZBB-9	815	1500	1.024	6730	88	0.052	88	0.525	46	9.947
ZBB-10	815	1500	1.024	6730	94	0.061	86	0.371	62	9.380
ZBB-11	815	1500	2.048	6730	99	0.073	84	0.402	58	9.872
ZBB-12	815	1500	2.048	6730	104	0.081	82	0.336	66	9.960

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 conditions.
d. Percent of sulfur, nitrogen, or hydrogen in liquid product.
e. % Removal = 100 (fraction in feed less fraction in product) / (fraction in feed)

Temperature	435C (815F)
Pressure	1500 psig ± 20
Space Time (Volume Hourly)	2.048, 1.024, 2.56 hr.
Hydrogen flow	6730 SCF/Bbl

The run was conducted for a period of 117 hours, the shut down was scheduled. The sample results are presented in Table V. Figure 1 presents the effect of space time on weight percent of nitrogen in the product oil. Rapid deactivation for nitrogen removal occurred after 100 hours of operation, negligible deactivation in sulfur removal was noticed. ASTM D1160 distillation data are presented in Table VIII. These results are essentially the same as those obtained in Run ZBB.

Run Series ZBD

This experimental run was carried out to access the effect of zoned catalyst bed on removal of sulfur and nitrogen from a coal derived liquid. The catalyst bed was made up of two sections superimposed on each other. The Ketjenfine-124 encountered the oil first. The zoned bed contained 50%, by volume, of Ketjenfine-124 and the rest was HDN-30 (Table II).

The typical run conditions were as follows:

Run Series	ZBD
Reactor	EN-1
Catalyst	Ketjenfine-124 (50% Volume) (Table II) HDN-30 (50% Volume)
Feedstock	Pamco Process Solvent (Table I)
Temperature	435C (815F)
Pressure	1500 psig ± 20
Space Time	2.56, 2.048, 1.024 hr.
Hydrogen flow	6730 SCF/Bbl

The run was conducted for 120 hours; the shut down was scheduled. The samples were analyzed for nitrogen, sulfur and hydrogen, and the results are presented in Table VI. Figure 2 presents the effect of space time on the weight percent of nitrogen in the product oil. The ASTM D1160 distillation was carried out on liquid samples taken between 40 to 60 hours of oil catalyst contact; results are presented in Table VIII. The zoned bed configuration provided no particular advantage over either of the single bed catalysts investigated.

TABLE V

RESULTS FROM REACTOR EN-1 WITH HDN-30 CATALYST
FEEDSTOCK: PAMCO PROCESS SOLVENT

Sample Number	Temp[a] (°F)	Pressure (psig)	Space Time[b] (Volume hrly)	Hydrogen (SCF/BBL)	Hours[c] on oil	%S[d]	%S[e] Removal	%N[d]	%N[e] Removal	%H[d]
Feed						0.438		0.977		7.110
ZBC-2	815	1500	2.048	6730	20	0.107	76	0.129	87	10.659
ZBC-3	815	1500	2.048	6730	30	0.020	96	0.062	94	10.849
ZBC-4	815	1500	2.048	6730	40	0.020	96	0.031	96	10.455
ZBC-5	815	1500	2.048	6730	50	0.020	96	0.133	86	9.323
ZBC-6	815	1500	2.048	6730	60	0.046	90	0.067	93	9.692
ZBC-7	815	1500	2.560	6730	70	0.020	96	0.067	93	10.858
ZBC-8	815	1500	2.560	6730	75	0.020	96	0.023	97	10.037
ZBC-9	815	1500	2.560	6730	83	0.020	96	0.068	93	10.381
ZBC-10	815	1500	1.024	6730	89	0.108	76	0.624	36	8.912
ZBC-11	815	1500	1.024	6730	94	0.050	86	0.541	45	8.134
ZBC-12	815	1500	1.024	6730	98	0.099	77	0.635	35	8.330
ZBC-13	815	1500	2.048	6730	106	0.020	96	0.266	73	9.243

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 conditions.
d. Percent of sulfur, nitrogen, or hydrogen in liquid product.
e. % Removal = 100 (fraction in feed less fraction in product) / (fraction in feed)

TABLE V
(continued)

RESULTS FROM REACTOR EN-1 WITH HDN-30 CATALYST
FEEDSTOCK: PAMCO PROCESS SOLVENT

Sample Number	Temp[a] (°F)	Pressure (psig)	Space Time[b] (Volume hrly)	Hydrogen (SCF/BBL)	Hours[c] on oil	%S[d]	%S[e] Removal	%N[d]	%N[e] Removal	%H[d]
ZEC-14	815	1500	2.048	6730	111	0.069	85	0.293	70	9.11
ZEC-15	815	1500	2.048	6730	117	0.038	92	0.380	61	9.44

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 conditions.
d. Percent of sulfur, nitrogen, or hydrogen in liquid product.
e. % Removal = 100 (fraction in feed less fraction in product) / (fraction in feed)

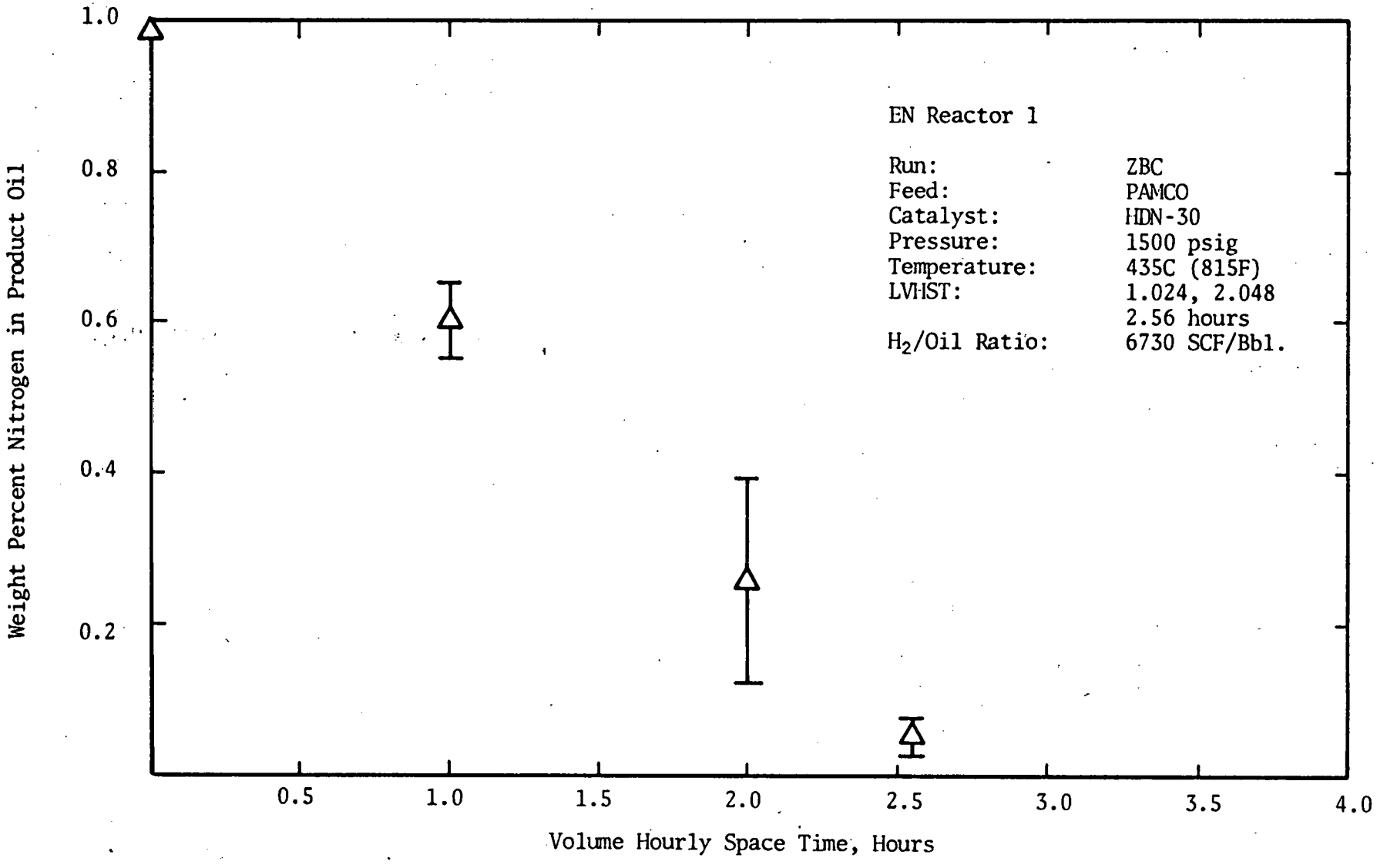


Figure 1. Nitrogen Content of Product Oil vs. Hourly Space Time

TABLE VI

RESULTS FROM REACTOR EN-1 WITH HDN-30 CATALYST
FEEDSTOCK: PAMCO PROCESS SOLVENT

Sample Number	Temp[a] (°F)	Pressure (psig)	Space Time[b] (Volume hrly)	Hydrogen (SCF/BBL)	Hours[c] on oil	%S[d]	%S[e] Removal	%N[d]	%N[e] Removal	%H[d]
Feed						0.438		0.977		7.110
ZBD-2	815	1500	2.048	6730	20	0.026	94	0.116	88	10.493
ZBD-3	815	1500	2.048	6730	30	0.020	96	0.118	86	9.349
ZBD-4	815	1500	2.048	6730	40	0.020	96	0.131	87	10.070
ZBD-5	815	1500	2.048	6730	50	0.028	94	0.091	91	9.481
ZBD-6	815	1500	2.048	6730	60	0.020	96	0.127	87	11.286
ZBD-7	815	1500	2.560	6730	70	0.020	96	0.083	92	10.843
ZBD-8	815	1500	2.560	6730	80	0.020	96	0.070	93	10.094
ZBD-9	815	1500	2.560	6730	88	0.020	96	0.125	87	10.009
ZBD-10	815	1500	1.024	6730	95	0.065	85	0.504	48	8.231
ZBD-11	815	1500	1.024	6730	100	0.020	96	0.576	41	8.595
ZBD-12	815	1500	1.024	6730	104	0.030	93	0.314	68	9.210
ZBD-13	815	1500	2.048	6730	109	0.020	96	0.193	80	10.042

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 conditions.
d. Percent of sulfur, nitrogen, or hydrogen in liquid product.
e. % Removal = 100 (fraction in feed less fraction in product) / (fraction in feed)

TABLE VI

(continued)

RESULTS FROM REACTOR EN-1 WITH HDN-30 CATALYST
FEEDSTOCK: PAMCO PROCESS SOLVENT

Sample Number	Temp[a] (°F)	Pressure (psig)	Space Time[b] (Volume hrly)	Hydrogen (SCF/BBL)	Hours[c] on oil	%S[d]	%S[e] Removal	%N[d]	%N[e] Removal	%H[d]
ZBD-14	815	1500	2.048	6730	114	0.02	96	0.143	85	8.401
ZBD-15	815	1500	2.048	6730	120	0.02	96	0.314	68	8.543

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 conditions.
d. Percent of sulfur, nitrogen, or hydrogen in liquid product.
e. % Removal = 100 (fraction in feed less fraction in product) / (fraction in feed)

Run Series ZBE

This run was conducted to determine the overall reproducibility of the experimental procedures and to determine the deactivation of the catalyst at a single space time, pressure, temperature and hydrogen flow rate. This was an attempt to reproduce the conditions and results of Run ZBC.

The run conditions were as follows:

Run Series	ZBE
Reactor	EN-1
Catalyst	HDN-30 (Table II)
Feedstock	Pamco Process Solvent (Table I)
Temperature	435C (815F)
Pressure	1500 psig ± 20
Space Time	2.048 hr.
Hydrogen flow	6730 SCF/Bbl

The run was conducted for 125 hours with a shut down scheduled. The samples were analyzed for sulfur, nitrogen and hydrogen. The results are presented in Table VII. The ASTM D1160 distillation results are presented on Table VIII. The weight percent nitrogen in the product oil is presented as a function of time in Figure 3. Note that the initial catalyst activity produced a product oil with 0.05 Wt% N (95% removal), after 125 hours of operation the catalyst decays rapidly to yield a product with 0.28 Wt% N (71% removal). Sulfur removal activity decay was not notable. The entire data set was a satisfactory replication of Run ZBC.

In summary, this set of five experimental runs conducted on the Pamco coal derived liquid indicated the following:

1) The new reactor systems, EN-1 performs satisfactorily.

2) High desulfurization and denitrogenation were achieved on both catalysts tested at conditions of 815F, 1500 psig.

3) Zoned bed of 50-50 volume % of the two catalysts tested revealed no advantages.

4) Nitrogen removal activity decay was significant over the operational interval of 100 hours.

TABLE VII

RESULTS FROM REACTOR EN-1 WITH HDN-30 CATALYST
FEEDSTOCK: PAMCO PROCESS SOLVENT

Sample Number	Temp[a] (°F)	Pressure (psig)	Space Time[b] (Volume hrly)	Hydrogen (SCF/BBL)	Hours[c] on oil	%S[d]	%S[e] Removal	%N[d]	%N[e] Removal	%H[d]
Feed						0.438		0.977		7.110
ZBE-2	815	1500	2.048	6730	20	0.020	96	0.125	87	10.624
ZBE-3	815	1500	2.048	6730	30	0.038	91	0.063	94	10.652
ZBE-4	815	1500	2.048	6730	40	0.048	89	0.050	95	10.202
ZBE-5	815	1500	2.048	6730	50	0.020	96	0.077	92	10.102
ZBE-7	815	1500	2.048	6730	70	0.020	96	0.045	95	9.786
ZBE-8	815	1500	2.048	6730	80	0.020	96	0.074	92	9.996
ZBE-9*	815	1500	2.048	6730	90	0.029	93	0.106	89	10.747
ZBE-10	815	1500	2.048	6730	100	0.020	96	0.2171	78	9.401
ZBE-11	815	1500	2.048	6730	110	0.029	93	0.224	77	9.836
ZBE-12	815	1500	2.048	6730	120	0.039	91	0.213	78	10.06
ZBE-13	815	1500	2.048	6730	125	0.020	96	0.281	71	9.03

* Oil flow was cut-off for 2.5 hours due to power failure.

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 conditions.
d. Percent of sulfur, nitrogen, or hydrogen in liquid product.
e. % Removal = 100 (fraction in feed less fraction in product) / (fraction in feed)

TABLE VIII

RESULTS FROM ASTM D 1160 DISTILLATION OF RUN ZBA, ZBB, ZBC, ZBD AND ZBE (50 mm Hg)

	FEEDSTOCK (C)	RUN* ZBA (C)	RUN* ZBB (C)	RUN* ZBC (C)	RUN* ZBD (C)	RUN* ZBE (C)
Initial	159	110	63	84	62	74
10 Vol %	166	165	128	134	125	136
20	170	168	148	152	150	154
30	181	178	168	169	164	169
40	192	190	179	181	174	182
50	213	211	191	194	192	191
60	230	229	210	216	208	219
70	249	252	235	242	234	243
80	265	275	274	253	296	269

*Product samples at 2.048 hr volume hourly space time

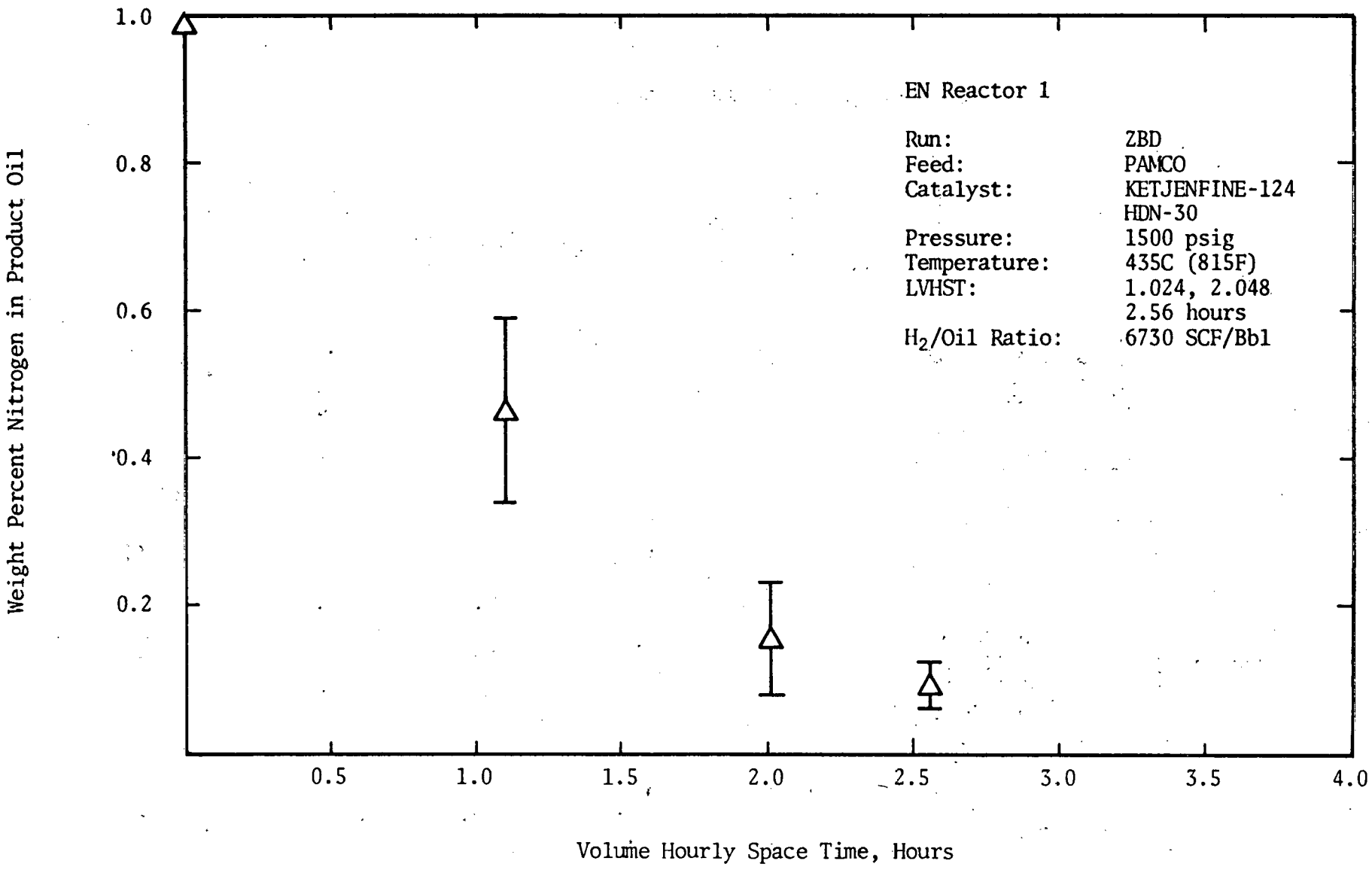


Figure 2. Nitrogen Content of Product Oil vs. Hourly Space Time

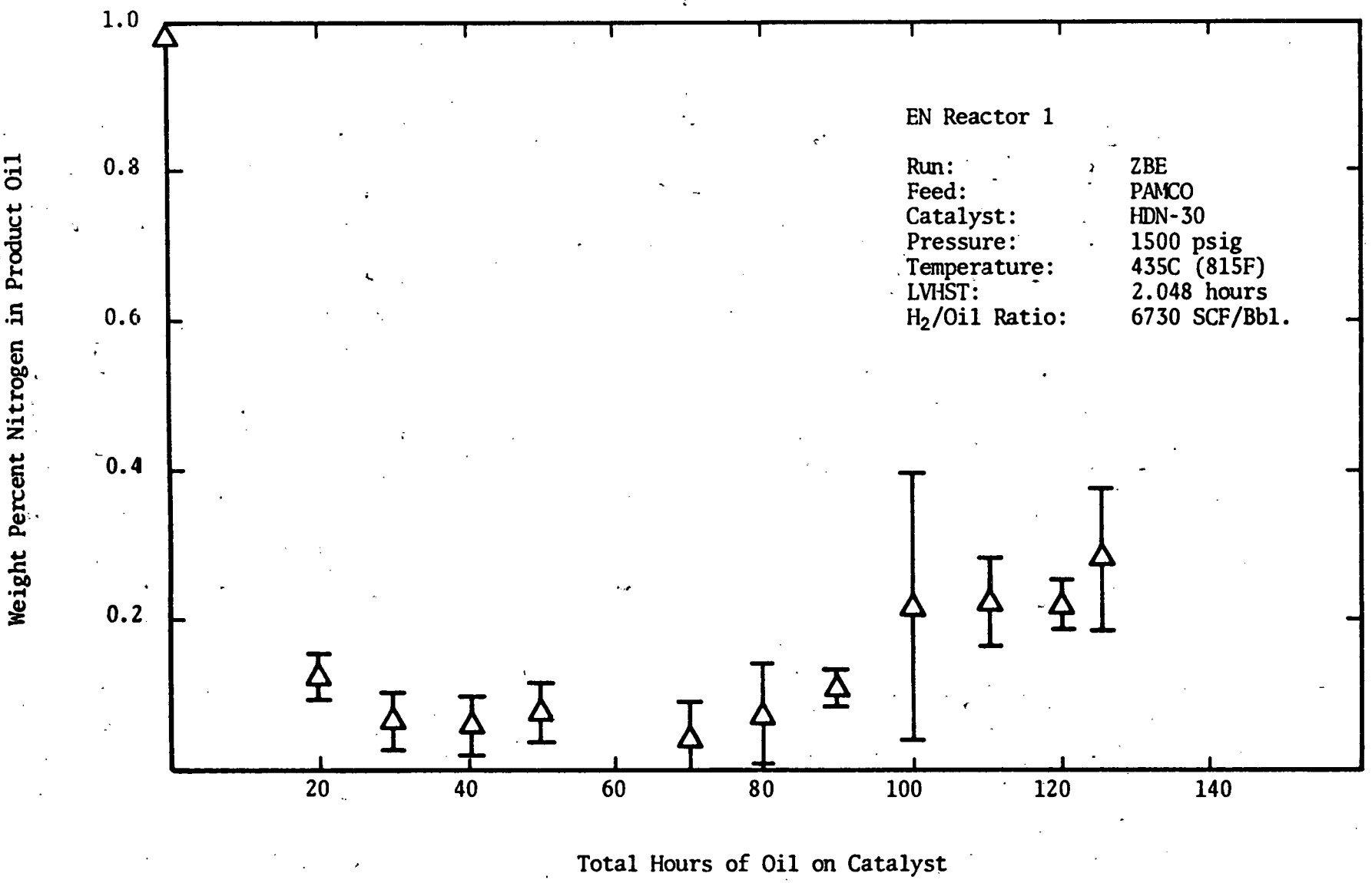


Figure 3. Nitrogen Content of Product Oil vs. Hours on Oil

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

Run Series CND and CNE

In the Catalyst Life Test Unit (CLTU), improvements have been made on the equipment to eliminate the problems of unstable pressure and temperature as indicated in the last quarterly report.* In this reporting quarter, two experimental runs, CND and CNE, have been completed.

The objective of these two experimental runs was to test the newly modified reactors and to check reactor performance using catalyst beds diluted with small size inert particles. Shell-324 NiMo/Al catalysts and Rasyn Oil (50 Vol. % Synthoil - 50 Vol. % Raw Anthracene) were used in both runs. The properties of the catalysts and feedstock are shown in Tables IX and X. Catalyst details were presented previously.*

The designed run conditions were as follows:

Run Series	CND	CNE
Reactor	2	2
Catalyst	Shell-324 1/16" extrud.	Shell-324 1/16" extrud.
Inert	0.250-0.595 mm sand	0.83-1.00 mm glass beads
Feedstock	Rasyn Oil	Rasyn Oil
Temperature	371C (700F)	371C (700F)
Pressure	1500 psig	1500 psig
Space time (Vol. Hrly.)	1.0 hr	1.0 hr
Hydrogen flow	10,000 SCF/Bbl	10,000 SCF/Bbl
Run duration	21	79

Recent literature** suggests that the reactors packed with undiluted 1.5mm (1/16") extrudate or spherical NiMo/Al catalysts could have poorer performance than those packed with the same catalysts but diluted with 0.25-0.83 mm inerts when hydrotreating gas oils. Therefore, in order to check our reactor performance on coal liquids, the reactor of Run CND was packed with an equal volume of 1/16" extrudate catalyst and 0.25-0.595mm of inert material (sand). Unfortunately, the pressure drop across the reactor increased significantly after only 10 hours operation.

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* "Quarterly Report for the period January 1 - March 31, 1980, DE-14876-2.

** "Bench Scale Testing and Presulfiding of Desulfurization Catalysts", Product Data Bulletin No. 76-4, Armak Catalyst Division, Pasadena, TX.

"J. Van Klinken and K. H. Van Dongen, "Catalyst Dilution for Improved Performance of Laboratory Trickle-Flow Reactor", Chemical Engineering Science, Vol. 35, p.59 (1980)

TABLE IX

PROPERTIES OF FEEDSTOCK

Oil	Rasyn Oil*
Composition; Wt%	
Carbon	84.92
Hydrogen	6.57
Sulfur	0.54
Nitrogen	1.21
Oxygen**	5.71
Ash	1.05
Normal boiling point***	
Initial	160C (320F)
10%	233C (451F)
30%	303C (577F)
50%	356C (673F)

* Equal volume mixture of Raw Anthracene oil and Synthoil II liquid (Western Kentucky Blend).

** By difference

*** Determined from ASTM D 1160 Data

TABLE X

CATALYST PROPERTIES

Catalyst Code	Shell-324
Manufacturer	Shell
Chemical Composition, wt%	
NiO	2.7*
MoO_3	13.2*
Physical Properties (1/16" Extrud.)	
surface area m^2/gm	146 (150*)
pore volume cc/gm	0.42 (0.48*)
Most frequent pore diameter (Å)	118

Å diameter	% pore volume in pore
35-70	12
70-100	21
100-150	57
150-200	2
200-400	1
400-600	1
>600	6
TOTAL	100

* Vendor's data

This was caused by the small inert particles plugging the screens which were used to support the bed. The reactor was shut-down after only 21 hours operation. Based on this experience, somewhat larger inert pellets, 0.83-1.00mm glass beads were used in Run CNE. In this later run, essentially no variations in pressure, temperature, liquid or gas flow rates were observed.

The results of Runs CND and CNE are summarized in Tables XI and XII and Figures 4 and 5 show the nitrogen and sulfur contents of the product oils as a function of time on stream for Run CNE. As the figures show, the activities of heteroatom removal tended to level off after 50-60 hours operation at one hour space time. When the space time was increased to 2.8 hours (the last points in Figures 4 and 5, the original removal levels were restored.

The first samples from both runs were at transient stages; extents of nitrogen removals were the same. This suggests that the 0.250-0.595mm inert particles are unnecessarily small for catalyst dilution. This observation results from the fact that the feedstock is relatively heavy and viscous and that nitrogen removal is not high. These two factors tended to mark off any deviation in our reactors from ideal plug flow reactors.

In summary:

1) Two experimental runs have been made to test the equipment and to check the diluted bed reactor performance.

2) Pressure, temperature, liquid and gas flow rates have been very stable during these runs.

3) When diluted catalyst beds were used, the smaller inert particles (0.250-0.595mm) offered no advantage over larger ones (0.83-1.00mm) in terms of heteroatom removal.

During the coming quarter, one or more experimental runs of 200-300 hours and less will be made using Shell-324 NiMo/Al catalyst and EDS process 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.

TABLE XI

RESULTS FROM CLTU REACTOR II WITH SHELL-324 CATALYST
FEEDSTOCK: RASYN OIL*

Run Number	Sample Number	Temp[a] (°F)	Pressure (psig)	Space Time[b] (Volume hrly)	Hydrogen (SCF/BBL)	Hours[c] on oil	%S[d]	%S[e] Removal	%N[d]	%N[e] Removal
	Feed						0.54		1.21	
061180	CND-1	400-700**	1500	1.0	10000	4	0.18	67	0.89	26
061280	CND-2	700	1500	1.0	10000	13	0.00	>96	0.46	62
061280	CND-3***	700	1500	1.0	10000	20	0.03	94	0.53	56

* Equal volume mixture of synthoil II and raw anthracene oils

** Transient stage

*** Unstable due to reactor plugging

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 conditions.
d. Percent of sulfur or nitrogen in liquid product.
e. % Removal = 100 (fraction in feed less fraction in product) / (fraction in feed)

TABLE XII

RESULTS FROM CLTU REACTOR II WITH SHELL-324 CATALYST
FEEDSTOCK: RASYN OIL

Run Number	Sample Number	Temp[a] (°F)	Pressure (psig)	Space Time[b] (Volume hrly)	Hydrogen (SCF/BBL)	Hours[c] on oil	%S[d]	%S[e] Removal	%N[d]	%N[e] Removal
061580	Feed						0.54		1.21	
061580	CNE-1	500-700	1500	1.0	10000	5	0.13	76	0.53	56
061580	CNE-2	700	1500	1.0	10000	12	0.11	80	0.46	62
061680	CNE-3	700	1500	1.0	10000	21	0.00	>96	0.66	45
061680	CNE-4	700	1500	1.0	10000	29	0.15	72	0.67	45
061680	CNE-5	700	1500	1.0	10000	36	0.27	50	0.86	29
061780	CNE-6	700	1500	1.0	10000	45	0.20	63	0.85	30
061780	CNE-7	700	1500	1.0	10000	53	0.31	43	0.98	19
061780	CNE-8	700	1500	1.0	10000	60	0.30	44	1.14	06
061880	CNE-9	700	1500	1.0	10000	69	0.30	44	1.09	10
06188-	CNE-10	700	1500	2.8	10000	77	0.03	94	0.59	51

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 conditions.
d. Percent of sulfur or nitrogen in liquid product.
e. % Removal = 100 (fraction in feed less fraction in product) / (fraction in feed)

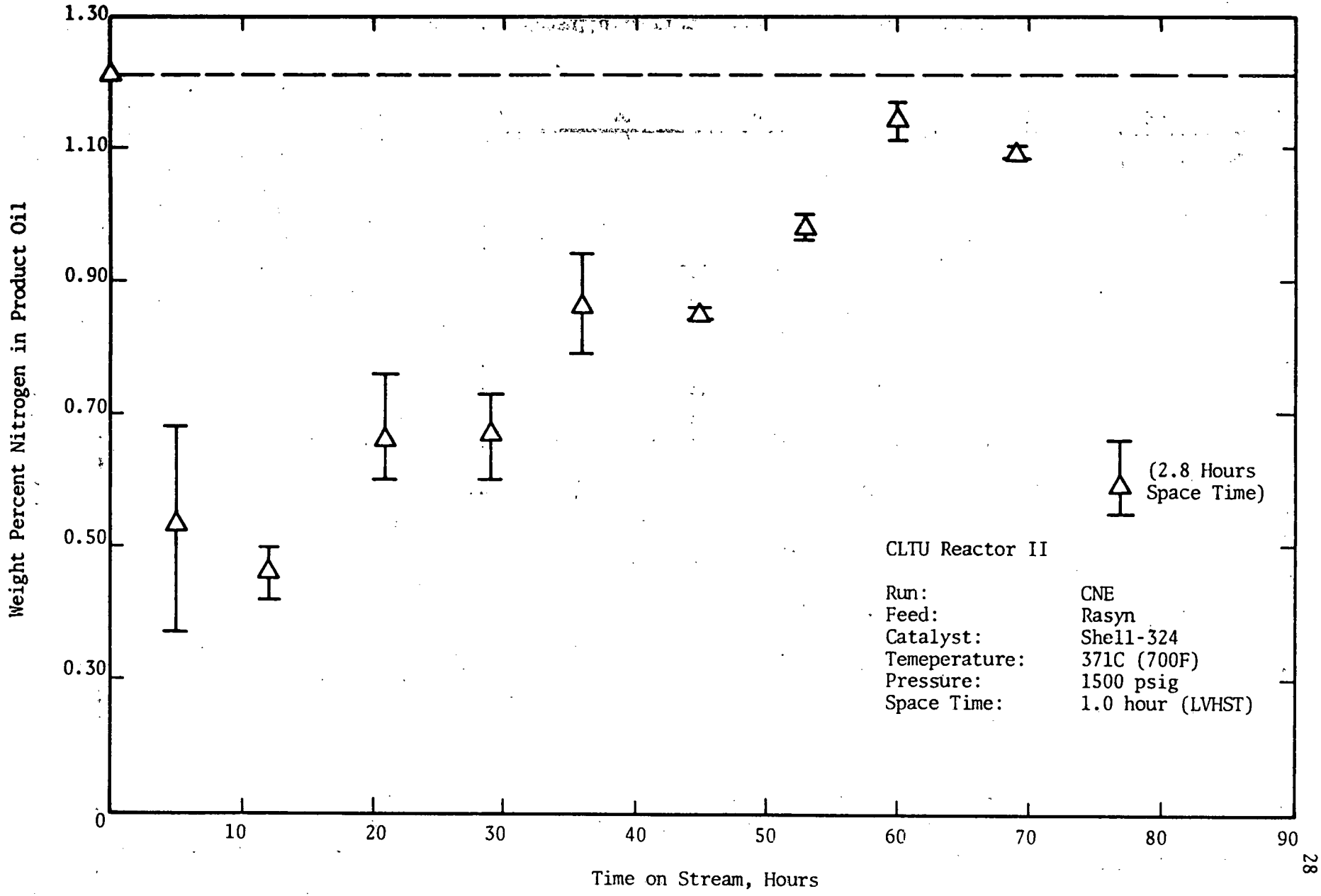

Figure 4. Hydrodenitrogenation Activity Response, Run CNE

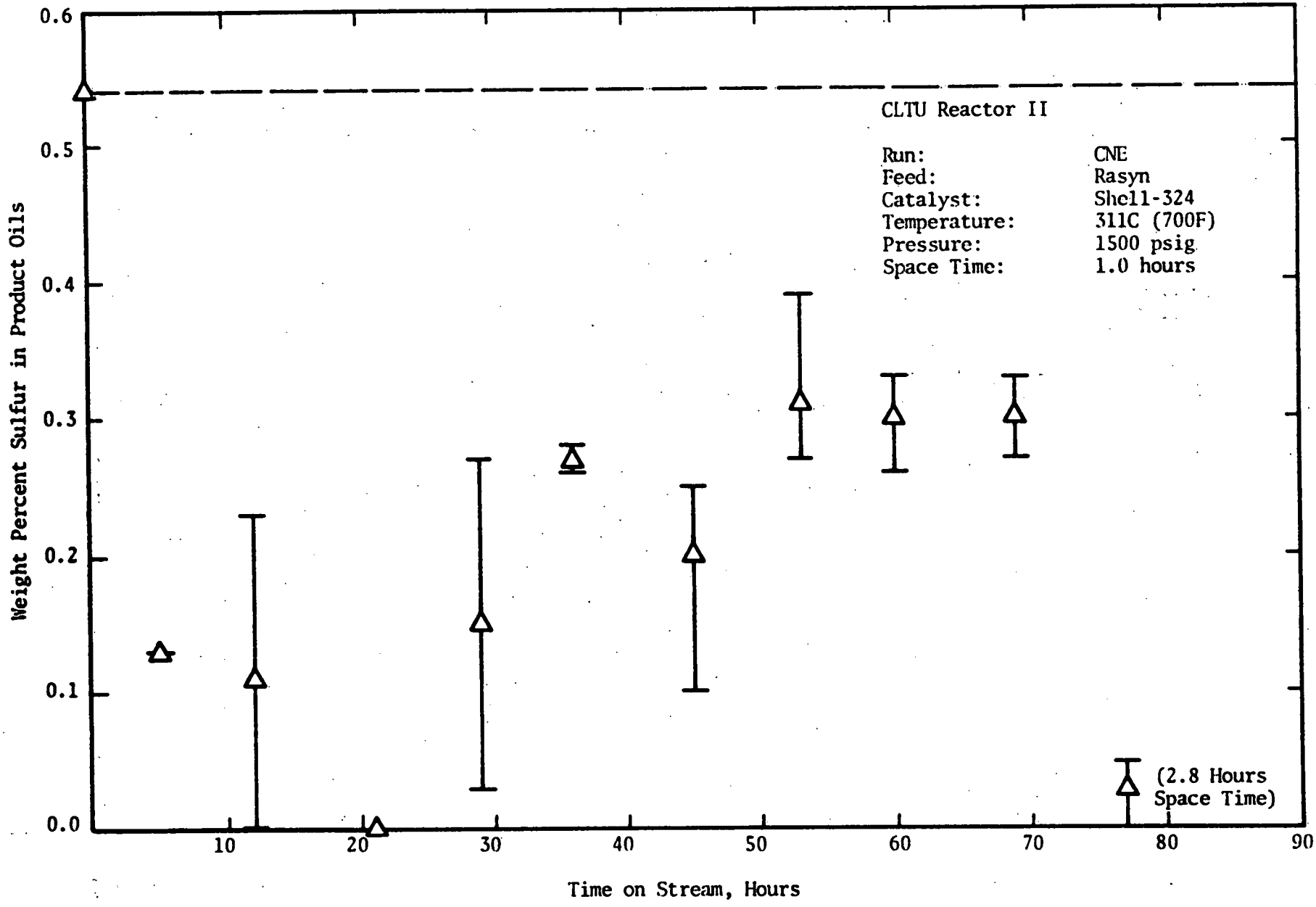

Figure 5. Hydrodesulfurization Activity Response, Run CNE