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CATALYTIC HYDROGENATION OF COAL-DERIVED LIQUIDS

Interim Report for the
Period March, 1977 - May, 1977

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OBJECTIVE

It is the object of this research to convert coal to clean distillate fuels. This program will be limited to research on the product from existing coal liquefaction processes. Liquified coal will be converted by a catalytic hydrogenation at elevated temperatures and pressures. Samples of the products from PAMCO, H-Oil, COED and SYNTHOIL will be obtained. They will be heated and pumped, with and without solvent, into a catalytic reactor in the presence of hydrogen and other reducing gases. Variables to be investigated will include temperature, pressure, space velocity, hydrogen-to-oil ratio, chemical nature of the solvent. The catalysts to be studied will include nickel molybdate and sulfide, nickel tungstate and other combinations on carriers such as mordanites and other molecular sieve types.

ABSTRACT

Nineteen batch and seven continuous runs on SRC Vacuum Flash Feed are reported with denitrogenation up to 38% and desulfurization up to 75% achieved. On COED Pyrolysis Oil, eight batch and four continuous runs are reported with denitrogenation up to 45% and desulfurization up to 90% accomplished. Twenty-eight batch and nine continuous runs on SYNTHOIL are reported with denitrogenation up to 32% and desulfurization up to 48% attained.

NUGGET

Shell's #344 cobalt molybdate catalyst gives 48% desulfurization, 32% denitrogenation and 50% conversion to distillate material from SYNTHOIL. It gives 65% desulfurization and 30% denitrogenation with SRC and 88% desulfurization and 20% denitrogenation with FMC tar.

Conversion of Solvent Refined Coal to Distillate Fuels - G. R. Hass

SUMMARY OF CATALYST SCREENING TASKS

Table I,appended to this report, summarizes heteroatom removal data of the batch catalyst screening tests made with PAMCO's Solvent Refined Coal Vacuum Flash Feed. Runs numbered 35B through 44B were tests completed during this quarter and runs numbered 26B through 34B are tests made previous to this quarter. Batch runs were made in a Parr rocking autoclave of 500 ml internal volume. Batch run conditions were as follows:

Vacuum Flash Feed Charged	=	200 gr.
Catalyst Charged	=	25 ml
Initial Hydrogen Pressure	=	2500 psig
Run Temperature	=	$420^{o}C \pm 5^{o}C$
Residence Time		1 hour at run temperature

From Table I it can be seen that Shell 324 E 1/16" catalyst (2.7% Ni, 13.2% Mo, on alumina) gave the best desulfurization in a batch run. Harshaw Co-Mo-0401 T1/8" (3% CoO, 9% MoO_3 on alumina) gave the best denitrogenation in a batch run. Of the batch screening runsmade this quarter, the most promising desulfurization catalyst is M.S.U. STK-14 E 1/16" (17.4% MoO_3, 2.3% NiO, 1.8% CuO on alumina). The most promising denitrogenation catalyst is M.S.U. STK-8-1 E 1/16" (8.6% MoO_3, 1.4% NiO, 11% Wo_3 on alumina). All catalysts in Table I labeled with the prefix M.S.U. STK were made in our laboratory using NORTON 6176 Alumina support (99.85% Al_2O_3, 0.014% Na_2O, .120% SiO_2, 0.065% Fe_2O_3, Pore Volume = .95cc/g, surface area = 250 ± 20 m^2/gr).

SUMMARY OF CONTINUOUS FIXED BED REACTOR RUNS

Table II, appended to this report, summarized heteroatom removal data obtained from continuous fixed bed reactor runs made with PAMCO's SRC Vacuum Flash Feed. Runs numbered C-7 and C-8 were completed this quarter and runs numbers C-1 through C-6 were made previous to this quarter. These continuous fixed bed reactor runs were made at the following conditions:

Pressure	=	1000 psig
Temperature	=	$450^{o} \pm 5^{o}C$
H_2 to oil ratio	=	10000 SCF/BBL
Catalyst bed	=	60 ml catalyst diluted with 60ml Denstone 1/8" inert support material
LHSV	=	1.0, 1.5, 2.0

From Table II it can be seen that the best average disulfurization over the three liquid hourly space velocities tested was obtained with Shell 344 E 1/16" catalyst (2.4% Co, 9.9% Mo on alumina). The best average denitrogenation over the space velocities tested was Harshaw HT-400 E 1/16" catalyst (3% CoO, 15% MoO_3 on alumina). At the lowest space velocity (LHSV= 1.0). Shell 344 E 1/16" catalyst has given the highest desulfurization to date (73.9%). At the lowest space velocity Shell 324 E 1/16" catalyst (2.7% Ni, 13.2% Mo on alumina) has given the highest denitrogenation to date (38.8%).

Other than heteroatom removal data obtained, probably the most significant data in Table II is the effect of macro-particle pore diffusion effects shown by runs C-4 and C-5. Runs C-4 and C-5 were made using the same catalyst with the only difference being the size of the catalyst particle. Clearly noticeable is the improved heteroatom removal with the smaller extrusion.

COMMENTS ON FIXED BED REACTOR PERFORMANCE

In order to facilitate easier cleaning of the one inch Inconel reactor used in these tests the reactor is de-pressurized and 30W motor oil is pumped through the catalyst bed. This procedure has prevented the catalyst particles from fusing together while cooling and makes for easier cleaning.

CONCLUSIONS FROM THIS QUARTER'S WORK

1. Shell 344 E 1/16" catalyst has given the best average disulfurization to date over the space velocities tested.

2. Harshaw HT-400 E 1/16" catalyst has given the best average denitrogenation to date over the space velocities tested.

3. Nickel-Molybdate catalyst combinations show promise as being good heteroatom removal catalysts.

FORECAST OF FUTURE WORK

Catalyst testing in batch autoclaves will continue in order to screen catalyst activity.

Catalyst testing in continuous fixed bed reactor will continue. Some of the catalysts to be tested will include:

Harshaw 4301	6% Ni, 19% W on silica alumina
Harshaw Co. Mo 0603	3% CoO, 12% MoO_3 on alumina
Cyanamid HDS-20A	5% CoO, 16.2% MoO_3 on alumina

A series of Ni-Co-W catalysts will be prepared in our laboratory and screened for activity.

Gas chromatographic techniques are now being prepared in order to analyze off-gas from our continuous reactors. Once this system has been debugged and the use of a mass flow meter to more accurately measure inlet hydrogen and wet test meters to measure off-gas floww rate, a more accurate mass balance can be made around our reactors.

TABLE I

DATA SUMMARY OF BATCH RUNS ON SRC VACUUM FLASH FEED

RUN	CATALYST	% DN*	% DS*
26 B	Harshaw HT-400 E 1/8", 3% CoO, 15% MoO_3, on alumina	25.4	34.8
27 B	Harshaw HT-500 E 1/8", 3% Nio, 15.5 MoO_3, on alumina	16.9	33.2
28 B	Ketjen HC-5-E 1/16", 6.5% NiO, 21% WO_3, on alumina	5.8	27.0
29 B	Ketjen 330-E 3/32", 6.6% NiO, 19.8 WO_3, 1.2% SiO_2 on alumina	12.3	37.3
30 B	Harshaw Co Mo-0401T 1/8", 3% CoO, 9% MoO_3, on alumina	29.5	36.0
31 B	M.S.U. STK-6 E 1/16", 1.2% NiO, 1.5% CoO, 18% MoO_3, on alumina	1.5	17.7
32 B	Shell 324 E 1/16", 1.7% Ni, 13.2% Mo on alumina	27.5	75.3
33 B	Shell 344 E 1/16", 2.4% Co, 9.9% Mo, on alumina	18.8	52.5
34 B	M.S.U. STK-5 E 1/16", 1.2% CoO, .4% NiO, 18.2% MoO_3, on alumina	20.2	44.1
35 B	Harshaw Ni-4401 T 1/8", 6% Ni, 19% W, 50% silica on alumina	20.4	35.7
36 B	M.S.U. STK-8-2 E 1/16", 9.5% MoO_3, 1.4% NiO, 11.2% WO_3 on alumina	21.5	47.7
37 B	M.S.U. STK-10 E 1/16", 12% MoO_3, 1.7% CoO, 2.6% NiO, 0.9% Fe_2O_3, on alumina	12.0	28.3
38 B	M.S.U. STK-11 E 1/16", 11.0% MoO_3, 3.7% CR_2O_3, 1.2% NiO, on alumina	12.0	38.9
39 B	Harshaw Ni-4303 T 1/8", 6% Ni, 19% W, on alumina	19.4	42.1
40 B	M.S.U. STK-14 E 1/16", 17.4% MoO_3, 2.3% NiO, 1.8% CuO, on alumina	10.2	50.8
41 B	M.S.U. STK-9 E 1/16", 21% MoO_3, 2% ENO, on alumina	14.9	8.7

T A B L E I (continued)

DATA SUMMARY OF BATCH RUNS ON

SRC VACUUM FLASH FEED

RUN	CATALYST	% DN*	% DS**
42-B	M.S.U. STK-12 E 1/16" 18% MoO_3, 2% NiO, 17% ~~Z~~NO^3 on alumina	16.1	46.7
43 B	M.S.U. STK-13 E 1/16" 11% MoO_3, 3% NiO .49% Fe_2O_3	21.7	21.0
44 B	M.S.U. STK-8-1 E 1/16" 8.6% MoO_3, 1.4% NiO, 11% WO_3 on alumina	29.4	15.7

* % DN - Weight Percent Denitrogenation

** % DS - Weight Percent Desulfurization

NOTE: SRC Vacuum Falsh Feed Contains:
.644% Sulfur and 1.30% Nitrogen

TABLE II

DATA SUMMARY OF CONTINUOUS RUNS ON SRC VACUUM FLASH FEEDS

RUN	CATALYST	LHSV*	% DN**	% DS***
C-1	Shell 324 E 1/16"	1.0	38.8	70.5
	2.7% Ni, 13.2% Mo,	1.5	15.4	61.8
	on alumina	2.0	8.5	49.5
C-3	Harshaw Co-MO-0401 T 1/8"	1.0	19.2	54.2
	3% CoO, 9% MoO_3	1.5	12.7	59.9
	on alumina	2.0	3.8	38.8
C-4	Harshaw HT-400 E 1/16"	1.0	33.8	67.1
	3% CoO, 15% MoO_3	1.5	32.3	53.9
	on alumina	2.0	26.2	55.3
C-5	Harshaw HT-400 E 1/8"	1.0	18.8	62.3
	3% CoO, 15% MoO_3	1.5	20.5	56.4
	on alumina	2.0	10.1	34.3
C-6	Harshaw HT-500 E 1/8"	1.0	18.5	53.1
	3% NiO, 15.5% MoO_3	1.5	20.0	58.8
	on alumina	2.0	13.1	53.6
C-7	Shell 344 E 1/16	1.0	31.1	73.9
	2.4% Co, 9.9% Mo	1.5	37.0	61.2
	on alumina	2.0	17.7	65.2
C-8	Harshaw Ni-4401 T 1/8"	1.0	15.2	66.3
	6% Ni, 19% W	1.5	17.8	38.2
	50% $S:O_2$ on alumina	2.0	13.5	41.5

* LHSV = Liquid Hourly Space Velocity

** % DN = Weight Percent Denitrogenation

*** % DS = Weight Percent Desulfurization

NOTE: SRC Vacuum Flash Feed Contains:
.644% Sulfur and 1.30% Nitrogen.

CATALYTIC CRACKING OF PAMCO SOLVENT-REFINED COAL - L. M. Henton

SUMMARY

Four continous runs each using a different catalyst were made this quarter. Three runs are completely analyzed and one is partially completed. Heteroatom removal:

1. Increases with temperature.

2. Decreases with space velocity.

3. Increases to a peak with hydrogen flow ratio.

An increase of temperature also increases hydrocracking.

CATALYST RESULTS

TABLE 3-1 lists the continuous run conditions and catalysts employed this quarter. Presented are conversions of solid SRC to liquids in each of three boiling ranges; sulfur and nitrogen removal data is also listed.

DISCUSSION

The first three continuous runs of the quarter are completely analyzed, and all samples of the fourth run have nitrogen analyses completed. The effect of temperature, hydrogen-to-liquid flow ratio, and liquid hourly space velocity (LHSV) were studied this quarter. Four different catalysts were tested: Harshaw HT-400, Ketjen HC-5, MSU STK-7, and MSU STK-5-2-1. Refer to Table 3-2 for catalyst descriptions.

The highest denitrogenation, 64%, was achieved by HT-400 Co-Mo catalyst. The highest desulfurization, 88%, was achieved by Ketjen HC-5 Wo_3-NiO catalyst.

Figures 3-A through 3-G display heteroatom removal data.

Nitrogen removal shows a greater dependency on temperature than does sulfur removal. Figure 3-D shows steep temperature effect between 420 and 445°C on nitrogen removal; Figure 3-A shows a more gradual effect on sulfur removal.

Heteroatom removal decreases with increased space velocity, as displayed in Figures 3-B and 3-E.

Figure 3-C shows desulfurization peaks or maximizes in the range of 10,000 to 13,000 SCF/BBL H_2-to-liquid ratio at LHSV=1 445°C. However, denitrogenation results from HC-5 and STK-7 conflicted. (See Figure 3-F) Results from STK-5-2-1 show the two MSU MoNiCo catalysts display a temporary high activity in the first sample of the run. Steady-state nitrogen removal maximizes at 10,000 SCF/BBL and decreases as hydrogen ratio decreases.

Figure 3-G shows that a given catalyst has different optimum hydrogen rate ratios at different space velocities: 7500 SCF/BBL is optimum at LHSV=2, and 10,000 SCF/BBL is highest at LHSV=1.

Figure 3-H displays HT-400 product distillations for three different space velocities. The curve for LHSV=2 shows the lowest curve, and LHSV=1 curve has the most overall conversion. The product of LHSV=3 is very much like the reactor feed.

Figure 3-I exhibits the effect of temperature on cracking. The 420°C product is similar to the feedstock, but the 445°C is much improved.

CONCLUSIONS

1. Harshaw HT-400 displayed highest nitrogen removal - 64%. Ketjen HC-5 displayed highest sulfur removal - 88%.

2. Heteroatom removal and hydrocracking both increase with temperature up to 445°C.

3. Heteroatom removal decreases as space velocity is increased from 1 to 3.

4. Maximum steady-state heteroatom removal is achieved at a hydrogen ratio of 10,000 SCF/BBL at LHSV=1 and 445°C.

5. Space velocities higher than 1 have maximum nitrogen removal at hydrogen ratios lower than 10,000 $\frac{\text{SCF}}{\text{BBL}}$.

FUTURE WORK

Analysis of continuous run will be completed.

TABLE 3-1

CONVERSION OF SRC TO LIQUID

CATALYST		LHSV	SCF/BBL H_2	TEMP. (^oC)	% deS	% deN	% NAPTHA IBP-425^oF	% FUEL OIL 425-600^oF	% GAS OIL 600-700^oF	RESIDUE
HARSHAW HT-400 E 1/16"	A.)	1	10,000	445	75%	64%	11%	35%	21%	33%
	B.)	2	10,000	445	67%	33%	58%	0%	0%	42%
	C.)	3	10,000	445	63%	12%	0%	31%	0%	69%
	D.)	1	10,000	420	71%	17%	-5%	22%	14%	69%
	E.)	1	10,000	400	59%	14%	0%	11%	14%	75%
KETJEN HC-5 E 1/16"	A.)	2	10,000	445	65%	46%	28%	33%	0%	39%
	B.)	1	10,000	445	85%	35%	11%	21%	24%	44%
	C.)	1	7,000	445	69%	25%	0%	28%	17%	55%
	D.)	1	13,000	445	88%	36%	0%	26%	18%	56%
MSU STK-7 E 1/8"	A.)	1	7,000	445	39%	55%	42%	11%	19%	28%
	B.)	1	9,200	445	57%	23%	5%	28%	14%	53%
	C.)	1	13,000	445	53%	21%	3%	31%	19%	47%
	D.)	3	10,000	445	41%	9%	0%	28%	14%	58%
	E.)	2	10,000	445	33%	9%	-3%	25%	19%	58%
	F.)	1	10,000	420	38%	0%	-5%	22%	11%	72%

CONTINUED

T A B L E 3-1- continued

CONVERSION OF SRC TO LIQUID

CATALYST		LHSV	SCF/BBL H_2	TEMP. (°C)	% deS	% deN	% NAPTHA IBP-425°F	% FUEL OIL 425-600°F	% GAS OIL 600-700°F	RESIDUE
MSU STK-5-2-1 E 1/16"	A.)	1	10,000	445		59%				
	B.)	2	5,000	445		17%				
	C.)	1	7,500	445		23%				
	D.)	1	5,000	445		20%				
	E.)	2	2,500	445		11%				
	F.)	1	2,500	445		18%				
	G.)	2	7,500	445		20%				
	H.)	2	10,000	445		15%				
	I.)	1	10,000	445		25%				

NOTE: 70 ml catalyst used in each continuous run, diluted 50-50 with inert 1/8" support.
Pressure of runs approximately 1000 psig.

DESULFURIZATION

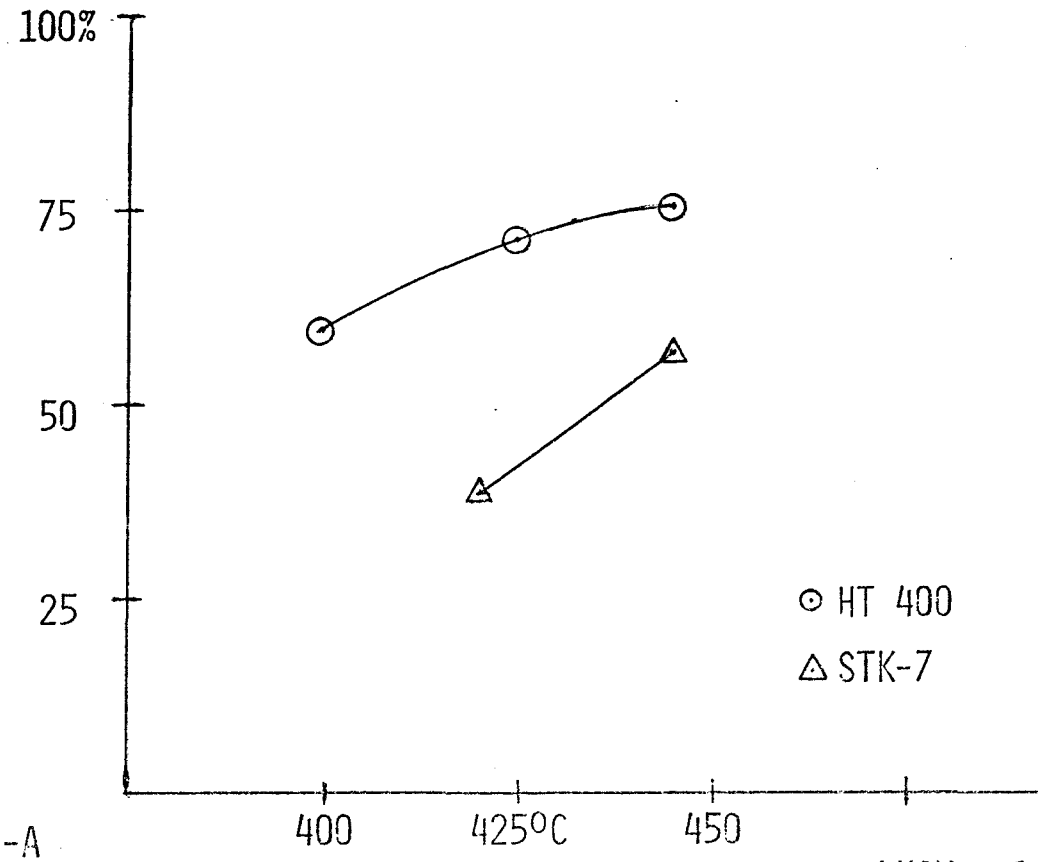


FIGURE 3-A

LHSV = 1, &
10,000 SCF
BBL

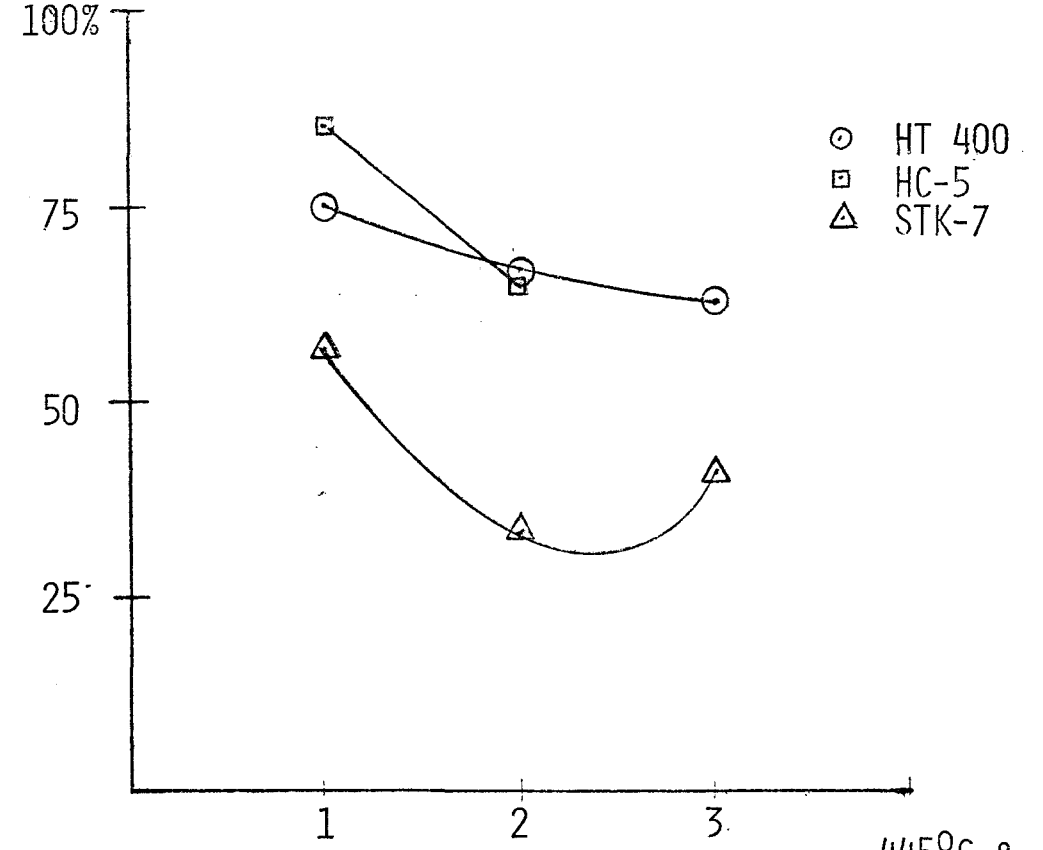


FIGURE 3-B

445°C &
10,000 SCF

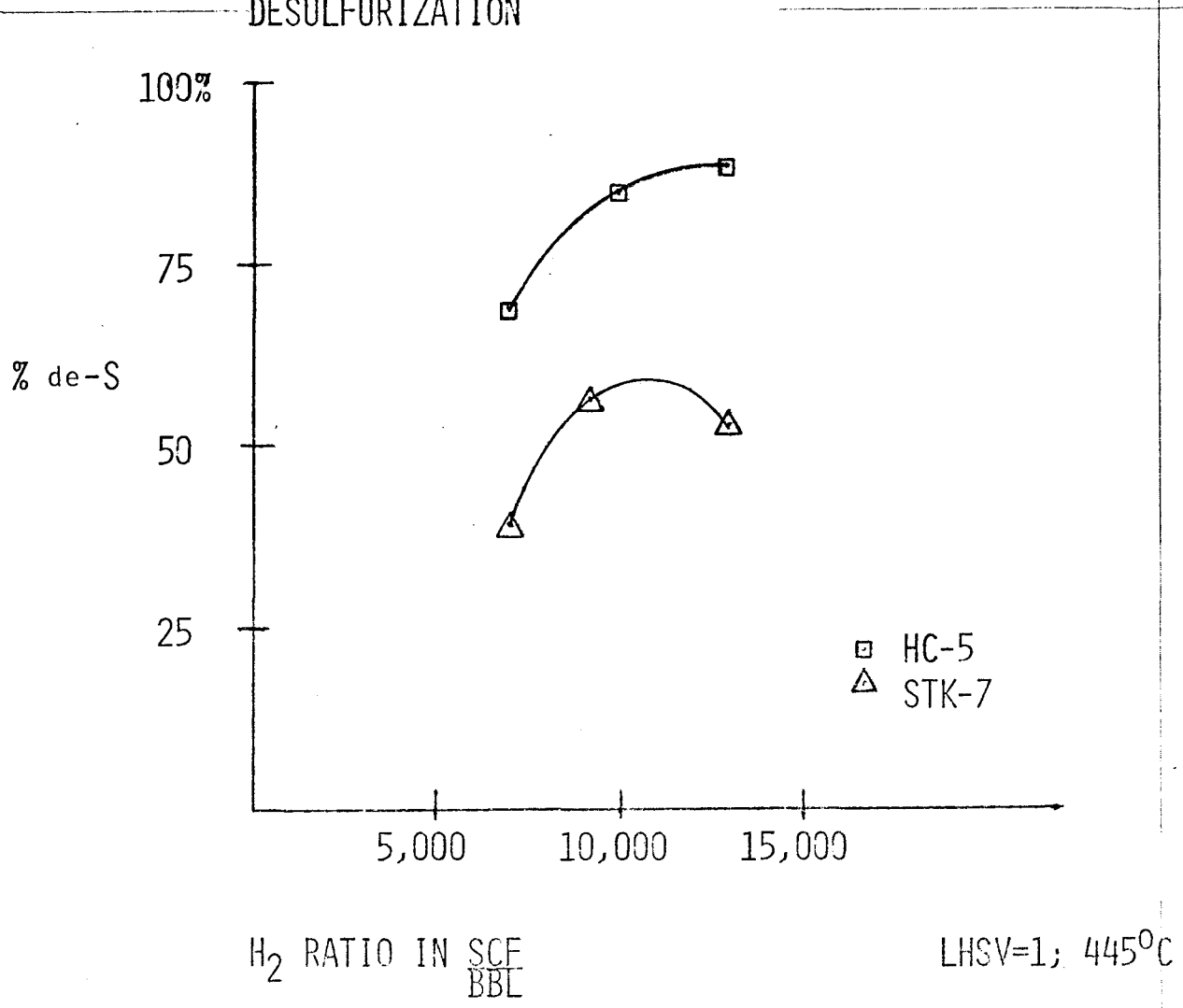

DESULFURIZATION
100%
75
50
25
% de-S
HC-5
STK-7
5,000
10,000
15,000
H_2 RATIO IN $\frac{SCF}{BBL}$
LHSV=1; 445°C

FIGURE 3-C

DENITROGENATION

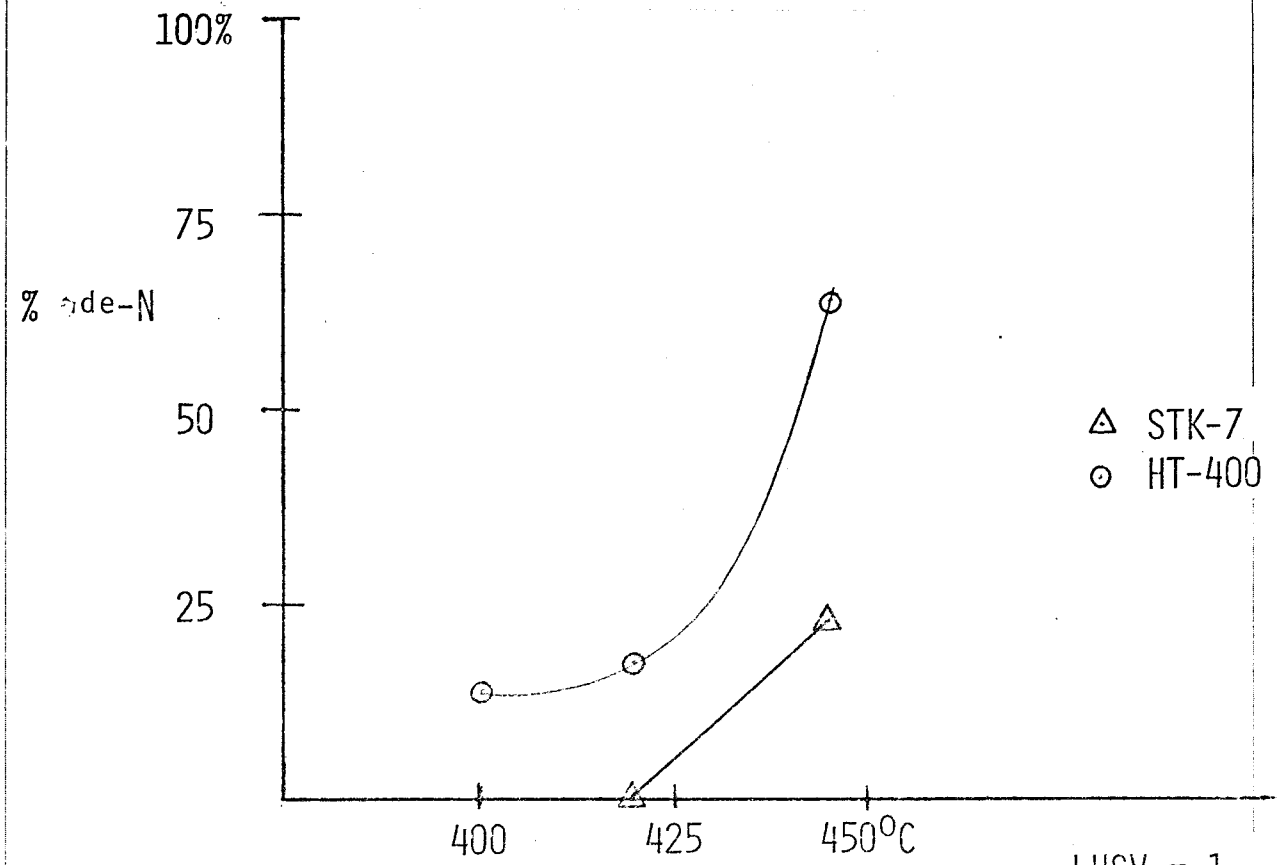


FIGURE 3-D

TEMPERATURE

LHSV = 1;
10,000 SCF/BBL

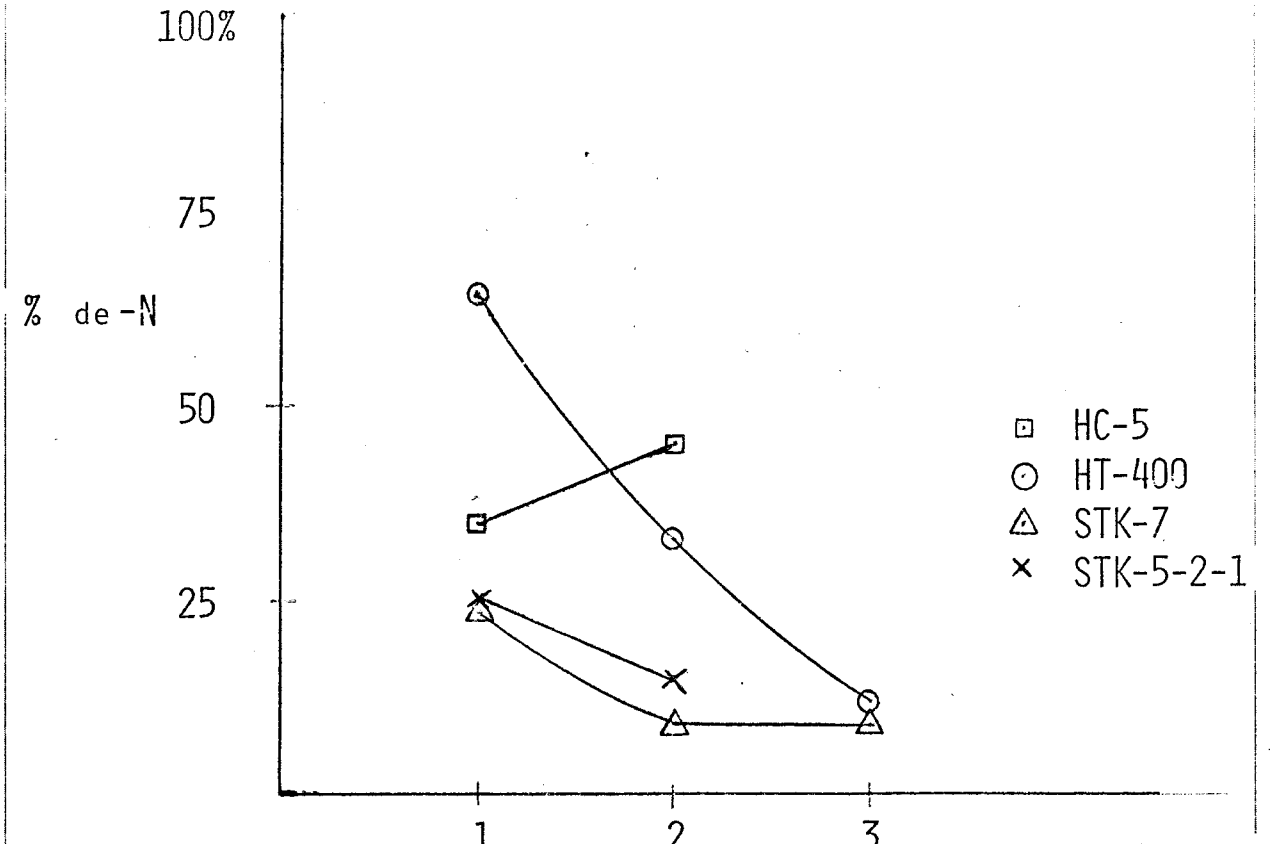


FIGURE 3-E

LHSV

445°C;
10,000 SCF
BBL

DENITROGENATION

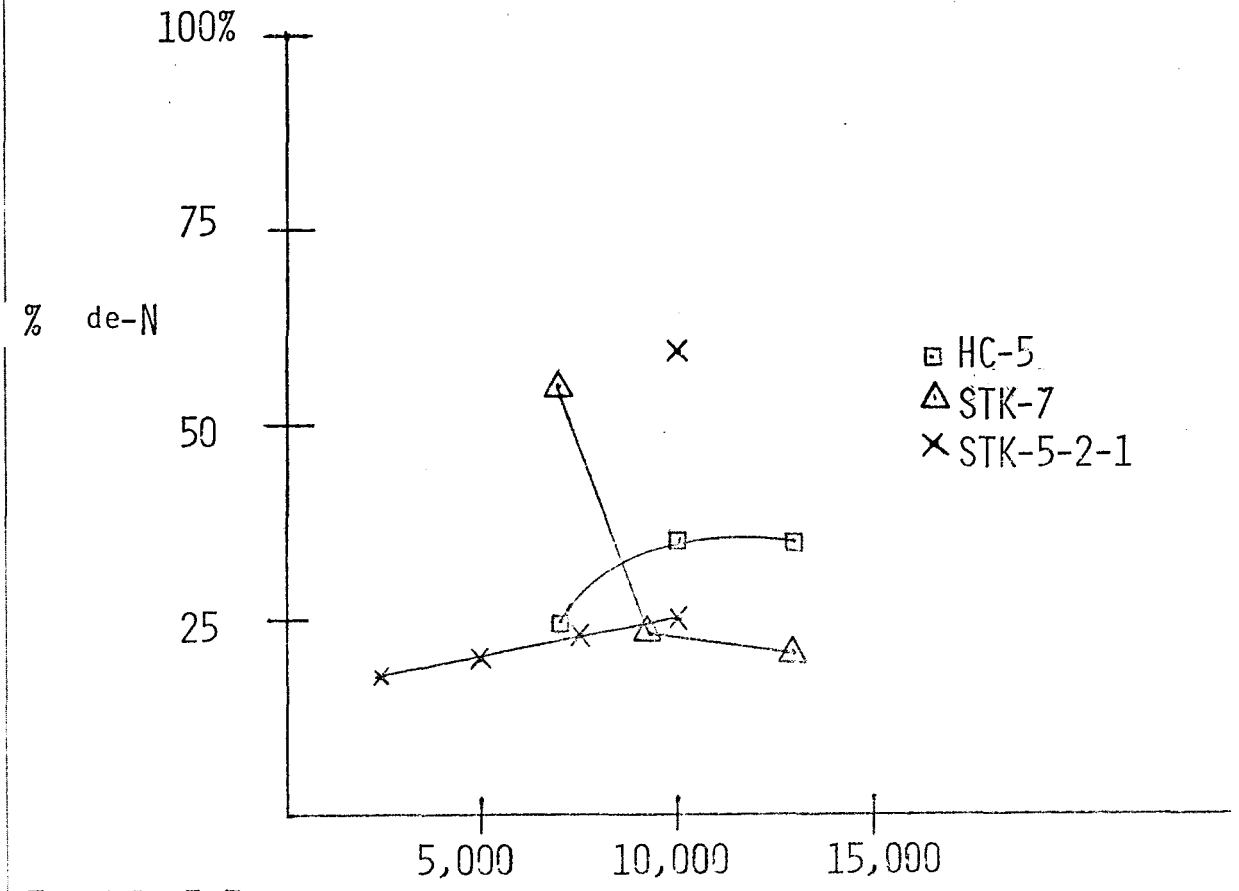


FIGURE 3-F

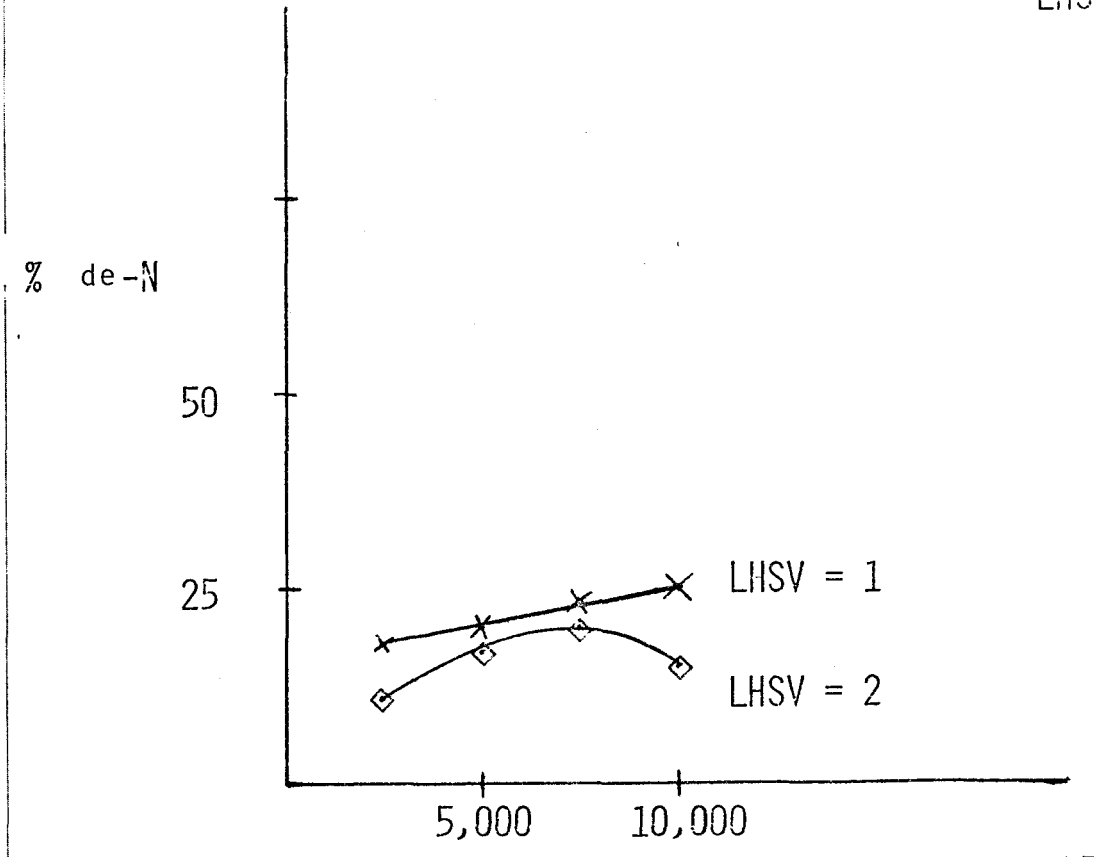
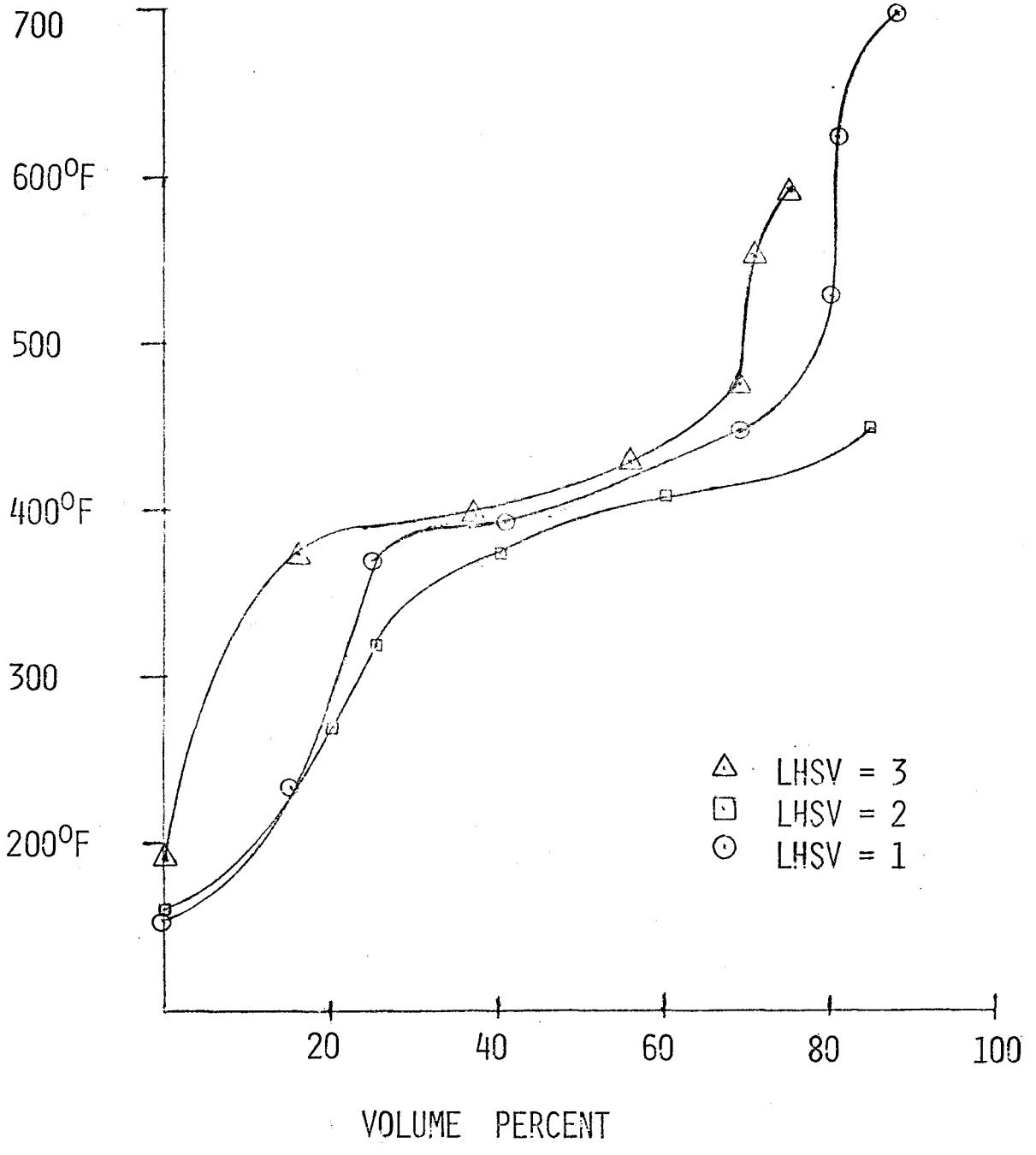


FIGURE 3-G



RUN C-HT 400

445°C
10,000 SCF/BBL

FIGURE 3-H

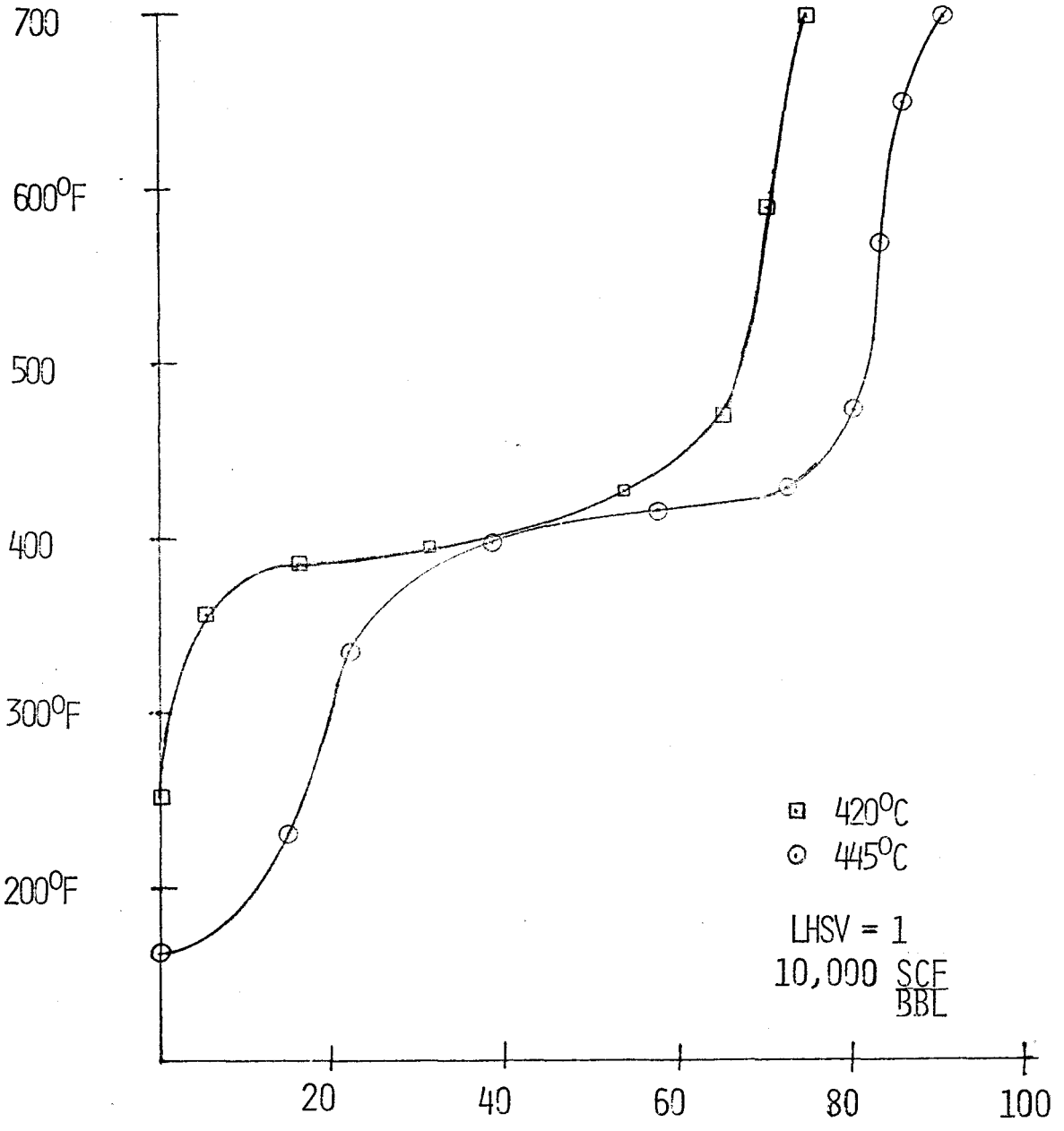

700
600°F
500
400
300°F
200°F
20
40
60
80
100
420°C
445°C
LHSV = 1
10,000 SCF/BBL
VOLUME PERCENT
RUN C-STK-7

FIGURE 3-I

T A B L E 3-2

CATALYST DESCRIPTION

HARSHAW	HT-400 E 1/16" on alumina	3% CoO, 15% MoO_3 Surface Area = 220 M^2/g Pore Volume = 0.55 cc/g
KETJEN	HC-5-1.5E (1/16") on alumina	21% Wo_3, 6.5% NiO, Surface Area = 200 M^2/g Pore Volume = 0.62 cc/g
MSU	STK-7 E 1/8"	17.1% MoO_3, 1.5% NiO, 1.4% Co_3O_4 on Norton 6176 alumina
MSU	STK-5-2-1 E 1/16"	23.9% MoO_x, .75% CoO_x, .48% NiO_x on Norton 6176 alumina

COED PYROLYSIS OIL - S. Kujawa

SUMMARY OF TECHNICAL PROGRESS

Tables 1-3 and 1-4 summarize progress previous to this quarter. Table 1-5 describes the catalysts used in this project.

For batch runs, a silica alumina nickel tungsten catalyst has given best all around performance, followed closely by a catalyst made at Montan State University consisting of colbalt, nickel, and molybdenum on alumina.

THe nickel tungsten catalyst has also shown best performance so far in a continuous run, however, the run conditions have been changed to reduce mass transfer effects, thus, the catalyst will have to be retested at the new conditions before any conclusions can be made about it.

Eight batch and four continuous tests were made during this reporting period. The batch tests were of catalysts made at MSU being primarily of nickel-moly on alumina with one or two additional promoters. The continuous tests were of four commercial cobalt molybdate catalysts of which Shell 344 and Harshaw HT-400 both removed over 90% of the sulfur in the tar feed when run at the conditions of 410^{o}C, 800 psi, and LHSV=1.5. Nitrogen removal for the two catalysts was 25-45% at LHSV=1.3.

OBJECTIVES DURING THIS QUARTER

During the period of March through May, 1977, the following was accomplished:

1. Batch tests were made on eight MSU-made nickel-moly plus promoter catalysts.

2. Continuous tests were performed on the cobalt-moly catalysts: Shell 344, Harshaw HT-400, Houdry HR-801, and CCI C20-6.

Sulfur and nitrogen removal are given for the above tests. Product distillations haven't been performed at the time of this report.

DETAILED RESULTS

1. Batch Tests

   Table 1-1 gives the results of heteroatom removal and hydrogen consumption for eight catalysts. The purpose of the work was to see if an additional promoter on a basic nickel-moly catalyst would improve nitrogen removal. Although none of these catalysts performed as well as the colbalt-nickel-moly catalysts previously reported (Table 3), five of them show sufficient promise to be tested continously.

2. Continuous Tests

Tests were made during the quarter previous to this that suggested that significant diffusion effects existed in the continuous runs. These effects could cause erroneous conclustions of catalytic activity in a screening project such as this. To reduce the diffusional effects two things were done:

a) The temperature that the catalysts were tested at was reduced. Hopefully, this will make film diffusion negligible; pore diffusion will still be a significant factor. This means that the pore volume distribution of the support will be as significant as the metal type and surface area of the catalyst.

b) The catalyst was diluted 1:1 with inert support in the reactor. This should give a better approximation to plug flow by cutting down back mixing and hotspots in the reactor.

The catalysts tested were presulfided similiarly in a separate sulfiding reactor before each run. The run conditions were:

Temperature:	400 - 410^{o}C Inlet
Pressure:	800 - 830 psig
H_2 Feed Rate:	10,000 SCF/BBL

The sulfur and nitrogen removal for these runs is present in Table 1-2 along with the significant run data. Figures 1-1 and 1-2 graphically depict the heteroatom removal versus space velocity for the colbalt molybdate catalysts tested.

A significant problem that arose during these runs and which is evident in Table II, is that the reactor temperatures are not easily controlled. At low space velocity, the reactor operates isothermally, while at higher space velocities the temperature rise became as much as 45 centigrade degrees through the bed. In future runs it will be attempted to reduce this rise as much as possible.

Colbalt molybdate catalysts are used primarily to remove sulfur from petroleum stocks. Harshaw HT-400 and Shell 344 are designed for gas oils and vacuum gas oils; Houdry H R-801 is designated for cracker and reformer pretreat of Naphthas and other light stocks; and CCI C20-6 is also used on light stocks. Since COED pyrolysis oil is somewhat similiar to heavy vacuum gas oil, it is to be expected that the Harshaw and Shell catalysts would perform better on this feed. As can be seen in Figure 1, this is exactly what happened. The Shell and Harshaw catalysts removed approximately the same amount of sulfur, which was about 30% higher in all cases than the Houdry and CCI catalysts.

The Shell and Harshaw catalysts were run at approximately a 10^{o} higher bed inlet temperature, which could account for their higher sulfur removal than the other two catalysts. Hbwever, by looking at specific space velocities, i.e., 2.46 in run 30 versus 2.13 in run 49, the temperatures and other conditions are close enough to show that the Harshaw catalyst is more active than the Houdry catalyst, and this can be done throughout the runs to show that the Shell and Harshaw catalysts are more active.

High nitrogen removal is not expected for colbalt-moly catalysts. The maximum removal was 44% at LHSV=1.27 for Harshaw HT-400, this being close to the best nitrogen removal in a continuous run at that space velocity so far.

The Shell catalyst performed similiar to the Harshaw catalyst for nitrogen removal, and removed more at the higher space velocities. The CCI and Houdry catalysts both left more nitrogen in the product than in the feed; this probably being due to selective cracking and desulfurization.

The reasons why the above catalysts performed as such are unclear as yet. The pore volume distribution and metal surface areas of these are not now known, so that all that can be said is that Harshaw HT-400 and Shell 344 are the best of the cobalt molybdate catalysts so far tested.

CONCLUSIONS FROM THIS QUARTERS WORK

1. Harshaw HT-400 and Shell 344 cobalt molybdate catalysts have so far given the best sulfur removal in continuous runs. Nitrogen removal for these two catalysts is as good as previous runs.

2. Five of the catalysts batch tested will be remade on smaller supports and tested in continuous runs. None of these removed as much nitrogen as the previously tested MSU cobalt-nickel-moly cata lyst.

PROJECT FORECAST - COED PYROLYSIS OIL

During the next quarter, continuous runs will be performed on cyanamides AERO HDS-20 cobalt moly catalyst, five various Harshaw and Ketjen nickel tungsten catalysts, and five nickel moly catalysts of various manufacture. Attempts will be made to run these at 410°C and as nearly isothermal as possible.

TABLE 1-1

BATCH[2] RUN DATA SUMMARY

RUN NO.	CATALYST DESCRIPTION				H_2 CONSUMPTION[3]	SULFUR[4]		NITROGEN	
		Mo	Ni	Promoter	p.s.i.	In Prod %	% Removal	In Prod %	% Removal
40	STK-10	18.9	2.6	1.7% Co 0.9% Fe	1710	.37	84	.76	16
41	STK-8-2	9.5	1.4	11.2% W	1740	.51	78	.77	14
42	STK-11	11.0	1.2	3.7% Cr	1650	.41	82	.82	9
43	STK-14	17.4	2.3	1.8% Cu	1790	.34	85	.77	15
45	STK-9	21.0	0	2.0% Zn	1690	.71	69	.83	8
46	STK-12	17.8	2.0	1.7% Zn	1640	.31	87	.76	16
47	STK-13	11.0	3.0	0.5% Fe	1850	.37	84	.75	17
48	STK-8-1	8.6	1.4	11.0% W	1710	.54	77	.79	12

1. All supports Norton 6176, 1/8" Alumina Pellets. Metal oxide weight percents shown. Presulfided before reaction.

2. Batch runs:2200 psi H_2 initial, 450C run temperature, 1/2 hour at 450C.

3. H_2 consumption is the difference between the cold charge and cold final pressure in p.s.i.

4. Containing 2.3% sulfur and 0.9% nitrogen in feed.

TABLE 1-2

CONTINUOUS RUN DATA SUMMARY(1)

RUN	CATALYST(3)	LHSV	H_2:OIL(2)	CAT. BED TEMP(4) TOP	BOTT.	SULFUR % In Prod.	% Removal	NITROGEN % In Prod.	% Removal
39	Harshaw, HT-400 Cobalt Moly	1.13	10,500	405	425	.12	95	.61	32
		1.27	9,400	410	430	.14	94	.5	44
		2.46	10,300	391	425	.27	88	.88	2
		2.56	8,000	405	435	.20	91	.98	0
		2.64	9,600	390	420	.29	87	.89	1
44	Shell 344 Cobalt Moly	1.27	9,700	410	410	.13	94	.64	29
		2.06	10,200	395	412	.27	88	.76	16
		2.84	7,300	390	430	.36	84	.81	10
49	Houdry, HR-801 Cobalt Moly	1.46	9,400	390	400	.83	64	.91	0
		1.49	9,200	385	395	.89	61	.94	0
		2.13	10,400	392	415	.86	63	.93	0
50	CCI, C20-6 Cobalt Moly	1.01	10,200	410	410	.59	74	.93	0
		1.82	10,300	400	415	.89	61	.96	0
		2.58	9,800	380	410	1.08	53	.94	0

1. Run condition catalyst presulfided, pressure:800 psig.
2. H_2:Oil in SCF/bbl
3. Catalysts described in Table 3
4. Bed temperature rise in degrees centigrade.

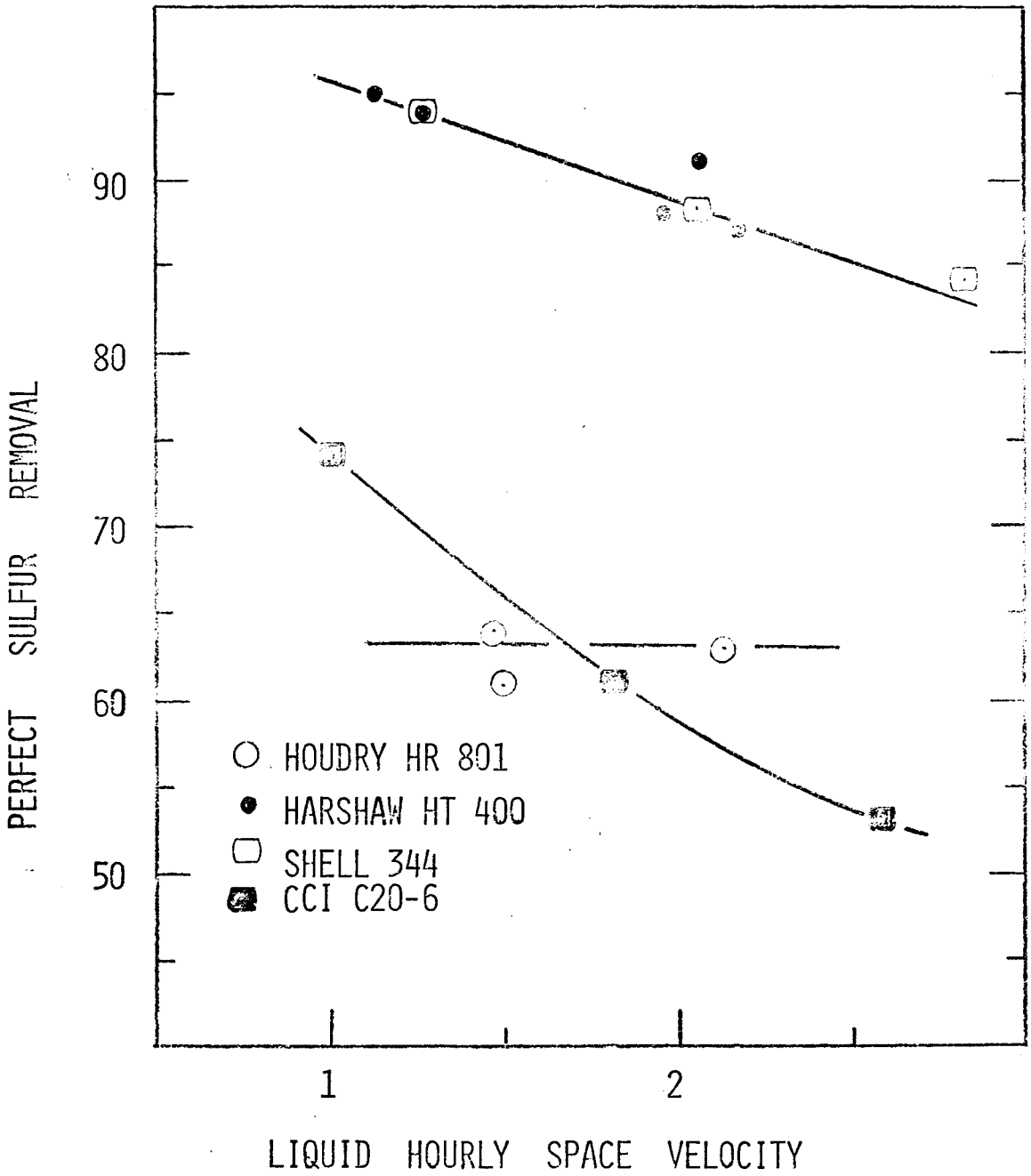

PERFECT SULFUR REMOVAL
90
80
70
60
50
HOUDRY HR 801
HARSHAW HT 400
SHELL 344
CCI C20-6
1
2
LIQUID HOURLY SPACE VELOCITY

FIGURE 1 - 1

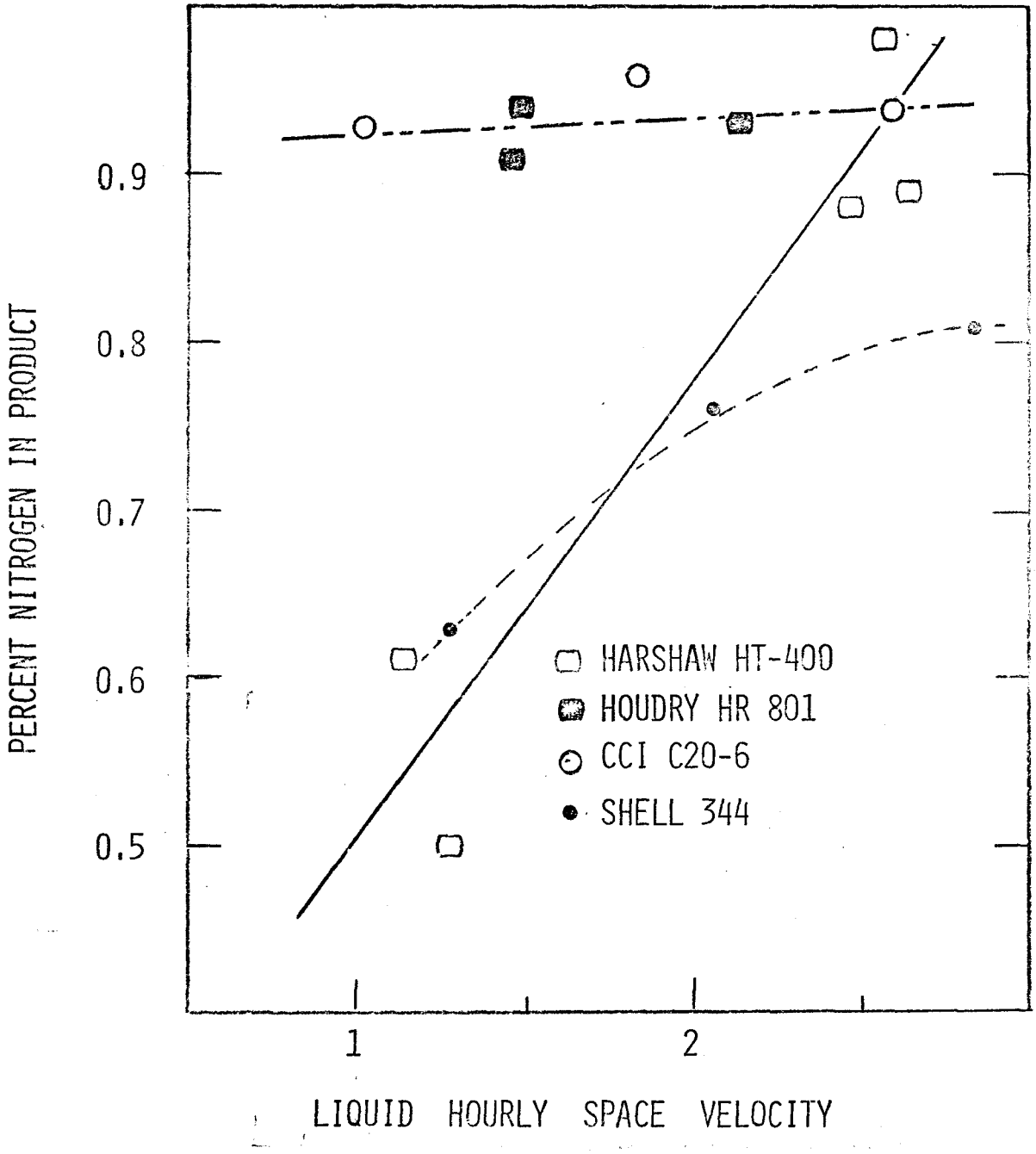

PERCENT NITROGEN IN PRODUCT
0.9
0.8
0.7
0.6
0.5
1
2
LIQUID HOURLY SPACE VELOCITY
HARSHAW HT-400
HOUDRY HR 801
CCI C20-6
SHELL 344

FIGURE 1 - 2

TABLE 1 - 111 BATCH RUN DATA SUMMARY[3] = COED TAR FEED

Run No.	Catalyst	% Desulfurization	% Denitrogenation[2]	ASTM DISTILLATION IBP-425F	425-600F	600-700F	D-86 (Vol %) Yield
Cobalt-Moly Catalysts[4]							
15	Harshaw CoMo 0401	80	28	16	29	22	67
37	Shell 344	86	29	19	26	24	69
Nickel-Moly Catalysts							
19	Harshaw HT-100	83	31	15	28.5	21.5	65
26	Harshaw HT-500	78	14	15	19	31	65
36	Shell 324	86	24	17	26	24	67
Nickel-Tungsten Catalysts							
7	Harshaw Ni4401	91	64	18	24	23	65
13	Harshaw Ni4301	80	24	16	28.5	21.5	66
18	Harshaw Ni4303	84	7	17.5	28.5	23	69
27	Ketjen HC-5	81	22	18	24	24	66
28	Ketjenfine 330-3E	85	22	17	25	25	67
Cobalt-Nickel-Moly Catalysts							
33	M.S.U. STK-5	86	29	18.5	24.5	28	71
34	M.S.U. STK-6	86	27	18	26	25	69
Others							
11	Harshaw Ni1601	44	23	9.5	24	24	57
14	Harshaw Ni3250	84	7	17.5	28	22	67
20	Harshaw Mo-1201	63	9	13	30	20	63
21	Harshaw W-0801	40	0	14	24	20	58

Notes: 1 yield:volume percent collected after drain of condenser as per ASTM D-86 at 700F, 640 mmHg

For COED Feed, ASTM D86 Data	IBP-425	425-600	600-700	yield
	3	22	31	53

2. COED feed contains 2.3 wt% sulfur and 0.9 wt % nitrogen
3. Batch run conditions: 2200 psig initial H_2, 450°C run temperature;1/2 hr at run temperature
4. See Table 1-V for catalyst description

Table 1 - 1V CONTINUOUS RUN DATA SUMMARY[2], COED TAR FEED

Run	Catalyst	LHSV	H_2:Oil[1]	%S in Prod.	% N in Prod.	ASTM D 86 Vol. % IBP-425F	426-600F	600-700F	Yield
4	CCI-C20-6	2.25	5000	.60	.602	13	28	17	59
		2.25	7000	.64	.84	16	31	25	72
6	Harshaw Ni4401	.8	6000	.56	.57	25	32	27	79
		1.7	11000	.70	.61	14	28	27	69
		3.1	9000	.78	.61	16	32	22	71
10	Harshaw Ni1600	.28	34000	1.2	.55	6.8	27.2	25	59
		.40	46000	1.39	.58	1.9	31.1	23	56
		.83	28000	1.51	-	6	32	23	61
25	Harshaw CoMo0401	4.26	10000	1.16	.95	not yet completed			
		3.72	10000	1.02	.92				
		2.5	10000	.86	.94				
		.93	10000	.36	.81				
35	Harshaw CoMo0401	.55	10000	.27	.4				
		.42	10000	.23	.58				
38	Harshaw CoMo0401	3.59	10000	1.1	.95				
		2.62	10000	1.08	.98				

Note: 1 H_2:Oil in scf of H_2 per bbl oil

2 run conditions: temperature 450°C for 4, 6, 10
temperature 420°C for 25, 35, 37
pressure: 1000 psi #6, others 800 psi.

TABLE 1-V

CATALYST DESCRIPTION

Harshaw CoMo 0401 T 1/8	3% CoO, 9% MoO_3 on silica alumina
Harshaw HT 100	3.8% NiO, 16.8% MoO_3 on silica alumina
Harshaw HT 500	3.2% NiO, 16% MoO_3 on alumina
Harshaw Ni 4401	6% NiO, 19% WO_3, 50% SiO_2, 25% Al_2O_3
Harshaw Ni 4301	6% NiO, 19% WO_3 on silica alumina
Harshaw Ni 4303	6% NiO, 19% WO_3 on alumina
Harshaw Ni 1601	3% NiO, 3%CoO, 3% Fe_2O_3 on alumina
Harshaw Ni 3250	50% Nickel
Harshaw Mo-1201	10% MoO_3 on alumina
Harshaw W 0801	10% WO_3 on alumina
Harshaw Ni 1600	3% CoO, 3% NiO, 3% Fe_2O_3 on silica alumina
Shell 324	3% NiO, 13% MoO_3
Shell 344	2.4% CoO, 9.9% MoO_3
Ketjen HC-5	6.5% NiO, 21% WO_3 on alumina
Ketjen Ketjenfine 330-3E	6.6% NiO, 19.8% WO_3, 1.2% SiO_2 on alumina
MSU-STK-5	1.2% CoO, 0.4% NiO, 18.2% MoO_3 on alumina
MSU STK-6	1.5% CoO, 1.2% NiO, 18% MoO_3 on alumina
CCI-C20-6	4% CoO, 15% WO_3 on alumina
Harshaw HT 400 E1/16"	3% CoO, 15% MoO_3, on alumina S.A. = 220 M^2/g, P.V. = .55cc/g
Houdry, HR 801	3% CoO. 15% MoO_3, on alumina S.A. = 300 M^2/g, 1/16" extrudates
Norton 6176 Alumina Supports	Alumina Supports. Al_2O_3(>99.85%) NaO_2(<0.014<) SiO_2(<0.12%) Fe_2O_3(<0.065%) S.A. = 250±20 M^2/g, P.V. - 0.8-101 cc/gr before impregnation.

CONVERSION OF SYNTHOIL TO CLEAN DISTILLATE FUELS - K. N. Runnion

RESULTS AND DISCUSSIONS

Twenty-eight rocking bomb autoclave tests were performed on twenty-four commercial catalysts and one chloride catalyst impregnated on a support at Montana State University. Continuous runs were made on eight catalysts in nine runs.

The products from each run were analyzed for cracking by ASTM atmospheric distillation. Heteroatom removal was determined by the quartz tube method for sulfur and the Macro Kjeldahl method for nitrogen.

The data and results from the runs are presented in the Appendix. All the catalysts tested in bomb runs are described by manufacturer, size, metal loading, support, and support properties in Appendix A. The data from the bomb runs is given in Appendix B. Appendix C lists the continuous run catalysts, data, and results.

This section will discuss the most important results from these appendices. The discussion is arranged mostly in chronological order with preliminary continuous runs, bomb runs, and then continuous runs.

Preliminary Continuous Runs

To determine if any hydrogenation and cracking have taken place and to give a quantitative comparison of the SYNTHOIL feed and run products, ASTM distillation of SYNTHOIL is used as a basis for comparison. Figure 1 is a distillation curve for SYNTHOIL. The percent SYNTHOIL is plotted vs. the temperature in degress Fahrenheit up to 700°F which is the end point for distillation at 640 mm. The

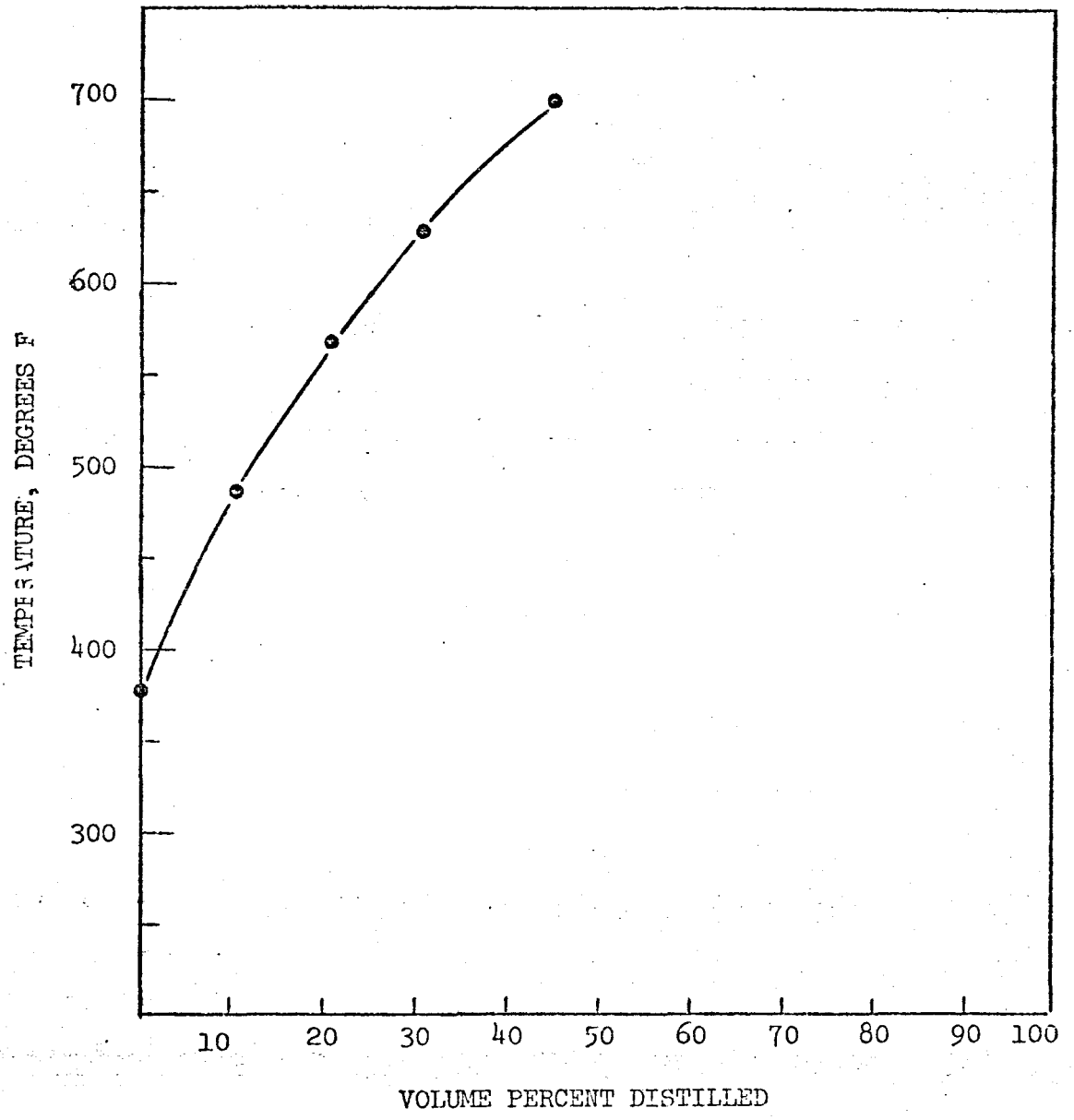


FIGURE 1. ASTM Distillation Curve for SYNTHOIL

objective of this research is to shift this curve to the lower right.

When the research was started, it was planned to test all catalysts in the continuous reactor. In the first reactor design both the liquid and gaseous products flowed through the back pressure regulator valve rather than being separated before the valve.

Figure 2 is a comparison of distillation of the SYNTHOIL feed and the product from Run 1. See Appendix C for continuous run data and results. SYNTHOIL was fed to the reactor at a liquid hourly space velocity (LHSV) of 4. The run conditions were a temperature of 450°C and a pressure of 800 psig. The catalyst was sulfided CCI catalyst C-20-6, Cobalt Molybdenum on silica activated alumina. A hydrogen flow rate of 5000 scf/bbl of feed was used.

Product 1 gave a small improvement in cracking in the lower range of distillation. The slope of the curve, however, is not as steep and gives an endpoint of 53%. This shows improvement in the higher boiling fractions and is a step in the right direction.

The run was ended before more variables could be tested due to plugging of the back pressure regulator valve with tar. It was theorized that uncracked SYNTHOIL tar was causing the plugging. So the run was repeated using a higher pressure and lower LHSV to try to increase conversion.

Run 2 was made using the same Co-Mo catalyst as in Run 1. Run conditions were 450°C and 1000 psig hydrogen pressure. A hydrogen

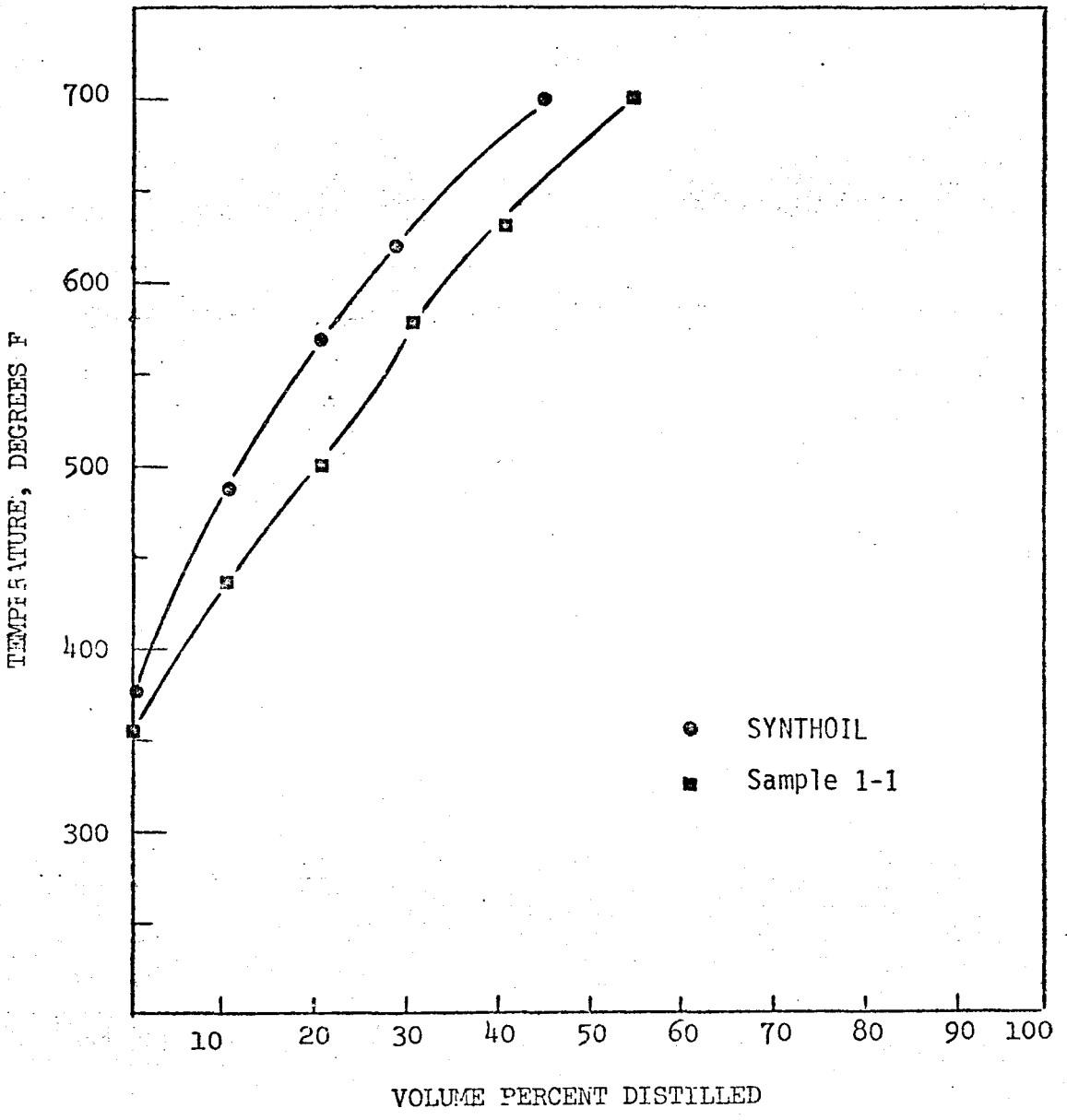


FIGURE 3. ASTM Distillation, Run 1
Catalyst: CCI C-20-6; 4% CoO, 15% MoO_3 on Alumina

flow rate of 10,000 scf/bbl was used.

Products 2-1 and 2-2 are graphed in Figure 3. For product 2-1, SYNTHOIL was fed at a LHSV of 1.4. This product was very noticeably liquid compared to SYNTHOIL and the product from Run 1. Distillate started coming off at 250°F and 70% distilled off by the end point 700°F. This is a good improvement over SYNTHOIL. Percent desulfurization was 70%, while 24% of the nitrogen was removed.

Product 2-2 is under the same conditions only with an increase in LHSV from 1.4 to 3.0. The graph shows no improvement over the SYNTHOIL. No denitrogenation was noted, but sulfur was reduced 43%.

Again the run was ended due to plugging of the back pressure valve. Since conversion seemed to drop off with time during the run, the unreacted SYNTHOIL that was plugging the valve might be due to carboning up of the reactor. To test this theory, a temperature decrease from 450°C to 400°C was decided on for the next run.

Run 3 was made using sulfided Harshaw catalyst Ni-4401, Nickel-Tungsten on silica alumina. Run conditions were a temperature of 400°C and a pressure of 800 psig. Hydrogen flow rate was 10,000 scf/bbl. SYNTHOIL was fed at a LHSV of 1. The product from Run 3 and the feed are plotted on Figure 4. Distillate started coming off at about the same temperature as SYNTHOIL. End point gave 62 volume percent distilled. Heteroatom removal was negligible.

Plugging of the back pressure regulator valve ended the run.

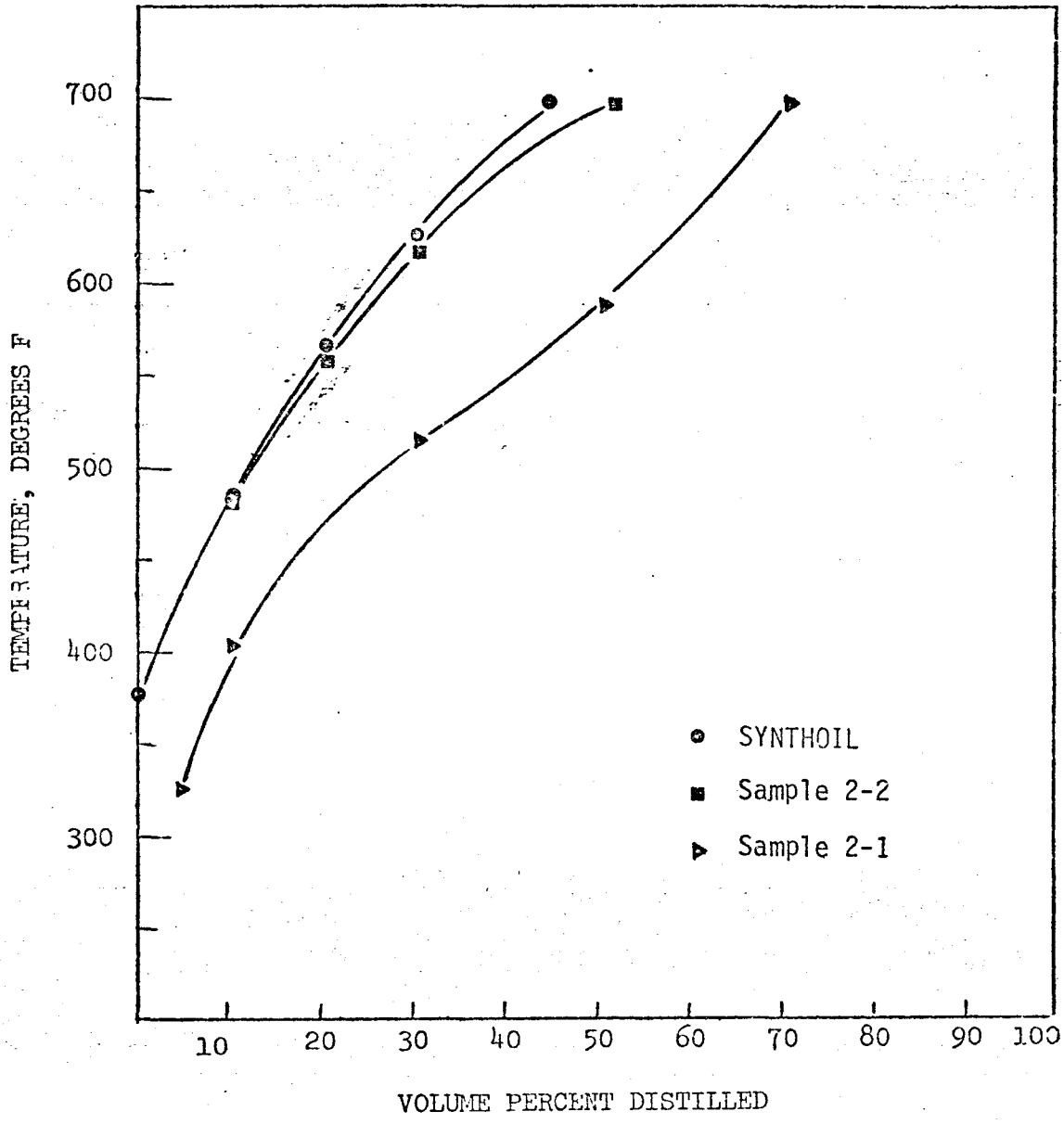


FIGURE 3. ASTM Distillation, Run 2
Catalyst: CCI C-20-6; 4% CoO, 15% MoO_3 on Alumina

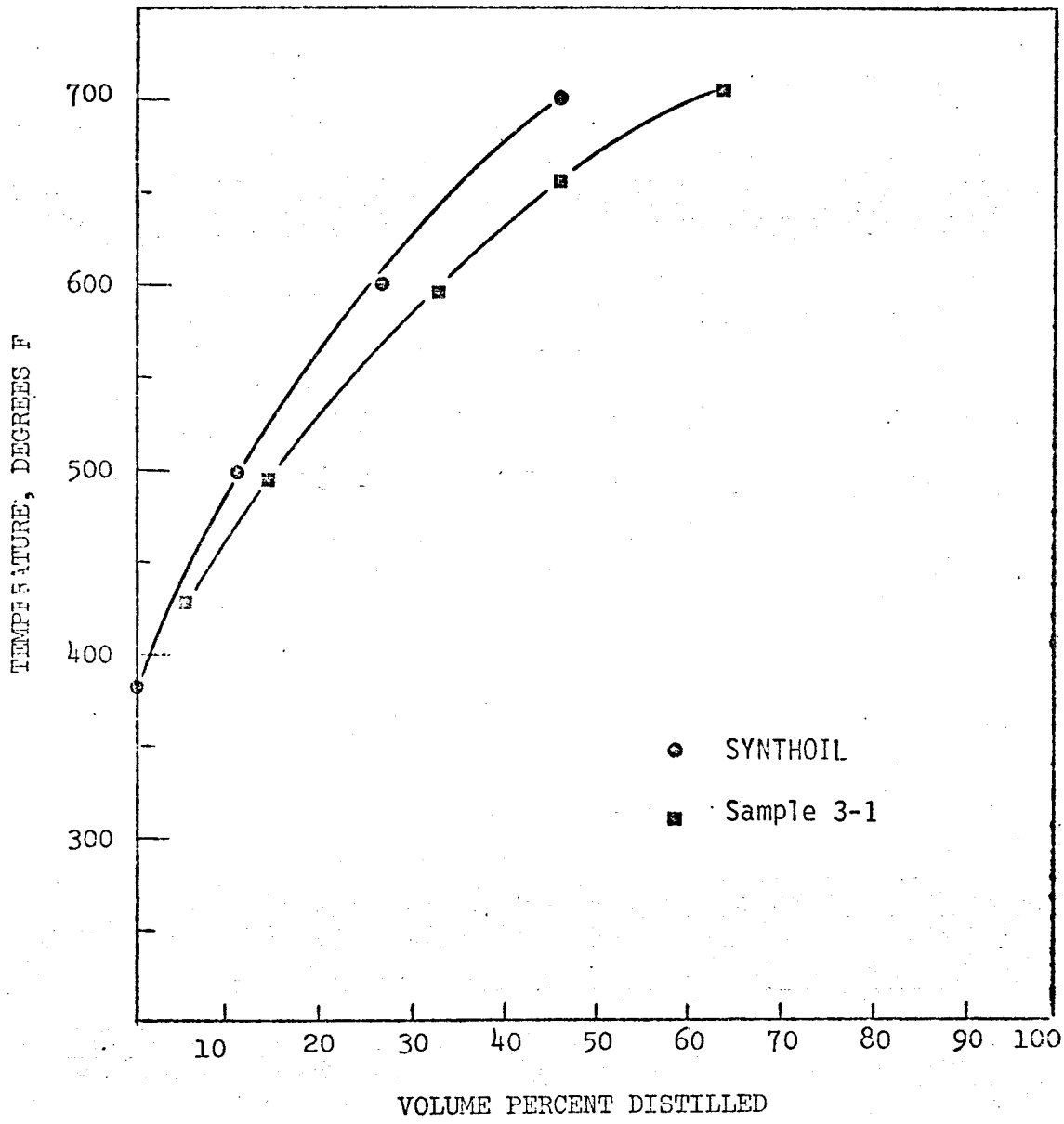


FIGURE 4. ASTM Distillation, Run 3
Catalyst: Harshaw Ni-4401; 6% Ni, 19% W on Silica Alumina

In these preliminary runs, the number one problem was plugging of the back pressure valve three to four hours into the run. This prevented any changing of parameters during the run, which would have supplied more data. Down time between runs to clean and recharge the reactor and to sulfide the catalyst was time consuming and cuts down on the number of runs that can be made.

Observations were made of the product collection and cleaning of the back pressure regulator valve and piping from the reactor to the valve. The first product that comes from the reactor was small continuous drops of oil. Gradually the drops change into spurts as the product surges out, then stops, then surges again. These spurts increase in intensity as they decrease in frequency. At the same time an increase in reactor pressure was noted from 10-50 psig between surges and then drops back to operating pressure with each surge of the product. The run is ended when the reactor pressure increases 100-200 psig above the back pressure without any product coming off. When the reactor was taken apart for cleaning, the back pressure valve and piping from the reactor were full of tar which had to be drilled out because it had solidified.

It was theorized that the plugging problem was because the lighter fractions from the SYNTHOIL feedstock are easily driven off and hydrotreated. Some of the heavier fractions are also cracked and hydrotreated, but the tar residue that was left was too thick and

viscous to flow through the back pressure regulator valve. The tar accumulates during the run until it blocks the flow of even the lighter oils.

To get around this problem the piping coming from the reactor was changed. Instead of running the gases and liquid product through the back pressure valve and collecting them, only the gases flowed through the valve. The gases and liquids were separated before the back pressure valve. The liquid product was collected at the bottom of the separator and the product drawn off in batches. No plugging problems were encountered in subsequent continuous runs using this modification.

Due to the time involved in setting up for a continuous run and cleaning up after, bomb autoclave tests were performed on several catalysts. The results from the bomb runs showed promise in predicting catalyst success, so it was decided that a bomb run should be made for each new catalyst tested. Data from the bomb runs would indicate if any improvement in cracking SYNTHOIL or heteroatom removal were made, and at what temperature reaction starts.

Bomb Runs

The twenty-five catalysts tested in bomb runs are listed in Appendix A. All catalysts tested except $SnCl_2$ (Run B11) are commercial catalysts. Most catalysts were dried and sulfided before

being loaded in the bomb. Non-sulfided catalysts will be pointed out in the discussion.

The bomb runs were operated at the same run conditions. An initial hydrogen pressure of 2000 ± 100 psig was used. The bomb was loaded in a rocking heater, heated to 450 ± 5°C, and held at this temperature for one hour. Runs B21, B23, and B24 were operated at lower temperatures.

Comparisons of the catalysts is a difficult problem. Each catalyst must be looked at in its entirety. The type, weight percent, and composition of promoters varies with each catalyst. The type and composition of the supports are also important, along with the physical properties of the support: form, surface area, and pore size. Looking at Appendix A, it can be seen how much the catalysts vary from each other. When one catalyst is said to be better than another, it must be remembered that these are specific catalysts so there may be problems in extrapolating the results to general classes of catalysts. This discussion will look at similarities among catalysts and try to draw some general conclusions where applicable.

The data for the bomb runs is presented in Appendix B. The hydrocracking results for each catalyst are listed as distillate yields in Table I . The ASTM distillation results are broken down into four products as follows: (1) % Naphtha (IBP - 425°F), (2) % Fuel oil (425-600°F), (3) % Gas Oil (600-700°F), and (4) % Residue

TABLE I BOMB RUN DISTILLATE YIELDS

Run #	Catalyst	% Naphtha IBP-425°F	% Fuel Oil 425-600°F	% Gas Oil 600-700°F	% Residue 700°F+	Total Vol. % Distilled
	SYNTHOIL	4	20	20	56	44
B8	Ni-1600	5	17	19	59	41
B17	Cr-0103	6	18	19	57	43
B18	Cr-0105	5	20	19	56	44
B13	W-0801	6	22	18	54	46
B23	Ni-4301	7	21	19	53	47
B19	Ni-3210	5	23	19	53	47
B14	Mo-1201	10	22	17	51	49
B27	HC-5-1.5E	6	20	23	51	49
B1	Ni-4401	6	23	20	51	49
B9	Ni-3250	8	20	21	51	49
B12	HT-100	10	22	18	50	50
B29	Shell 344	8	21	21	50	50
B3	Ni-1800	4	23	24	49	51
B21	W-0101	6	25	20	49	51
B2	Ni-1601	7	22	22	49	51
B11	$SnCl_2$	8	24	21	59	51
B28	Shell 324	10	21	21	48	52
B24	Ni-4301	7	22	23	48	52
B7	Ni-4303	12	22	20	46	54
B26	330-3E	12	22	20	46	54
B10	Ni-0104	9	23	22	46	54
B6	C-20-6	10	21	25	44	56
B15	W-0101	23	25	9	43	57
B20	CoMo-0603	9	25	27	39	61
B5	Ni-4301	9	24	28	39	61
B22	HT-400	10	24	30	36	64

TABLE I (Cont). BOMB RUN DISTILLATE YIELDS

Run #	Catalyst	% Naphtha IBP-420°F	% Fuel Oil 425-600°F	% Gas Oil 600-700°F	% Residue 700°F+	Total Vol. % Distilled
B4	CoMo-0401	11	23	31	35	65
B25	HT-500	11	25	29	35	65

Note: Catalysts listed by run numbers and manufacturers identification numbers. Catalyst descriptions given in Appendix A.

(700°F+). The catalysts are arranged in increasing order of total volume percent distilled. The first line is the SYNTHOIL feed distillation results.

Looking at Table I, no general trends as to what makes a good catalyst are obvious. Of the six best hydrocracking catalysts, all are made by Harshaw. Three are CoMo catalysts (CoMo-0603, HT-400, CoMo-0401) and there are one each of W (W-0101), Ni-W (Ni-4301) and Ni-Mo (HT-500). Two catalysts have supports of silica alumina (CoMo-0401 and Ni-4301). The other four supports are alumina. The products from these catalysts were liquid at room temperature and flowed easily.

Cracking shows about the same trend for all the "best" hydrocracking catalysts except W-0101. Good yields in Naphtha and gas oil ranges were obtained, with a small increase in fuel oil. W-0101 gives more than twice the yield of Naphtha and less than half the yield of gas oil.

The two best hydrocracking catalysts, Harshaw catalysts CoMo-0401 and HT-500, are graphed in Figure 5. The distillation graph for W-0101 is shown in Figure 6.

Harshaw Ni-W catalysts were tested in Runs B5 (Ni-4301) and B7 (Ni-4303). Both catalysts contain 6% Ni and 19% W. Ni-4301 on silica alumina support gives better hydrocracking than Ni-4401 on alumina support. The same trend can be seen for Ketjen catalysts

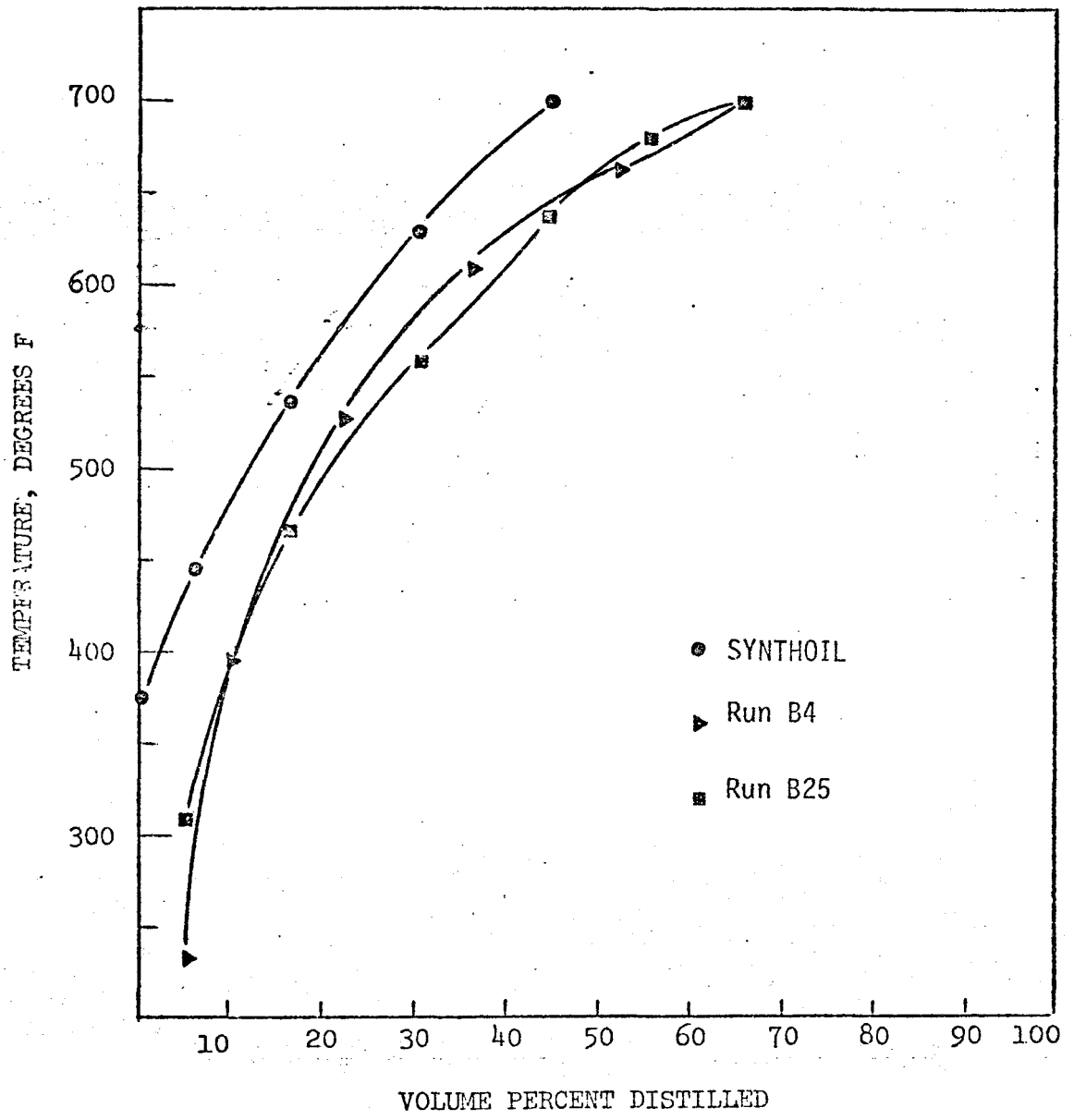


FIGURE 5. ASTM Distillation, Run B4 and Run B25
Run B4 Catalyst: Harshaw CoMo-0401
Run B25 Catalyst: Harshaw HT-500

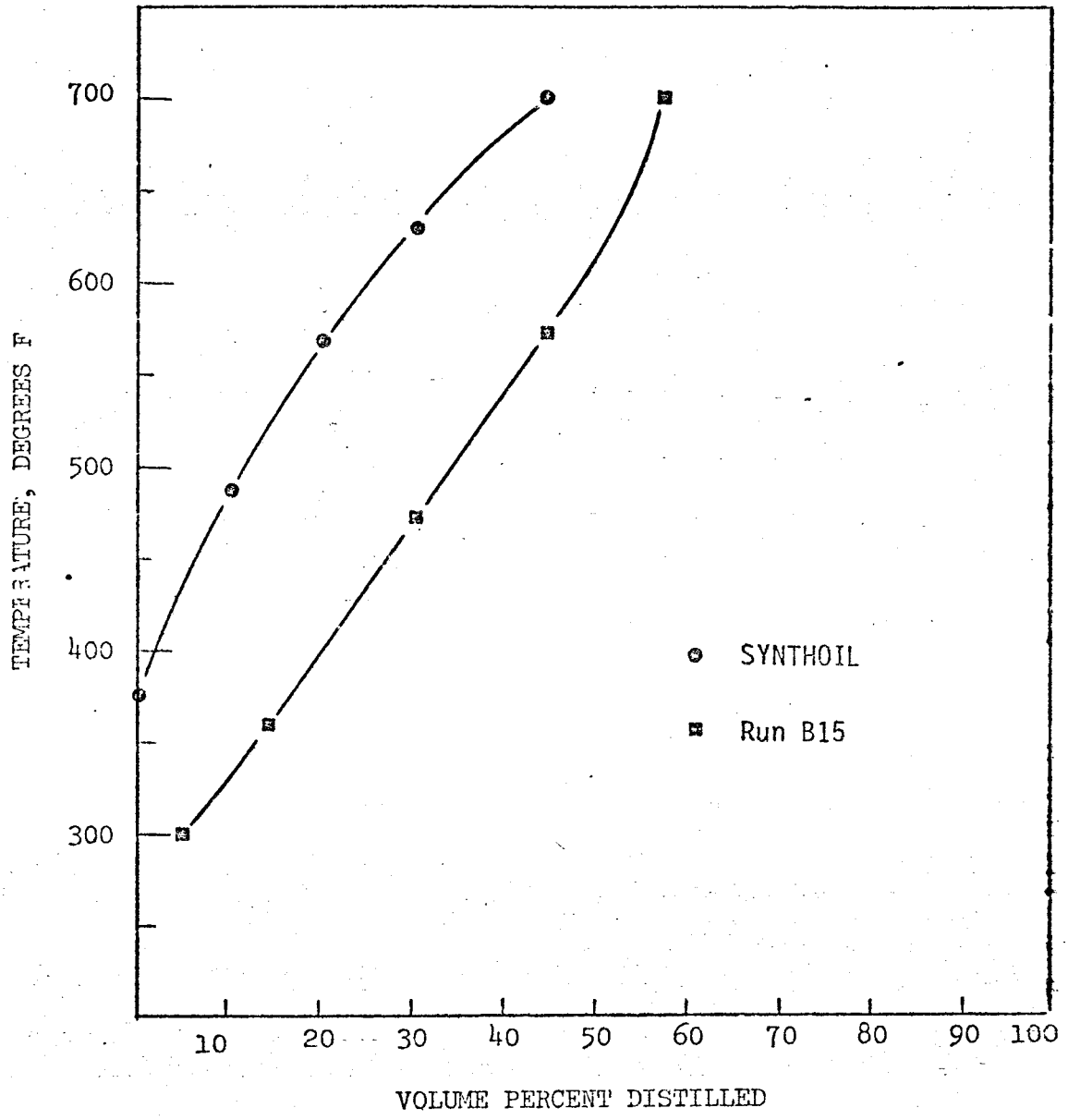


FIGURE 6. ASTM Distillation, Run B15
Catalyst: Harshaw W-0101; 10% WO_3 on Alumina

330-3E (6.2% NiO, 20% WO_3 on silica alumina) and HC-5-1.5E (6.5% NiO, 21% WO_3 on alumina). The silica alumina support did a better job of hydrocracking.

Heteroatom removal is also important in upgrading SYNTHOIL. Table V lists the heteroatom removal for bomb runs in order of increasing hydrocracking. No trends are obvious from the table.

The best desulfurization catalyst is Ni-0104, which is a powder containing 60% Ni on Kieselguhr. This catalyst was not presulfided. At the end of the run, the powder catalyst had to be chipped out of the bomb. A serious plugging problem would probably be encountered if a powder catalyst were tried in the continuous fixed bed reactor.

One other catalyst that was not presulfided Ni-3250, also gave good desulfurization results. This catalyst is very interesting because it has an alkaline support while most catalysts are slightly acidic.

Sulfided catalysts Shell 324 (NiMo) and Harshaw CoMo-0603 gave better than 50% desulfurization.

Denitrogenation is much more difficult than desulfurization. The two best hydrocracking catalysts gave the best denitrogenation results. The catalysts are CoMo-0401 and HT-500 (NiMo).

Shell catalyst 344 (CoMo on alumina) gave the best heteroatom removal (48% deS and 32% deN). However, hydrocracking results with this catalyst were not very good.

TABLE 2. BOMB RUN HETEROATOM REMOVAL

Run #	Catalyst	Vol. % Distilled	% DeS	% DeN
B8	Ni-1600	41	07	10
B17	Cr-0103	43	00	05
B18	Cr-0105	44	05+	00
B13	W-0801	46	27	04
B23	Ni-4301	47	41	17
B19	Ni-3210	47	05	25
B14	Mo-1201	49	36	19
B27	HC-5-1.5E	49	25	23
B1	Ni-4401	49	41	18
B9	Ni-3250	49	50+	17
B29	Shell 344	50	48	32
B12	HT-100	50	36	18
B3	Ni-1800	51	16	00
B21	W-0101	51	09	00
B2	Ni-1601	51	07+	06
B11	$SnCl_2$	51	20+	10
B28	Shell 324	52	55	21
B24	Ni-4301	52	23	28
B7	Ni-4303	54	45	18
B26	330-3E	54	30	12
B10	Ni-0104	54	57+	16

TABLE 2 (Cont.) BOMB RUN HETEROATOM REMOVAL

Run #	Catalyst	Vol. % Distilled	% DeS	% DeN
B6	C-20-6	56	18	25
B15	W-0101	57	25	03
B20	CoMo-0603	61	52	25
B5	Ni-4301	61	32	29
B22	HT-400	64	34	13
B4	CoMo-0401	65	16	33
B25	HT-500	65	32	33

+ Catalysts not sulfided

Note: Catalysts listed by run numbers and manufacturers identification numbers. Catalyst descriptions given in Appendix A.

% DeS based on SYNTHOIL containing .44% S

% DeN based on SYNTHOIL containing 1.06% N

Bomb runs also supply data on temperature effects. ASTM distillation curves of Runs B5, B23, and B24 are graphed in Figure 10. These runs were made using the same Harshaw Ni-4301 catalyst and keeping all run conditions the same except the reaction temperature. Run B5 was operated at 450°C which is the usual reaction temperature. A decrease in hydrocracking is noted in going from 450°C to 418°C and finally to 400°C.

The heteroatom removal vs. temperature is also given in Figure 10. The percent denitrogenation decreases with decreasing temperature. The sulfur removal starts to show this trend, but the highest percent desulfurization is at the lowest temperature.

The bomb runs do a good job of screening catalysts to be tested in the continuous reactor.

Continuous Runs

Catalysts were tested in the continuous reactor to determine the effects of varying the LHSV, temperature, and hydrogen flow. The catalysts, data, and results for these runs are given in Appendix C.

Preliminary continuous reactor runs were plagued with plugging problems that caused the runs to end after only a short time on stream. A gas-liquid separator was installed after the reactor to alleviate the problem.

Comparing the bomb runs, Appendix B, to the "best" continuous

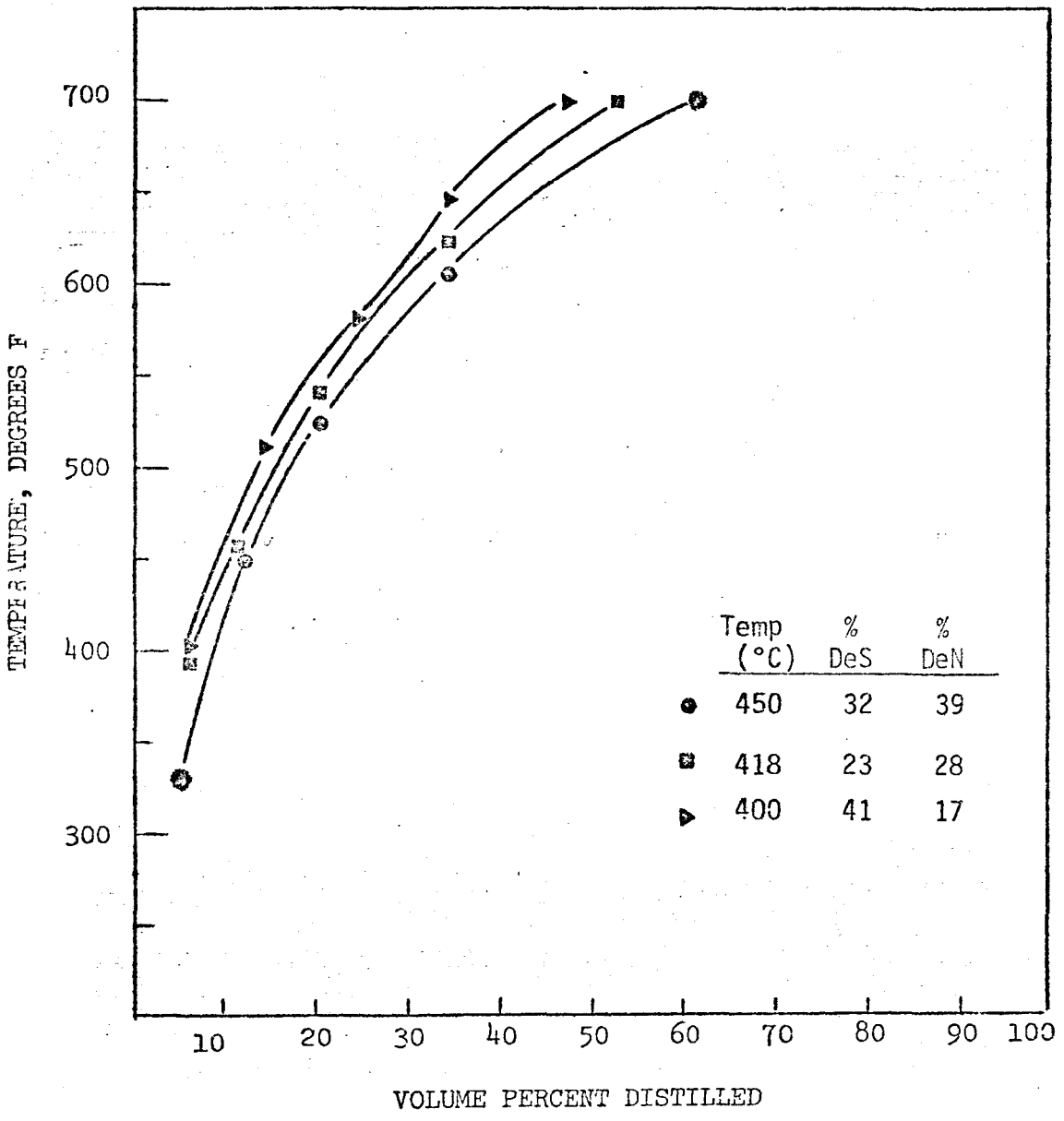


FIGURE 7 . Temperature Effects on Bomb Runs
Catalyst: Harshaw Ni-4301; 6% Ni, 19% W on Silica Alumina

products from Runs 4 through 9, Appendix C, for the same catalysts shows an improvement in hydrocracking and desulfurization for the continuous runs. Denitrogenation did not increase and in some cases decreased. The "best" continuous products were usually at LHSV around one.

Figures 8 and 9 are graphs of two of the "best" catalysts, in both the bomb and continuous runs.

Looking at Figure 8 for CoMo-0401 shows an increase in cracking in the middle fractions. Desulfurzation more than doubled from 16% to 50%. Denitrogenation decreased from 33% to an insignificant 4%.

Figure 9, for HT-500, indicates an increase in hydrocracking all along the curve. Again desulfurization more than doubled from 32% to 70%. The percent denitrogenation stayed approximately the same at 33% compared to 32%.

Four samples from Run 4 with the same hydrogen flow rate and varying LHSV are plotted in Figure 10. The graph shows that as LHSV is increased there is a trend of decreasing cracking. Sample 4-2 and 4-5 contradict, but the distillations are close together and so are LHSV's.

Figure 11 is a plot of the three samples from Run 5, at different LHSV with constant hydrogen flow rate. The trend of a decrease in cracking with an increase in LHSV is not observed for all samples. Sample 5-1 with a LHSV of 2.17 gives a better distillate than

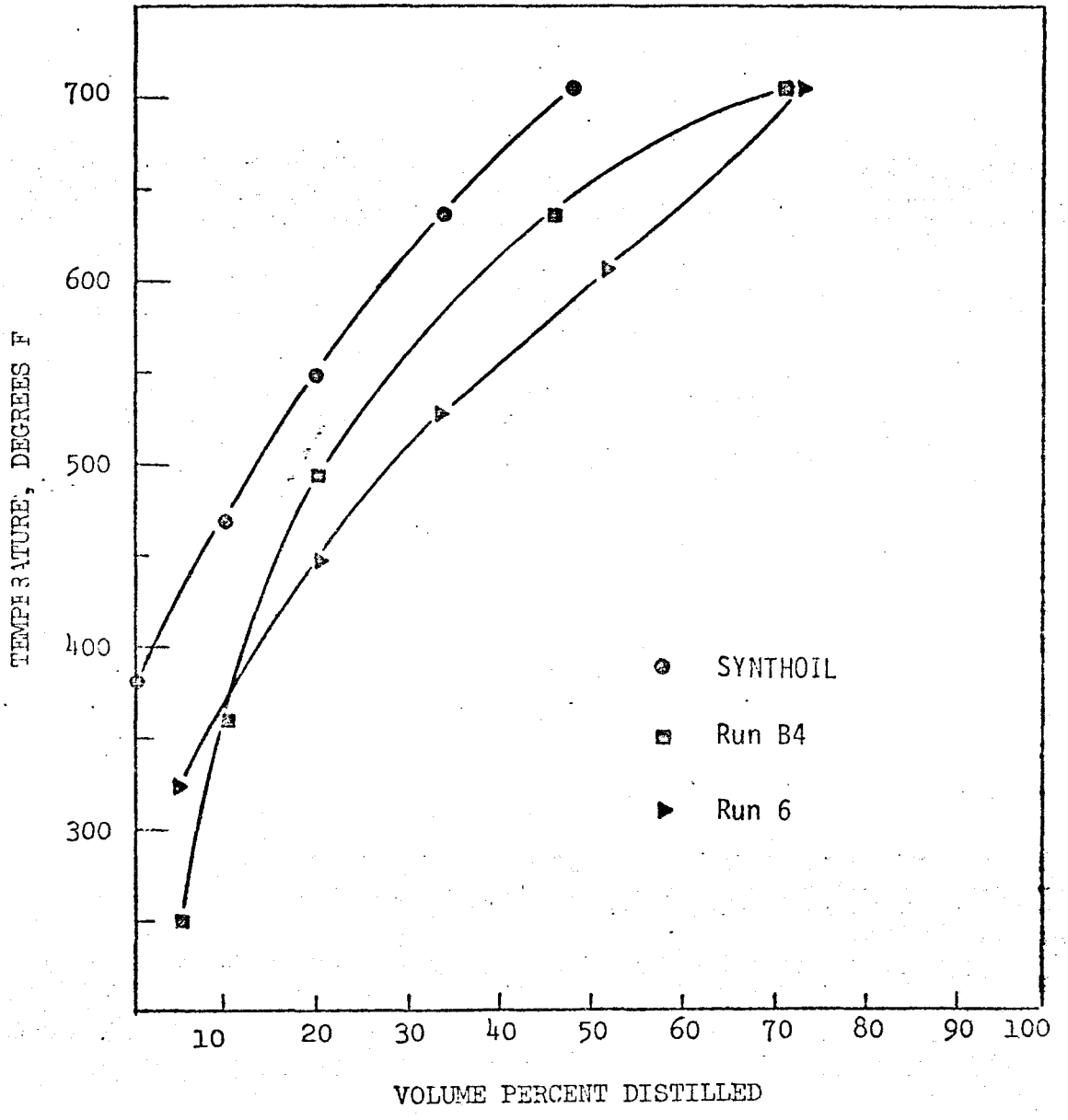


FIGURE 8 . ASTM Distillation, CoMo-0401
Catalyst: 3% CoO, 9% MoO_3 on Alumina

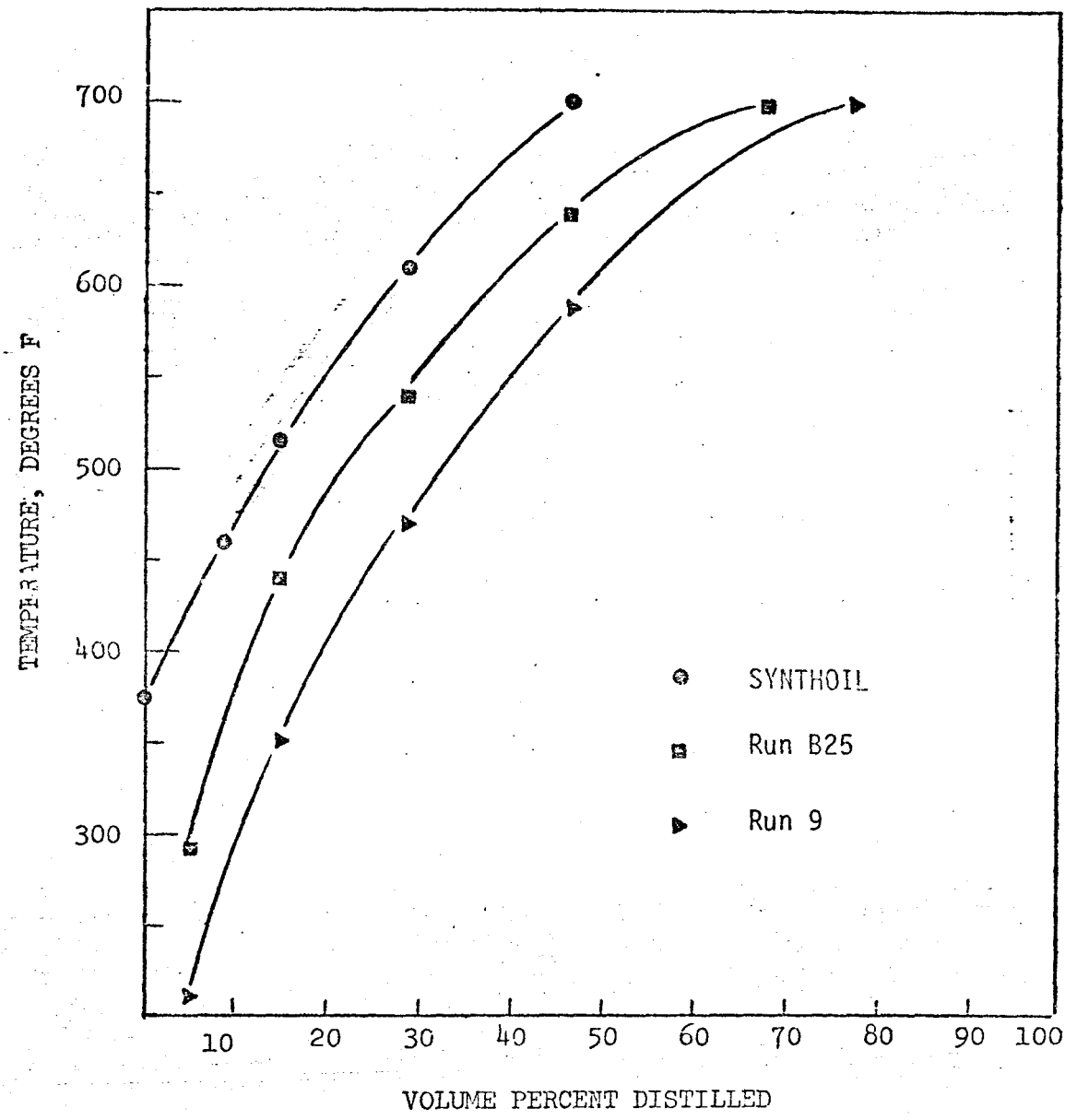


FIGURE 9. ASTM Distillation, HT-500
Catalyst: 3% NiO, 15.5% MoO_3 on Alumina

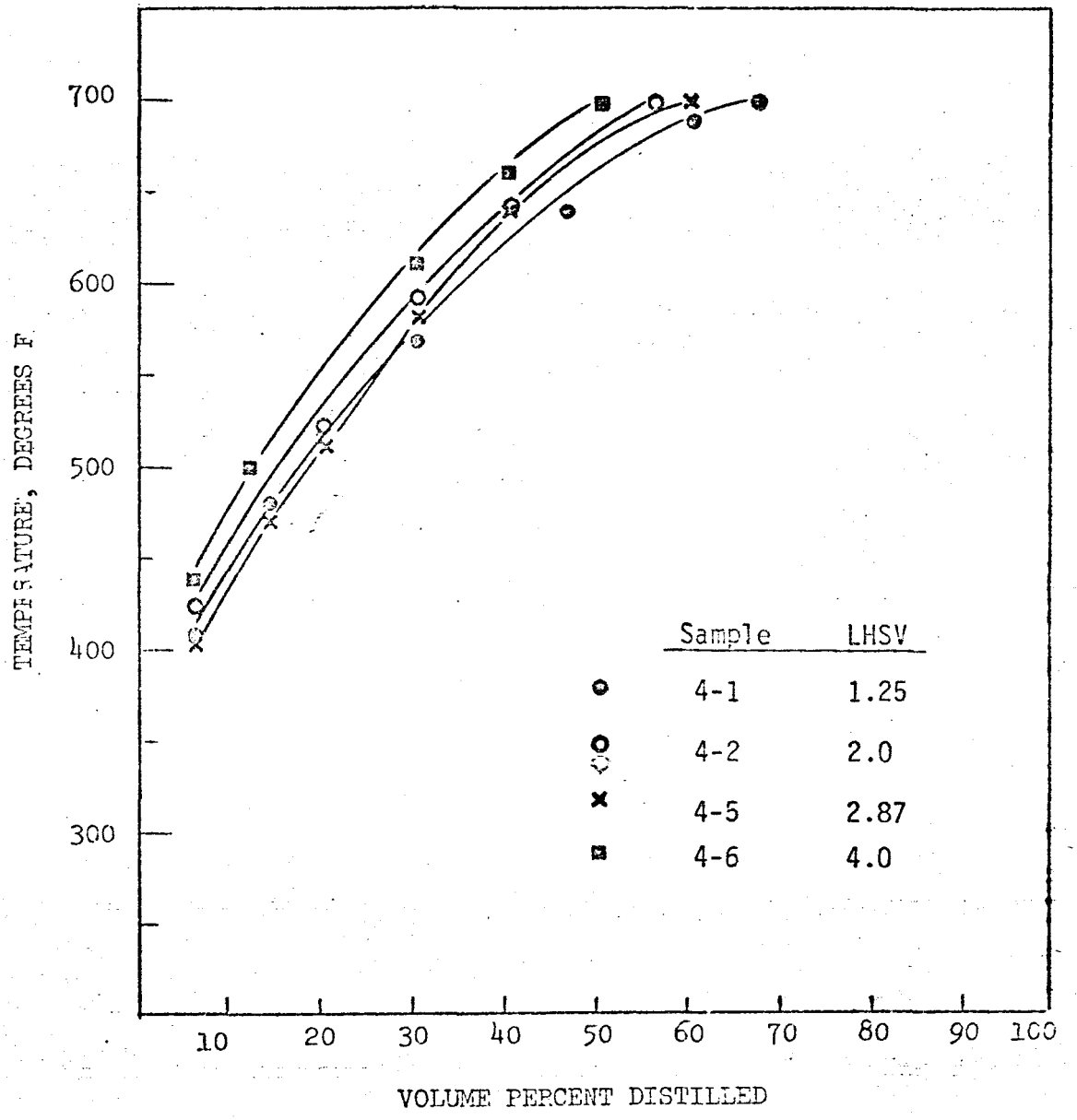


FIGURE 10. ASTM Distillation, Run 4
Catalyst: Harshaw Ni-1601
3% Ni, 3% Co, 3% Fe on Alumina

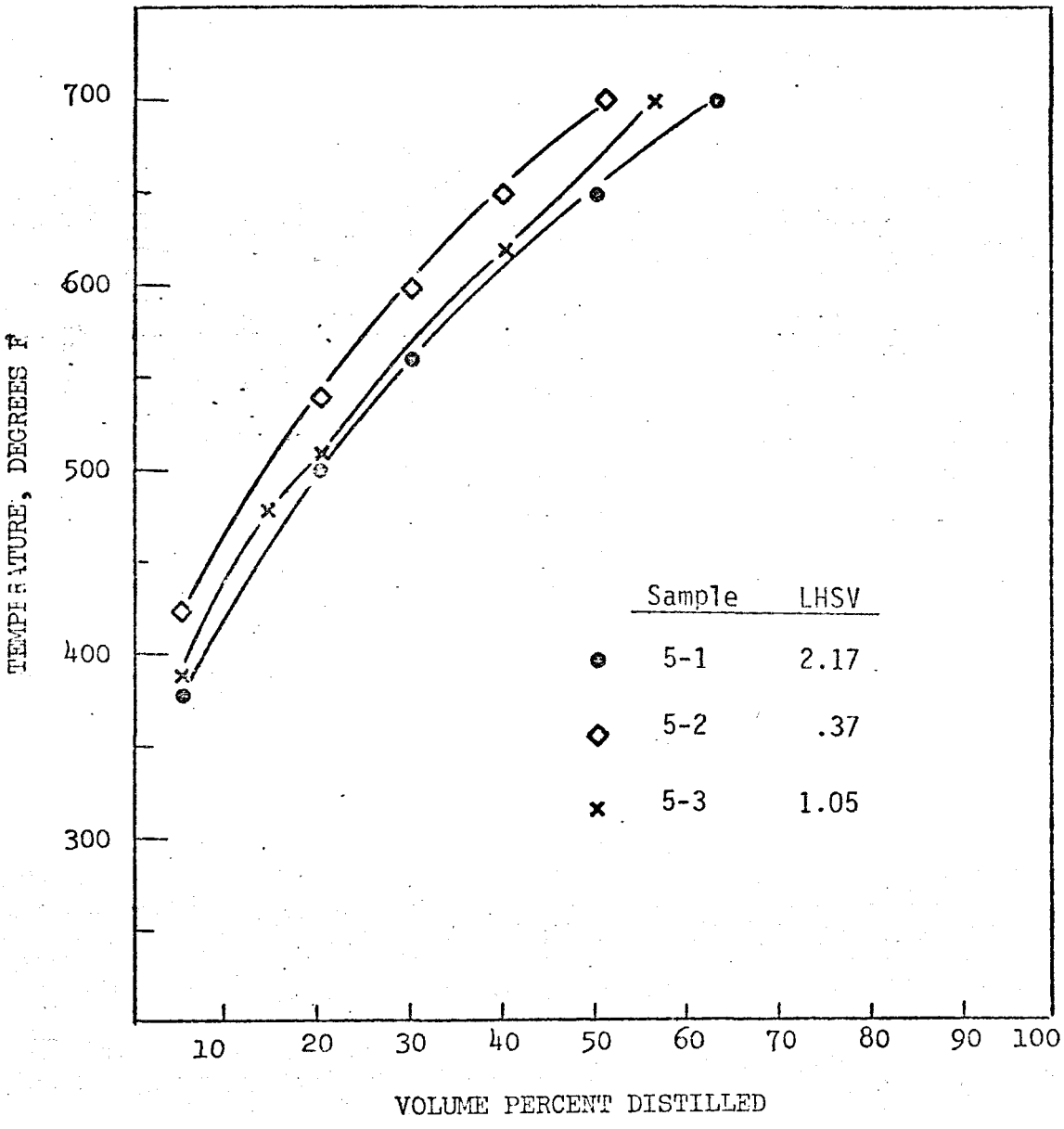


FIGURE 11. ASTM Distillation, Run 5
Catalyst: Harshaw Ni-3210
35% Ni on Proprietary Support

sample 5-3 with a LHSV of 1.05. No explanation is readily obvious. Looking at sample 5-2 with a LHSV of 0.37, its distillation curve is not very much improved over sample 5-1 as would be expected with the difference in LHSV. Some other phenomenum such as deactivity of the catalyst with time or possibly a decrease in hydrogen flow rate with time could produce these results. Hydrogen flow is controlled by a very fine micro-metering valve. This valve is calibrated before each run with a wet test meter and a calibration curve is drawn. Some variable could change during the run changing this calibration. For example, a restriction in the reactor which produces a larger back pressure than indicated on the back pressure regulator valve, would cause a decrease in hydrogen flow.

Run 6 looked at one of the better catalysts CoMo-0401. With constant hydrogen flow rates, the feed was varied to give different LHSV. The results are presented in Figure 12. It is quite evident that distillation results are inversely proportional to LHSV.

Figures 13-16 try to show some trends in heteroatom removal. Figure 13 is a plot of percent desulfurization vs. LHSV for three different catalysts. As can be seen the percent desulfurization decreases as the LHSV increases. The percent denitrogenation graphed in Figure 14 vs. the LHSV shows a general trend of increasing with increasing LHSV. Two data points contradict this statement, however.

Heteroatom removal vs. hydrogen flow rate is graphed in Figures

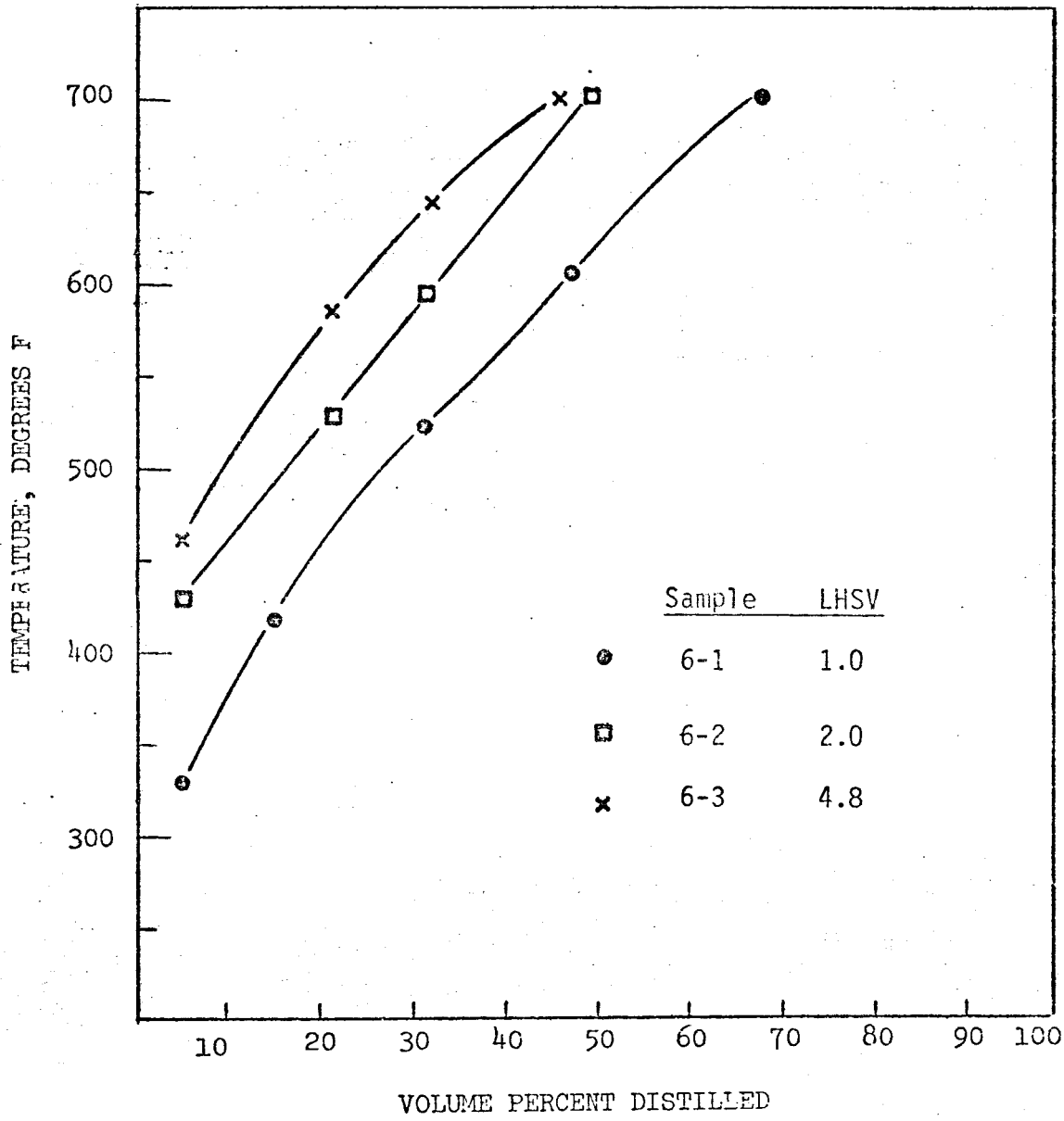


FIGURE 12. ASTM Distillation, Run 6
Catalyst: Harshaw CoMo-0401
3% CoO, 9% MoO_3 on Silica Alumina

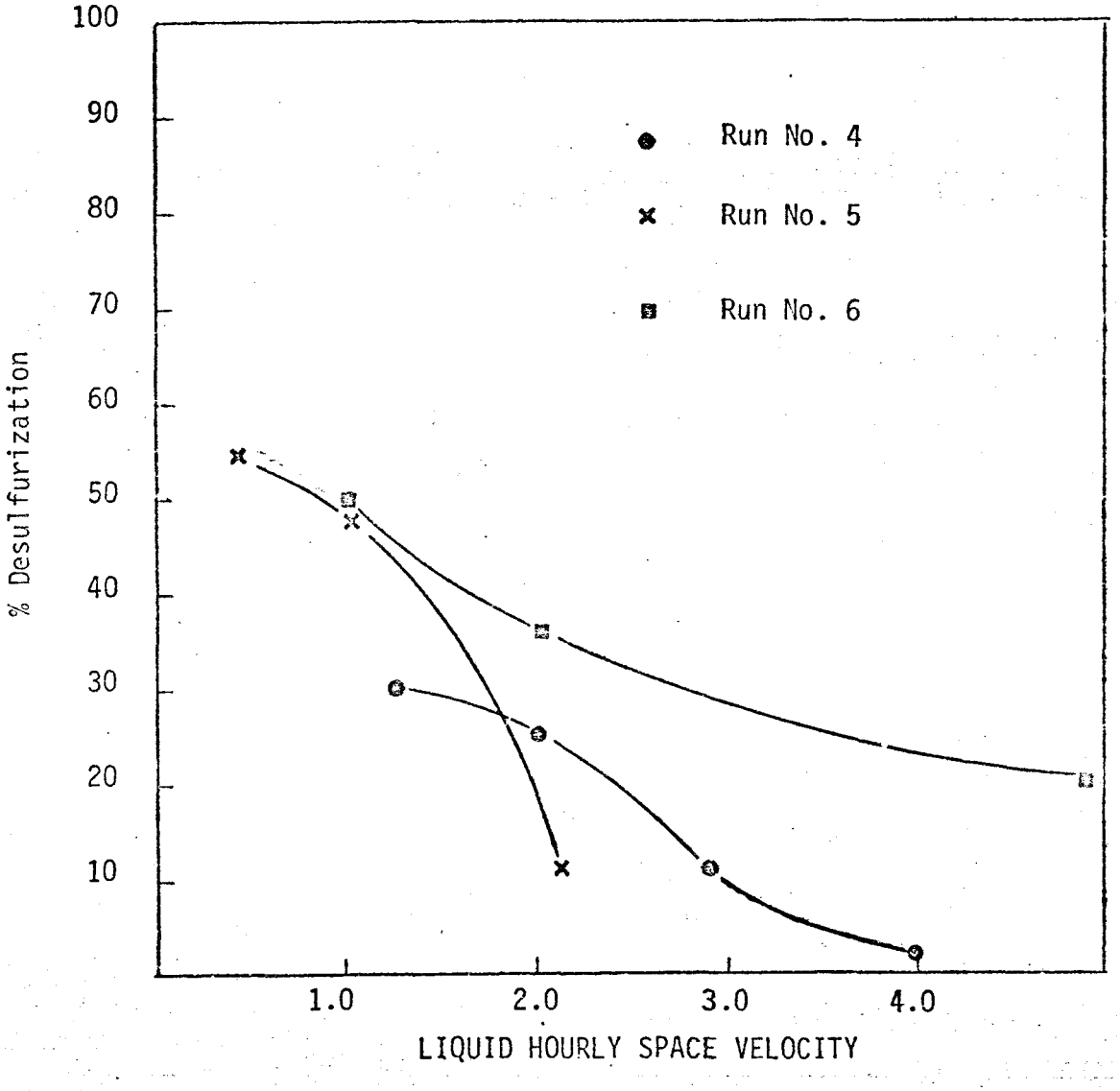


FIGURE 13. Percent Desulfurization vs. LHSV

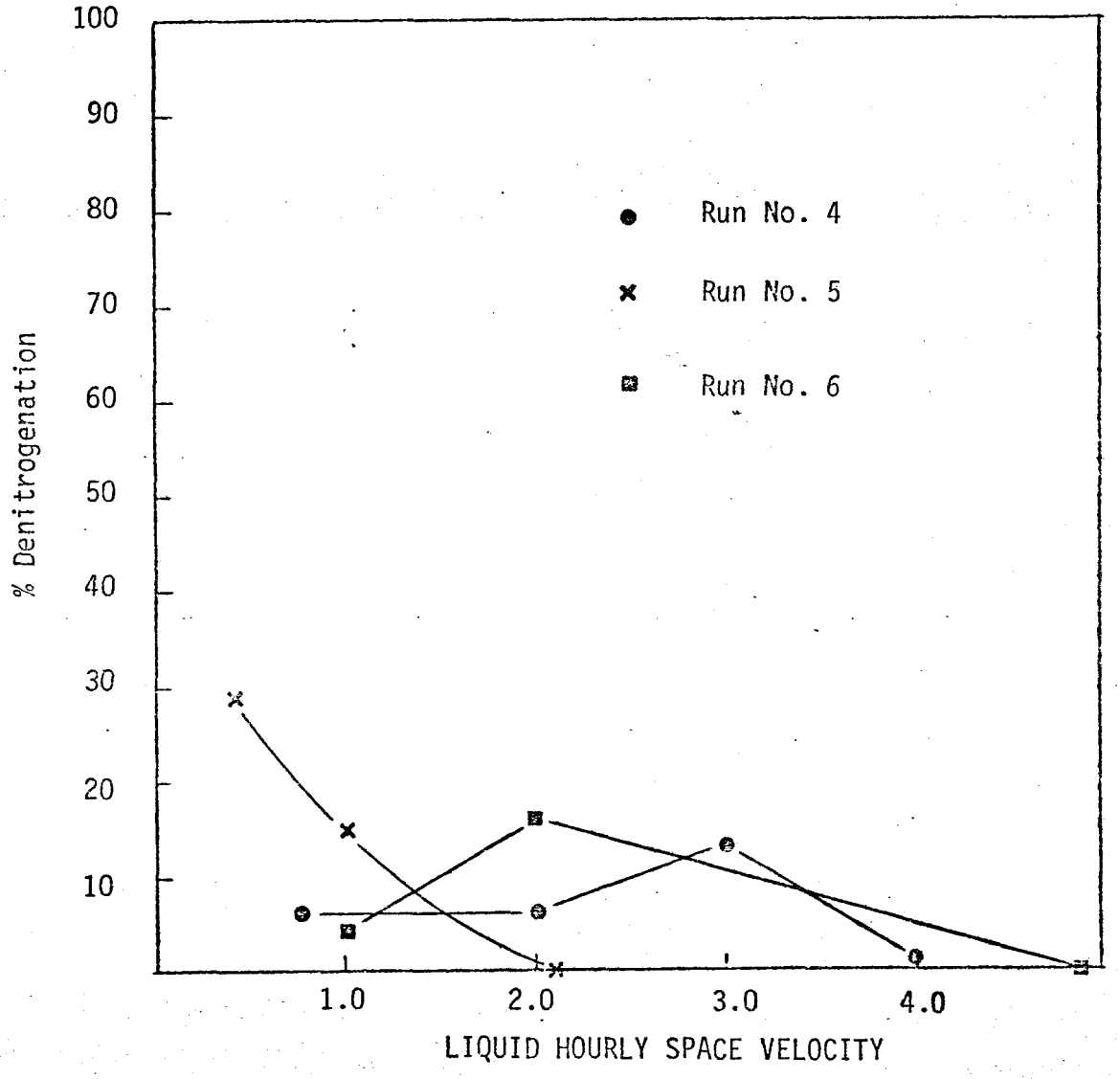


FIGURE 14. Percent Denitrogenation vs. LHSV

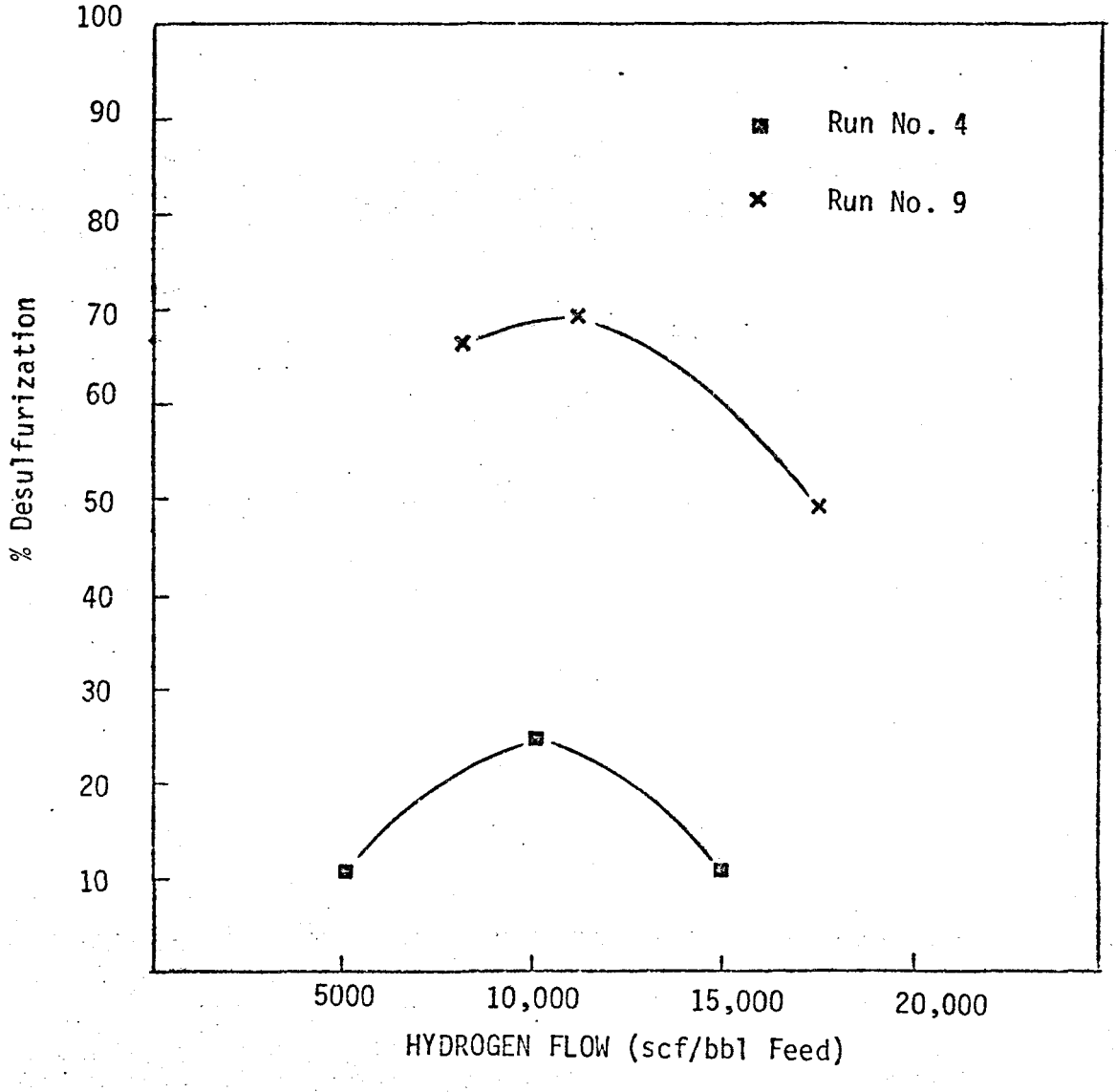


FIGURE 15. Percent Desulfurization vs. Hydrogen Flow

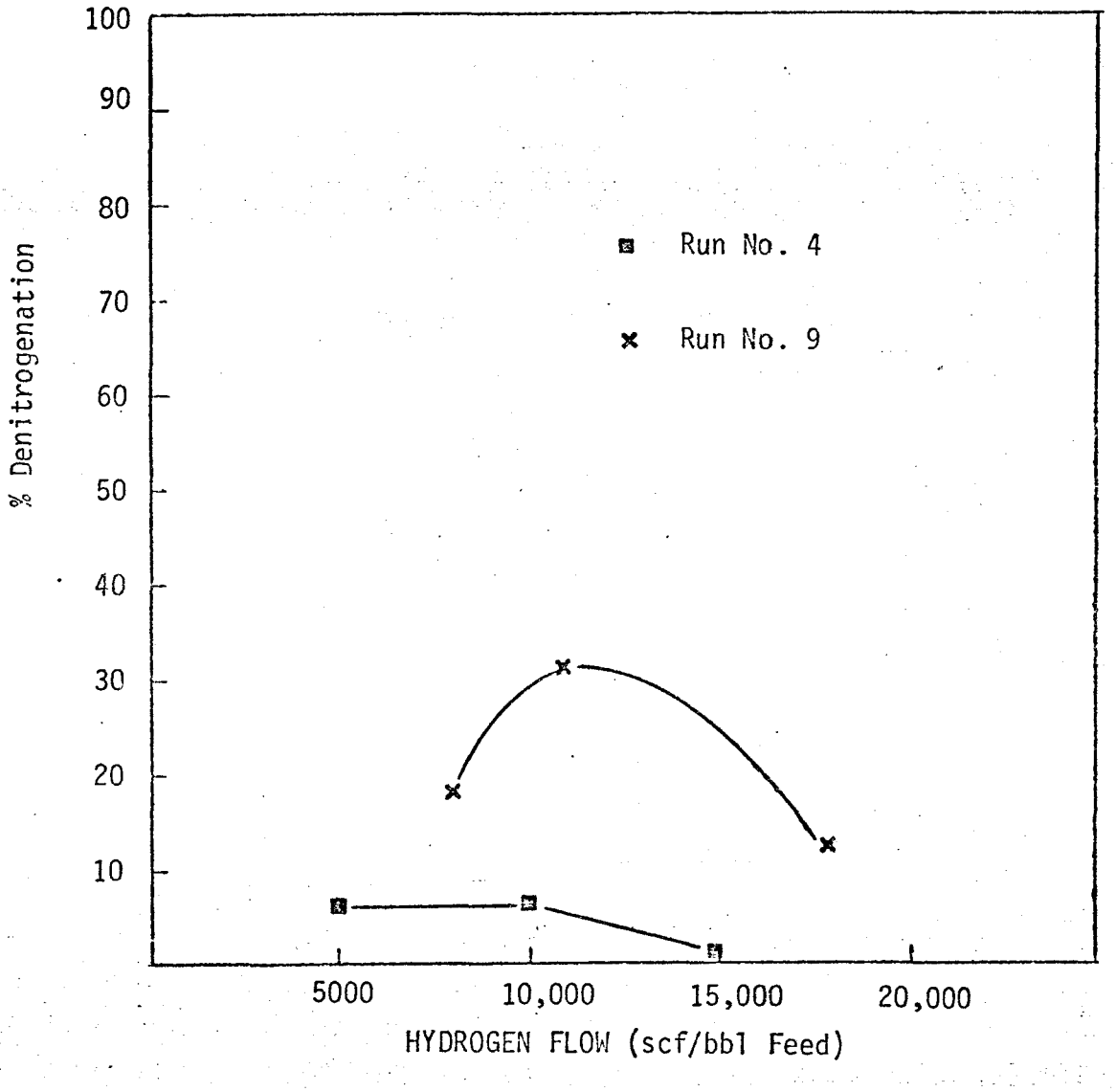


FIGURE 16. Percent Denitrogenation vs. Hydrogen Flow

18 and 19 for Run 4 (Ni-1601) and Run 9 (HT-500). The LHSV was approximately constant. In Figures 18 and 19 the percent desufluriza-tion and percent denitrogenation, respectively, reach a maximum at approximately 10,000 scf/bbl and then decrase. The worst results were at hydrogen flow rates greater than 15,000 scf/bbl. At these high flow rates the hydrogen must blow the SYNTHOIL through the catalyst bed so fast that good contacting and reaction do not occur.

Run 9, catalyst HT-500, was made to determine the effect of hydrogen flow rate. Figure 17 shows that a hydrogen flow rate of 11,000 scf/bbl gives the best hydrocracking results. This agrees with the flow rate for heteroatom removal given above.

Run 7 was made using a Ni-W catalyst Ni-4301. Four different temperatures were tested. The ASTM distillation results are graphed in Figure 18. It is noted that hydrocracking decreases with a decrease in temperature.

Figure 19 is the heteroatom removal for the continuous run. In this graph percent desulfurization and percent denitrogenation show the same general trend of decrease with a decrease in temperature.

The data from Run 8 (Ni-4303) is given in Appendix C. The object of the run was to determine if there was any deactivation of the catalyst during a 12 hour run (normal one day run). Samples 8-1, 8-2, and 8-3 were taken the first day of the run. All operating parameters were kept as consistent as possible for the 12 hour run.

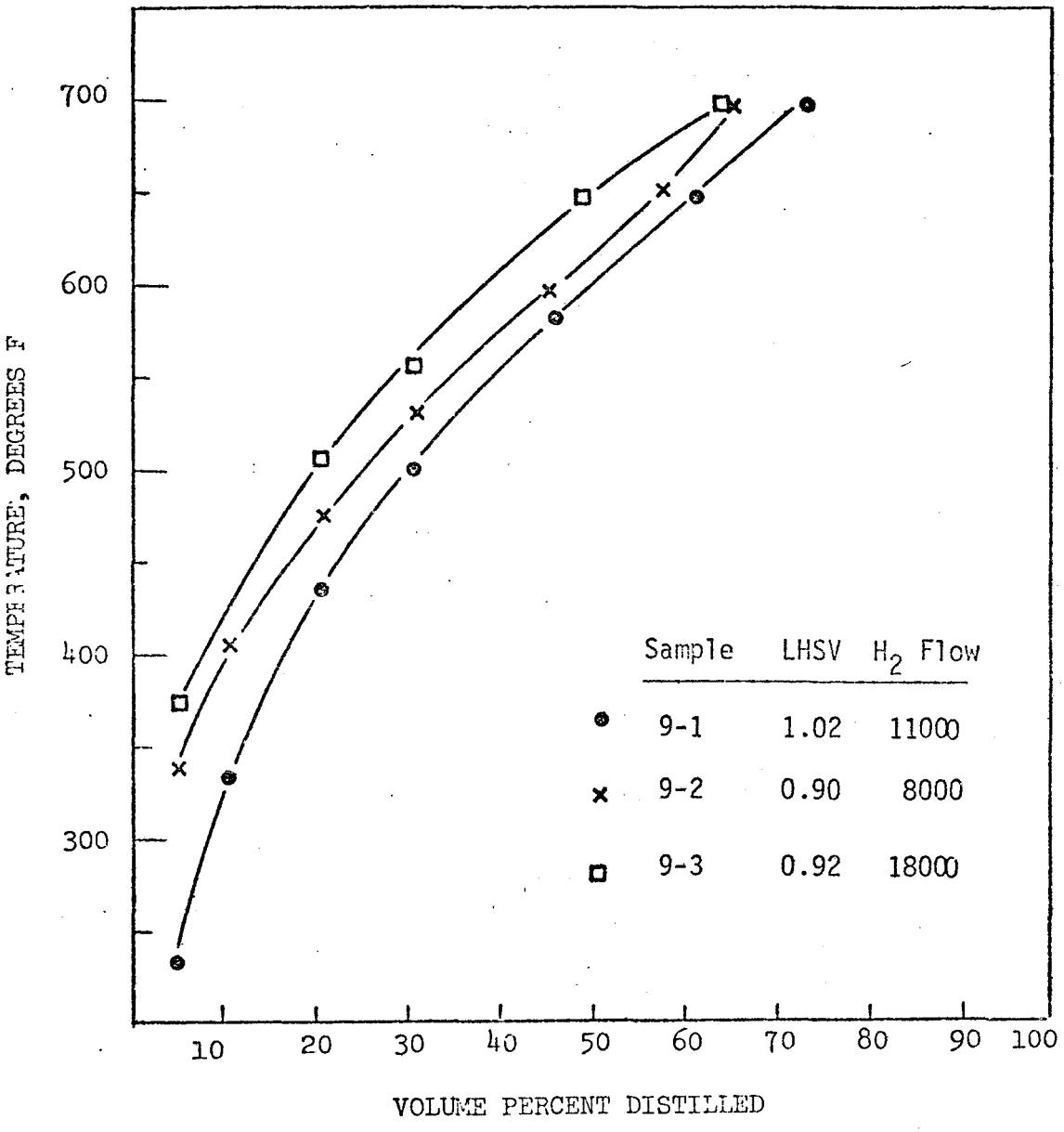


FIGURE 17. ASTM Distillation, Run 9
Catalyst: Harshaw HT-500; 3% NiO, 15.5% MoO_3 on Alumina

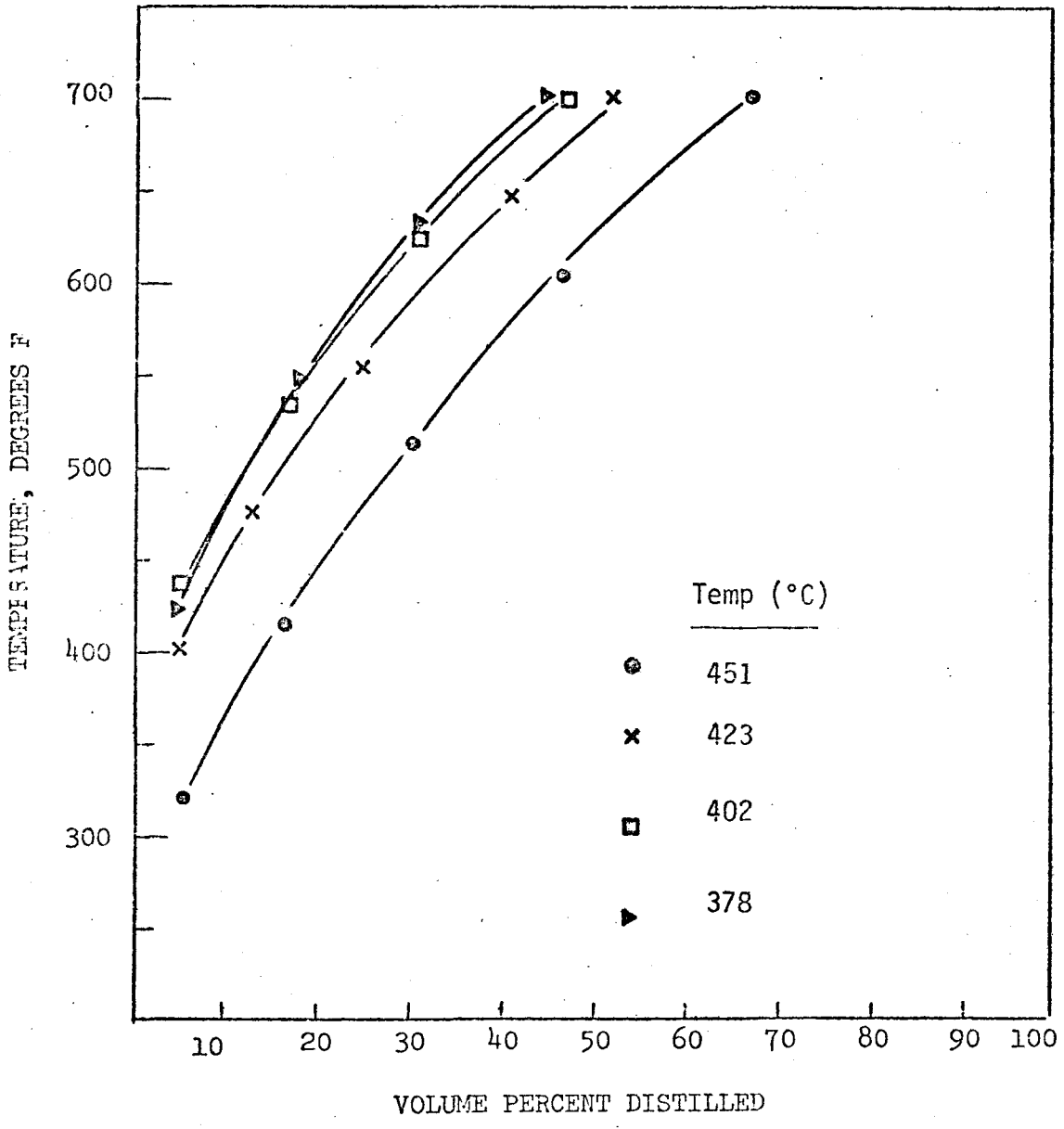


FIGURE 18. ASTM Distillation, Run 7
Catalyst: Harshaw Ni=4301; 6% NiO, 19% WO_3 on Silica Alumina

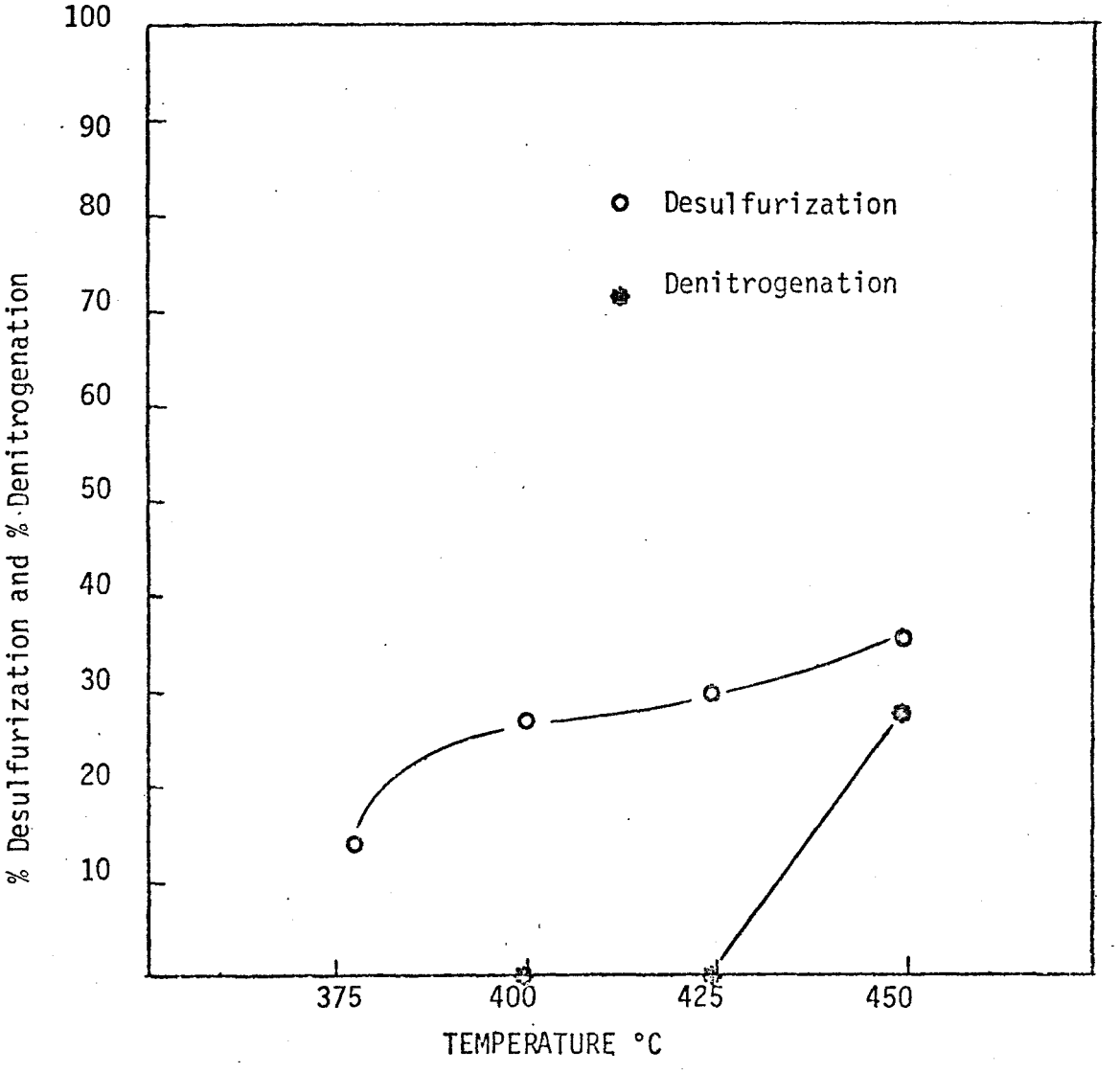


FIGURE 19. Percent Desulfurization and Denitrogenation vs. Temperature

Run No. 7
Catalyst: Harshaw Ni-4301

No deactivation of the catalyst was noted in hydrocracking, desulfurization, or denitrogenation during the 12 hours. The SYNTHOIL feed to the reactor was then stopped and a stream of hydrogen was trickled through the reactor overnight. Samples 8-4 and 8-5 were taken the second day. The hydrogen flow rate was doubled from 5000 to 10,000 scf/bbl. All other operating parameters remained the same. A decrease was noted from the first day in hydrocracking, desulfurization and denitrogenation. It was hoped that this test would allow runs to be made on consecutive days with no deactivation of the catalyst. But while no deactivation of the catalyst seems to occur in a 12 hour run, the catalyst does see degradation from SYNTHOIL residue in sitting overnight.

The discrepancies in the data show a need to get a better fix on the flow rates through the reactor. The Hills-McCanna chemical proportioning pump was unreliable. Flow varied for no apparent reason. Repeatability was difficult due to the inaccuracy in setting the pump stroke.

Hydrogen flow was even more of a problem to measure and control. Changing any pressure in the system would affect the hydrogen flow. As an example the back pressure increased due to plugging and also due to increased pressure drop across the reactor once SYNTHOIL was pumped through the reactor. A wet test meter was connected to the gas outlet after the scrubber in runs 8 and 9. By assuming that 90%

of the gases coming off were hydrogen, relative changes in hydrogen flow could be determine. A hydrogen flow meter is necessary to give accurate quantitative numbers for hydrogen flow.

No material balances were made on the system because of the problems with the hydrogen and SYNTHOIL feeds as mentioned above. Sensitive chromatograph analysis of the exit gases is also necessary.

CONCLUSIONS

1. Hydrocracking, desulfurization, and denitrogenation of SYNTHOIL can be accomplished to some degree using commercial hydrotreating catalysts.
2. No general statements can be made as to what makes a "good" catalyst.
3. Harshaw catalyst HT-500 (Ni-Mo on alumina) gave the best hydrocracking and denitrogenation results in both the bomb and continuous run.
4. Shell catalyst 344 (CoMo on alumina) gave the best heteroatom removal in a bomb (48% desulfurization and 32% denitrogenation).
5. Nitrogen is the more difficult heteroatom to remove.
6. Continuous runs at LHSV $\simeq$ 1 give better hydrogenation and desulfurization results than the bomb run for the same catalyst.
7. Hydrocracking and heteroatom removal decrease as the LHSV increases.
8. A hydrogen flow rate of approximately 10,000 scf/bbl showed the best hydrocracking and heteroatom removal.
9. A reaction temperature of 450°C and a pressure of 800 psig gives the best results in hydrocracking and heteroatom removal.

APPENDIX A. BATCH RUN CATALYST DESCRIPTION

Run #	Catalyst
B1	Harshaw catalyst Ni-4401 (1/10" extrusions) 6% NiO, 19% WO_3 on Silica Alumina.
B2	Harshaw catalyst Ni-1601 (1/8" tablets) 3% NiO, 3% CoO, 3% FeO on activated Alumina. Surface area = 78 m^2/g Pore volume = .28 cc/g
B3	Harshaw catalyst Ni-1800 (4-8 mesh granules) 10% Ni), 1% CuO on Silica. Surface area = 3 m^2/g
B4	Harshaw catalyst CoMo-0401 (1/8" tablets) 3% CoO, 9% MoO_3 on Silica Alumina. Surface area = 160 m^2/g Pore volume = 0.40 cc/g
B5	Harshaw catalyst Ni-4301 (1/12" extrusions) 6% NiO, 19% WO_3 on Silica Alumina. Surface area = 228 m^2/g Pore volume = .37 cc/g
B6	Catalyst and Chemical Co. catalyst C-20-6 4% CoO, 15% MoO_3 on Alumina.
B7	Harshaw catalyst Ni-4303 (1/12" extrusions) 6% NiO, 19% WO_3 on Alumina. Surface area = 152 m^2/g Pore volume = 0.54 cc/g
B8	Harshaw catalyst Ni-1600 (1/4" spheres) 3% NiO, 3% CoO, 3% FeO on inert Silica Alumina. Surface area = 1 m^2/g

Run #	Catalyst
B9	Harshaw catalyst Ni-3250 (1/8" tablets) 50% Ni on alkaline support. Surface area = 150 m^2/g Pore volume = 0.34 cc/g
B10	Harshaw catalyst Ni-0104 (powder) 60% Ni on Kieselguhr Surface area = 150 m^2/g Pore volume = .2 cc/g
B11	Catalyst impregnated on support in house 26% $SnCl_2$ on Silica. Support: Johns-Manville cellite 408 (5/32" pellets) Surface area = 3 m^2/g Pore volume = 0.65 cc/g Pore diameter (mean) = .98μ
B12	Harshaw catalyst HT-100 (1/12" extrusions) 3.8% NiO, 16.8% MoO_3 on 1.5% Silica promoted Alumina. Surface area = 175 m^2/g Pore volume = 0.54 cc/g
B13	Harshaw catalyst W-0801 (1/8" tablets) 10% WO_3 on high activity Alumina Surface area = 145 m^2/g Pore volume = 0.36 cc/g
B14	Harshaw catalyst Mo-1201 (1/8" tablets) 10% MoO_3 on high activity Alumina. Surface area = 160 m^2/g Pore volume = 0.36 cc/g
B15	Harshaw catalyst W-0101 (1/8" tablets) 10% WO_3 on Alumina. Surface area = 75 m^2/g Pore volume = 0.37 cc/g

B17 Harshaw catalyst Cr-0103 (1/8" tablets) 12% CrO_3 on active Alumina.

Surface area = 63 m^2/g Pore volume = 0.35 cc/g

B18 Harshaw catalyst Cr-0105 (1/8" tablets) 9% Cr_2O_3, 1.5% K_2O on active Alumina.

Surface area = 67 m^2/g Pore volume = 0.34 cc/g

B19 Harshaw catalyst Ni-3210 (3/16" tablets) 35% Ni on proprietary support.

Surface area = 175 m^2/g Pore volume = 0.45 cc/g

B20 Harshaw catalyst CoMo-0603 (1/8" tablets) 3% CoO, 9% MoO_3 on Alumina.

Surface area = 160 m^2/g Pore volume = 0.40 cc/g

B21 Same catalyst as Run #B15

B22 Harshaw catalyst HT-400 (1/16" extrusions) 3% CoO, 15% MoO_3 on Alumina.

Surface area = 220 m^2/g Pore volume = 0.55 cc/g

B23 Same catalyst as Run #B5

B24 Same catalyst as Run #B5

B25 Harshaw catalyst HT-500 (1/8" extrusions) 3% NiO, 15.5% MoO_3 on Alumina.

Surface area = 210 m^2/g Pore volume = .44 cc/g

Run #	Catalyst
B26	Ketjen catalyst Ketjenfine 330-3E, 6.62% NiO, 19.8% WO_3 on Silica Alumina Surface area = 193 m^2/g Pore volume = 0.43 cc/g
B27	Ketjen catalyst HC-5-1.5E; 6.5% NiO, 21% WO_3 on Alumina. Surface area = 200 m^2/g Pore volume = 0.62 cc/g
B28	Shell Catalyst 324 (1/116" extrusions) 2.7% Ni, 13.2% Mo, on Alumina. Surface area = 160 m^2/g Pore volume = 0.5 cc/g
B29	Shell catalyst 344 (1/16" extrusions) 2.4% Co, 9.9% Mo on Alumina. Surface area = 195 m^2/g Pore volume = 0.6 cc/g

APPENDIX B. BATCH RUN DATA

Run #B1

Catalyst	H_2 take-up Psig	Distillate Yield Vol. %	Wt. %	% DeS	% DeN
Ni-4401	800	49	49	41	18

ASTM Distillation:	Vol. %	Temp (°F)	Vol. %	Temp (°F)
	5	395	30	608
	10	450	40	662
	20	540	49	700

Run #B2

Catalyst	H_2 take-up Psig	Distillate Yield Vol. %	Wt. %	% DeS	% DeN
Ni-1601	150	51	51	07	06

ASTM Distillation:	Vol. %	Temp (°F)	Vol. %	Temp (°F)
	5	410	40	660
	10	450	50	697
	20	540	51	700
	30	610		

Run #B3

Catalyst	H_2 take-up Psig	Distillate Yield Vol. %	Wt. %	% DeS	% DeN
Ni-1800	100	51	50	16	20

ASTM Distillation:	Vol. %	Temp (°F)	Vol. %	Temp (°F)
	5	445	30	620
	10	480	40	665
	29	553	51	700

Run #B4

Catalyst	H_2 take-up Psig	Distillate Yield Vol. %	Wt. %	% DeS	% DeN
CoMo-0401	1300	65	61	16	33

ASTM Distillation:	Vol. %	Temp (°F)	Vol. %	Temp (°F)
	5	200	40	630
	10	410	50	660
	20	510	60	685
	30	580	65	700

Run #B5

Catalyst	H_2 take-up Psig	Distillate Yield Vol. %	Wt. %	% DeS	% DeN
Ni-4301	700	61	59	32	29

ASTM Distillation:	Vol. %	Temp (°F)	Vol. %	Temp (°F)
	5	350	40	630
	10	445	50	668
	20	530	61	700
	30	590		

Run #B6

Catalyst	H_2 take-up Psig	Distillate Yield Vol. %	Wt. %	% DeS	% DeN
C-20-6	675	56	53	18	25

ASTM Distillation:	Vol. %	Temp (°F)	Vol. %	Temp (°F)
	5	355	40	650
	10	420	50	685
	20	515	56	700
	30	590		

Run #B7

Catalyst	H_2 take-up Psig	Distillate Yield Vol. %	Wt. %	% DeS	% DeN
Ni-4303	90	54	49	45	18

ASTM Distillation:

Vol. %	Temp (°F)	Vol. %	Temp (°F)
5	360	40	642
10	405	50	685
20	515	54	700
30	585		

Run #B8

Catalyst	H_2 take-up Psig	Distillate Yield Vol. %	Wt. %	% DeS	% DeN
Ni-1600	275	41	41	07	10

ASTM Distillation:

Vol. %	Temp (°F)	Vol. %	Temp (°F)
5	430	30	660
10	490	41	700
20	590		

Run #B9

Catalyst	H_2 take-up Psig	Distillate Yield Vol. %	Wt. %	% DeS	% DeN
Ni-3250	700	49	50	50	17

ASTM Distillation:

Vol. %	Temp (°F)	Vol. %	Temp (°F)
5	390	30	620
10	440	40	670
20	540	49	700

Run #B10

Catalyst	H_2 take-up Psig	Distillate Yield Vol. %	Wt. %	% DeS	% DeN
Ni-0104	600	54	53	57	16

ASTM Distillation:	Vol. %	Temp (°F)	Vol. %	Temp (°F)
	5	355	40	645
	10	430	50	686
	20	520	53	700
	30	580		

Run #B11

Catalyst	H_2 take-up Psig	Distillate Yield Vol. %	Wt. %	% DeS	% DeN
$SnCl_2$	775	51	50	20	10

ASTM Distillation:	Vol. %	Temp (°F)	Vol. %	Temp (°F)
	5	390	30	585
	10	445	40	640
	20	522	51	700

Run #B12

Catalyst	H_2 take-up Psig	Distillate Yield Vol. %	Wt. %	% DeS	% DeN
HT-100	800	50	50	36	18

ASTM Distillation:	Vol. %	Temp (°F)	Vol. %	Temp (°F)
	5	300	30	590
	10	425	40	650
	20	521	50	700

Run #B13

Catalyst	H_2 take-up Psig	Distillate Yield Vol. %	Wt. %	% DeS	% DeN
W-0801	500	46	47	27	04

ASTM Distillation:	Vol. %	Temp (°F)	Vol. %	Temp (°F)
	5	410	30	615
	10	463	40	670
	20	543	46	700

Run #B14

Catalyst	H_2 take-up Psig	Distillate Yield Vol. %	Wt. %	% DeS	% DeN
Mo-1201	500	49	46	36	19

ASTM Distillation:	Vol. %	Temp (°F)	Vol. %	Temp (°F)
	5	365	30	390
	10	430	40	650
	20	520	49	700

Run # B15

Catalyst	H_2 take-up Psig	Distillate Yield Vol. %	Wt. %	% DeS	% DeN
W-0101	800	57	55	25	03

ASTM Distillation:	Vol. %	Temp (°F)	Vol. %	Temp (°F)
	5	305	40	620
	10	338	50	680
	20	405	57	700
	30	475		

Run #B17

Catalyst	H_2 take-up Psig	Distillate Yield Vol. %	Wt. %	% DeS	% DeN
Cr-0103	200	43	41	00	05

ASTM Distillation:	Vol. %	Temp (°F)	Vol. %	Temp (°F)
	5	405	30	635
	10	485	40	685
	20	570	43	700

Run #B18

Catalyst	H_2 take-up Psig	Distillate Yield Vol. %	Wt. %	% DeS	% DeN
Cr-0105	250	44	43	05	00

ASTM Distillation:	Vol. %	Temp (°F)	Vol. %	Temp (°F)
	5	425	30	628
	10	480	40	680
	20	560	44	700

Run #B19

Catalyst	H_2 take-up Psig	Distillate Yield Vol. %	Wt. %	% DeS	% DeN
Ni-3210	400	47	45	05	25

ASTM Distillation:	Vol. %	Temp (°F)	Vol. %	Temp (°F)
	5	425	30	610
	10	470	40	670
	20	540	47	700

Run #B20

Catalyst	H_2 take-up Psig	Distillate Yield Vol. %	Wt. %	% DeS	% DeN
CoMo-0603	700	61	57	52	25

ASTM Distillation:	Vol. %	Temp (°F)	Vol. %	Temp (°F)
	5	355	40	628
	10	432	50	675
	20	504	61	700
	30	570		

Run # B21

Catalyst	H_2 take-up Psig	Distillate Yield Vol. %	Wt. %	% DeS	% DeN
W-0101	400	51	50	09	00

ASTM Distillation:	Vol. %	Temp (°F)	Vol. %	Temp (°F)
	5	415	30	595
	10	467	40	665
	20	540	51	700

Run #B22

Catalyst	H_2 take-up Psig	Distillate Yield Vol. %	Wt. %	% DeS	% DeN
HT-400	1000	64	62	34	13

ASTM Distillation:	Vol. %	Temp (°F)	Vol. %	Temp (°F)
	5	355	40	630
	10	418	50	670
	20	510	60	693
	30	580	64	700

Run # B23

Catalyst	H_2 take-up Psig	Distillate Yield Vol. %	Wt. %	% DeS	% DeN
Ni-4301	250	47	45	41	17

ASTM Distillation:	Vol. %	Temp (°F)	Vol. %	Temp (°F)
	5	400	30	618
	10	475	40	675
	20	540	47	700

Run #B24

Catalyst	H_2 take-up Psig	Distillate Yield Vol. %	Wt. %	% DeS	% DeN
Ni-4301	400	52	51	23	28

ASTM Distillation:	Vol. %	Temp (°F)	Vol. %	Temp (°F)
	5	395	30	605
	10	470	40	665
	20	540	52	700

Run #B25

Catalyst	H_2 take-up Psig	Distillate Yield Vol. %	Wt. %	% DeS	% DeN
HT-500	1000	65	64	32	34

ASTM Distillation:	Vol. %	Temp (°F)	Vol. %	Temp (°F)
	5	315	40	622
	10	410	50	668
	20	500	60	692
	30	560	65	700

Run #B26

Catalyst	H_2 take-up Psig	Distillate Yield Vol. %	Wt. %	% DeS	% DeN
330-3E	700	54	51	30	12

ASTM Distillation:

Vol. %	Temp (°F)	Vol. %	Temp (°F)
5	340	40	628
10	405	50	688
20	512	54	700
30	573		

Run #B27

Catalyst	H_2 take-up Psig	Distillate Yield Vol. %	Wt. %	% DeS	% DeN
HC-5	500	49	48	25	23

ASTM Distillation:

Vol. %	Temp (°F)	Vol. %	Temp (°F)
5	415	30	623
10	468	40	675
20	560	49	700

Run #B28

Catalyst	H_2 take-up Psig	Distillate Yield Vol. %	Wt. %	% DeS	% DeN
Shell 324	700	51	52	55	21

ASTM Distillation:

Vol. %	Temp (°F)	Vol. %	Temp (°F)
5	325	30	592
10	422	40	660
20	435	51	700

Run #B29

Catalyst	H_2 take-up Psig	Distillate Yield Vol. %	Wt. %	% DeS	% DeN
Shell 344	800	50	47	48	32

ASTM Distillation:	Vol. %	Temp (°F)	Vol. %	Temp (°F)
	5	330	30	610
	10	450	40	670
	20	540	50	700

NOTES:

1. SYNTHOIL Feed Analysis

Distillate Yield Vol. %	Wt. %	Weight % S	Weight % N
44	43	.44	1.06

ASTM Distillation:	Vol. %	Temp (°F)	Vol. %	Temp (°F)
	0	380	30	632
	5	440	40	682
	10	490	44	700
	20	570		

2. Catalysts listed by run numbers and manufacturuers identification numbers. Catalyst descriptions given in Appendix A.
3. H_2 take-up is calculated by taking the difference between the charge pressure ≈2000 psig of hydrogen and the pressure upon cooling the bomb to room temperature after the run.
4. ASTM Distillation data can be graphed with volume percent as the abscissa and the temperature as the ordinate. Use a volume percent of 5 as start because distillate started coming off all samples at <200°F. End point for distillation is 700°F.

5. Bomb run conditions: 450°C for 1 hour.

   Except - Run #B21 run at 427°C

   Run #B23 run at 400°C

   Run #B24 run at 418°C

APPENDIX C. CONTINUOUS RUN DATA

Run #1

Catalyst and Chemical Company catalyst C-20-6
4% CoO, 15% MoO_3 on Alumina

Temperature: 450°C Pressure: 800 psig

Sample #	LHSV	H_2 Flow scf/bbl	Distillate Yield Vol.%	Wt. %	%DeS	%DeN
1-1	4	5000	54	51	27	19

ASTM Distillation:

Vol. %	Temp (°F)	Vol. %	Temp (°F)
0	360	30	582
5	404	40	631
10	440	50	680
20	502	54	700

Run #2

Same catalyst as in Run #1

Temperature: 450°C Pressure: 1000 psig

Sample #	LHSV	H_2 Flow scf/bbl	Distillate Yield Vol.%	Wt. %	%DeS	%DeN
2-1	1.4	10,000	70	67	70	24
2-2	3.0	10,000	51	50	43	01

ASTM Distillation:

Sample #2-1 Vol. %	Sample #2-1 Temp (°F)	Sample #2-2 Vol. %	Sample #2-2 Temp (°F)
0	252	0	370
5	332	5	444
10	441	10	494
20	460	20	556
30	520	30	628
40	565	40	682
50	594	50	698
60	657	51	700
70	700		

Run #3

Harshaw Catalyst Ni-4401 (1/10" extrusions)
6% NiO, 19% WO_3 on Silica Alumina

Temperature: 400°C Pressure: 800 psig

Sample #	LHSV	H_2 Flow scf/bbl	Distillate Yield Vol. %	Wt. %	%DeS	%DeN
3-1	1.0	10,000	62	61	09	13

ASTM Distillation:	Vol. %	Temp (°F)	Vol. %	Temp (°F)
	0	301	30	576
	5	429	40	633
	10	471	50	670
	20	532	62	700

Run #4

Harshaw catalyst Ni-1601 (1/8" tablets)
3% NiO, 3% CoO, 3% FeO on active Alumina
Surface area = 78 m^2/g Pore volume = 0.28 cc/g

Temperature: 450°C Pressure: 800 psig

Sample #	LHSV	H_2 Flow scf/bbl	Distillate Yield Vol. %	Wt. %	%DeS	%DeN
4-1	1.25	10,000	67	65	30	06
4-2	2.00	10,000	55	52	25	06
4-3	2.24	5,000	54	52	11	06
4-4	2.14	15,000	60	57	11	01
4-5	2.87	10,000	59	57	11	13
4-6	4.00	10,000	54	52	02	01

Run #4 (cont)

ASTM Distillation:

4-1		4-2		4-3	
Vol.%	Temp (°F)	Vol. %	Temp (°F)	Vol. %	Temp (°F)
0	215	0	300	0	218
5	415	5	410	5	428
10	453	10	466	10	464
20	525	20	531	20	531
30	575	30	594	30	606
40	620	40	645	40	650
50	657	50	685	50	692
60	683	55	700	54	700
67	700				

4-4		4-5		4-6	
Vol.%	Temp (°F)	Vol. %	Temp (°F)	Vol. %	Temp (°F)
0	216	0	218	0	250
5	428	5	420	5	425
11	458	10	458	10	454
20	522	20	515	20	540
30	579	30	581	30	598
40	630	40	642	40	660
50	670	50	680	50	692
60	700	59	700	54	700

Run #5

Harshaw catalyst Ni-3210 (3/16" tablets)
35% Ni on proprietary support
Surface area = 175 m^2/g Pore voluem = 0.45 cc/gm

Temperature: 450°C Pressure: 800 psig

Sample #	LHSV	H_2 Flow scf/bbl	Distillate Yield Vol. %	Wt. %	% DeS	%DeN
5-1	2.17	10,000	57	54	11	00
5-2	.37	10,000	63	60	55	29
5-3	1.05	10,000	51	50	48	15

ASTM Distillation:

5-1		5-2		5-3	
Vol. %	Temp (°F)	Vol. %	Temp (°F)	Vol. %	Temp (°F)
0	380	0	<200	0	<200
10	462	5	390	5	436
20	508	10	427	10	470
30	564	20	501	20	541
40	615	30	560	30	597
50	679	40	606	40	648
57	700	50	654	50	698
		60	695	51	700
		63	700		

Run #6

Harshaw catalyst CoMo-0401 (1/8" tablets)
3% CoO, 9% MoO_3 on Silica Alumina
Surface Area = 160 m^2/g Pore volume = 0.40 cc/g

Temperature: 450°C Pressure: 800 psig

Sample #	LHSV	H_2 Flow scf/bbl	Distillate Yield Vol. %	Wt. %	% DeS	% DeN
6-1	1.00	10,000	65	62	50	04
6-2	2.03	10,000	48	51	36	16
6-3	4.80	10,000	43	50	20	00

ASTM Distillation:

6-1		6-2		6-3	
Vol. %	Temp (°F)	Vol. %	Temp (°F)	Vol. %	Temp (°F)
0	<200	0	220	0	360
5	336	5	440	5	468
10	399	10	466	10	510
20	466	20	540	20	580
30	530	30	595	30	642
40	574	40	654	43	700
50	620	48	700		
60	688				
65	700				

Run #7

Harshaw Catalyst Ni-4301 (1/12" extrusions)
6% NiO, 19% WO_3 on Silica Alumina
Surface area = 228 m^2/g Pore volume = 0.37 cc/g

Temperature: varies Pressure: 800 psig

Sample #	Temp (°C)	LHSV	H_2 Flow scf/bbl	Distillate Yield Vol.%	Wt. %	%DeS	%DeN
7-1	451	1.71	10,000	65	65	36	28
7-2	423	1.70	10,000	51	48	30	00
7-3	402	2.0	10,000	45	45	27	00
7-4	378	1.67	10,000	46	44	16	18

ASTM Distillation:

7-1 Vol.%	7-1 Temp. (°F)	7-2 Vol. %	7-2 Temp (°F)	7-3 Vol. %	7-3 Temp (°F)
0	225	0	340	0	330
5	330	5	404	5	437
10	370	10	462	10	476
20	458	20	528	20	560
30	514	30	591	30	614
40	572	40	644	40	680
50	628	51	700	45	700
60	689				
65	700				

7-4 Vol. %	7-4 Temp (°F)
0	370
5	430
10	487
20	570
30	630
40	685
46	700

Run #8

Harshaw catalyst Ni-4303 (1/12" extrusions)
6% NiO, 19% WO_3 on alumina
Surface area = 152 m^2/g Pore volume = 0.54 cc/g

Temperature: 450°C Pressure: 800 psig

Sample #	LHSV	H_2Flow scf/bbl	Distillate Yield Vol. %	Wt. %	%DeS	%DeN
8-1	1.00	5,000	57	54	68	17
8-2	0.98	5,000	56	54	61	03
8-3	1.00	5,000	62	57	68	17
8-4	1.03	10,000	53	52	50	00
8-5	.96	10,000	48	47	20	12

ASTM Distillation:

8-1		8-2		8-3	
Vol. %	Temp (°F)	Vol. %	Temp (°F)	Vol. %	Temp (°F)
0	190	0	180	0	200
5	254	5	360	5	350
10	410	10	408	10	405
20	500	20	500	20	475
30	552	30	577	30	528
40	629	40	632	40	590
50	680	50	690	50	630
57	700	56	700	62	700

8-4		8-5	
Vol. %	Temp (°F)	Vol. %	Temp (°F)
0	200	0	300
5	410	5	437
10	468	10	480
20	527	20	550
30	576	30	604
40	625	40	680
53	700	48	700

Run #9

Harshaw Catalyst HT-500 (1/8" extrusions)
3% NiO, 15.5% MoO_3 on Alumina
Surface area = 210 m^2/g Pore volume = 0.44 cc/g

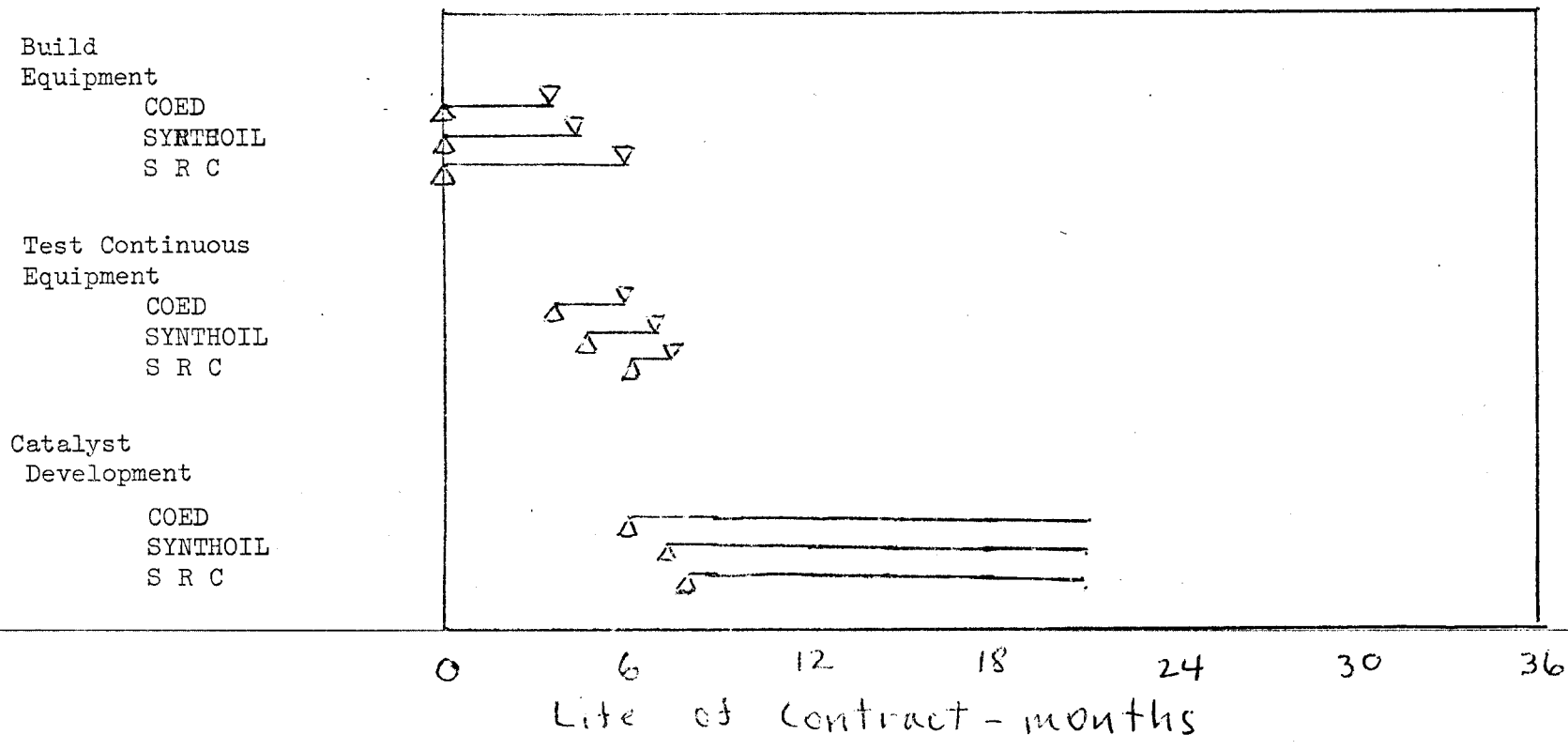
Temperature: 450°C Pressure: 800 psig

Sample #	LHSV	H_2 Flow scf/bbl	Distillate Yield Vol. %	Wt. %	% DeS	% DeN
9-1	1.02	11,000	72	69	70	31
9-2	0.90	8,000	64	61	67	18
9-3	0.92	18,000	64	61	50	12

ASTM Distillation:

9-1		9-2		9-3	
Vol. %	Temp (°F)	Vol. %	Temp (°F)	Vol. %	Temp (°F)
0	200	0	200	0	200
5	200	5	344	5	380
10	340	10	410	10	430
20	440	20	480	20	510
30	505	30	535	30	554
40	564	40	580	40	595
50	600	50	630	50	557
60	650	60	692	60	690
72	700	64	700	64	700

PICTORIAL PROGRESS REPORT



G & C PROJECT FINANCIAL REPORT NO. 789 03/31/1977

DEPT 6131 BERG DISTILLATE FUELS BEGIN DATE 07-01-75 END DATE 6-19-78

	CURRENT MO.	TOTAL TO DATE		AMT. AUTH.
RECEIPTS	.00	61727.44		155932.00
			ENCUMBRANCES	TOTAL COMMITTED	BUDGET
EXPENDITURES					
SALARY AND WAGES	1707.80	31733.15	2250.00	33983.15	68657.
BENEFITS	58.01	1487.20		1487.20	4255.
REP & MAINT		8.00		8.00	
TRAVEL	361.60	1349.29		1349.29	3000.
COMMUNICATIONS	243.60	274.07		274.07	
COMPUTER					3000.
SUPPLIES	589.45	10735.66		10735.66	12750.
SUBCONTRACT	18.00	150.97		150.97	
EQUIPMENT	781.00	4395.86		4395.86	12700.
AWARDS	120.20	1386.45		1386.45	6000.
INDIRECT CHARGES	1207.99	22726.04	22843.96	45570.00	45570.
TOTAL	5087.65	74246.69	25093.96	99340.65	155932.

BALANCE CASH -12519.25 FREE BALANCE 56591.35

DETAIL TRANSACTION	DATE	NUMBER	DESCRIPTION	AMOUNT	TOTAL
	= -7		BERG LLOYD	350.00	
	= -7		TEIGEN SHARON L	60.00	
	= -7		RUNNION KENNETH N	400.00	
	= -7		HENTON LEE M	400.00	
	= -7		KUJAWA STEPHAN T	400.00	
	= -7		ANDERSON MARK D	30.00	

DETAIL TRANSACTION	DATE	NUMBER	DESCRIPTION	AMOUNT	TOTAL
	03-11-77	J700897	STU FIN AID WRK STU	51.30	
	03-17-77	J700925	FIN AID WRK STUDY	16.50	
					1707.80
	03-02-77	J700797	MT I A	2.08	
	03-02-77	J700803	JAN UCC	1.05	
	03-04-77	J700812	FEB SOCIAL SECURITY	20.47	
	03-04-77	J700818	FEB TRS	21.87	
	03-04-77	J700823	FEB UCC	1.05	
	03-04-77	J700829	FEB MT I A	5.64	
	03-11-77	J700891	FEB GROUP MED INS	1.33	
	03-11-77	J700897	STU FIN AID WRK STU	3.42	
	03-17-77	J700925	FIN AID WRK STUDY	1.10	
					58.01
	03-08-77	J700847	CHEM STORES	167.51	
	03-09-77	J700863	XEROX CHEM ENGR	11.32	
	03-04-77	7406897	IDAHO VALVE & FITTNG	24.86	
	03-04-77	7406898	H-R OXYGEN & SUPPLY	98.62	
	03-16-77	7407339	VWR SCIENTIFIC	163.84	
	03-23-77	7407642	COLE-PARMER	123.30	
					589.45
	03-08-77	J700848	TECHNICAL SERVICES	18.00	
					18.00
	03-17-77	J700935	PBX LONG DISTANCE	.80	
	03-23-77	J700953	XEROX REVOLV CHE	242.80	
					243.60
	03-01-77	7406801	LLOYD BERG	113.84	
	03-01-77	7406802	F P MCCANDLESS	113.84	
	03-21-77	J700943	MOTOR POOL	133.92	
					361.60
	03-15-77	7407290	NW PIPE FITTINGS	781.00	
					781.00
	03-18-77	7407489	MONT STATE UNIV	60.10	
	03-23-77	7407653	MONTANA STATE UNIV	60.10	
					120.20

DETAIL	DATE	NUMBER	DESCRIPTION	AMOUNT	TOTAL
ENCUMBRANCE	03-31-70		SALARY ENCUMBRANCE	1050.00	
	03-31-70		SALARY ENCUMBRANCE	1200.00	
					2250.00

G & C PROJECT FINANCIAL REPORT NO. 789 04/30/1977

DEPT 6131 BERG DISTILLATE FUELS BEGIN DATE 07-01-75 END DATE 6-19-78

	CURRENT MO.	TOTAL TO DATE	AMT. AUTH.
RECEIPTS	7431.60	69159.04	155932.00

EXPENDITURES			ENCUMBRANCES	TOTAL COMMITTED	BUDGET
SALARY AND WAGES	478.00	32211.15	800.00	33011.15	68657.
BENEFITS	47.82	1535.02		1535.02	4255.
REP & MAINT		8.00		8.00	
TRAVEL		1349.29		1349.29	3000.
COMMUNICATIONS	4.25	278.32		278.32	
COMPUTER					3000.
SUPPLIES	365.25	11100.91		11100.91	12750.
SUBCONTRACT		150.97		150.97	
EQUIPMENT		4395.86		4395.86	12700.
AWARDS		1386.45		1386.45	6000.
INDIRECT CHARGES	359.71	23085.75	22484.25	45570.00	45570.
TOTAL	1255.03	75501.72	23284.25	98785.97	155932.
BALANCE	CASH -6342.68		FREE BALANCE	57146.03	

DETAIL TRANSACTION	DATE	NUMBER	DESCRIPTION	AMOUNT	TOTAL
	03-30-77	E007571	US TREAS 97003987	3491.84	
	04-05-77	E008904	US TRES 97103170	3939.76	
					7431.60
	- -7		TEIGEN SHARON L	39.00	
	- -7		HAUGEN MARILYN M	30.00	
	- -7		KORWALD DEIDRA L	9.00	
	- -7		KUJAWA STEPHAN T	400.00	
					478.00
	04-15-77	J701047	MAR MT IA	3.10	
	04-15-77	J701053	MAR SOCIAL SECURITY	20.47	
	04-15-77	J701058	MAR UCC	1.05	
	04-15-77	J701062	MAR TRS	21.87	
	04-19-77	J701085	MAR GROUP MED INS	1.33	
					47.82
	04-04-77	J700982	CHEM STORES	83.56	
	04-13-77	7408157	COLE-PARMER	36.10	
	04-11-77	J701024	LIBRARY LOAN	5.50	

DETAIL	DATE	NUMBER	DESCRIPTION	AMOUNT	TOTAL
TRANSACTION	04-18-77	7408165	MSU BOOKSTORE	27.75	
	04-20-77	7408266	FRONTIER AIRLINES	28.60	
	04-20-77	J701097	CHEM STORES	84.71	
	04-21-77	J701104	XEROX REVOLV CH E	99.03	
					365.25
	04-19-77	J701090	FEB PBX	4.25	
					4.25
ENCUMBRANCE	04-30-70		SALARY ENCUMBRANCE	800.00	
					800.00

G E C PROJECT FINANCIAL REPORT NO. 789 05/31/77

DEPT 6131 BERG DISTILLATE FUELS BEGIN DATE 07-01-75 END DATE 6-19-78

	CURRENT MO.	TOTAL TO DATE	AMT. AUTH.
RECEIPTS	5087.65	74246.69	155932.00

	CURRENT MO.	TOTAL TO DATE	ENCUMBRANCES	TOTAL COMMITTED	BUDGET
EXPENDITURES					
SALARY AND WAGES	3899.38	36110.53	900.00	37010.53	68657.
BENEFITS	5.09	1540.11		1540.11	4255.
REP & MAINT		8.00		8.00	
TRAVEL		1349.29		1349.29	3000.
COMMUNICATIONS		278.32		278.32	
COMPUTER					3000.
SUPPLIES	551.90	11652.81		11652.81	12750.
SUBCONTRACT		150.97		150.97	
EQUIPMENT	1023.30	5419.16		5419.16	12700.
AWARDS	63.70	1450.15		1450.15	6000.
INDIRECT CHARGES	2671.05	25756.80	19813.20	45570.00	45570.
TOTAL	8214.42	83716.14	20713.20	104429.34	155932.
BALANCE	CASH -9469.45		FREE BALANCE	51502.66	

DETAIL TRANSACTION	DATE	NUMBER	DESCRIPTION	AMOUNT	TOTAL
	05-20-77	F005895	US TREAS #98338492	5087.65	
					5087.65
	- -7		HAUGEN MARILYN M	153.00	
	- -7		HASS GARY R	100.00	
	- -7		HEATON LEE M	400.00	
	- -7		HENTON LEE M	400.00	
	- -7		KUJAWA STEPHAN T	400.00	
	- -7		ANDERSON MARK D	37.50	
	05-03-77	J701160	FIN AID WRK STUDY	8.88	
	05-24-77	J701285	CORR P/R-GARY HASS	800.00	
	05-24-77	J701286	CORR P/R-L HENTON	1600.00	
					3899.38
	05-03-77	J701160	FIN AID WRK STUDY	.59	
	05-10-77	J701291	APR MT IA	1.54	
	05-24-77	J701285	CORR P/R-GARY HASS	.96	
	05-24-77	J701286	CORR P/R-L HENTON	2.00	
					5.09

DETAIL	DATE	NUMBER	DESCRIPTION	AMOUNT	TOTAL
TRANSACTION	05-02-77	7408520	ACADEMIC PRESS INC	91.93	
	05-03-77	J701158	READER PRINTER COPY	15.45	
	05-12-77	J701235	CHEMISTRY STORES	37.44	
	05-19-77	7408925	VWR SCIENTIFIC INC	58.32	
	05-23-77	7408984	MSU BOOKSTORE	4.75	
	05-19-77	J701281	CHEM STORES	344.01	
					551.90
	05-20-77	7408956	VWR SCIENTIFIC INC	1023.30	
					1023.30
	05-16-77	J701240	BUSINESS OFFICE	63.70	
					63.70
ENCUMBRANCE	05-31-70		SALARY ENCUMBRANCE	900.00	
					900.00