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CATALYTIC HYDROGENATION OF COAL-DERIVED LIQUIDS

Interim Report for the

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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

For COED pyrolysis oil the evaluation of commercially available hydrotreating catalysts showed that the best denitrogenation catalysts are Cyanamid HDS9A and Harshaw HT 500 but only about 30% nitrogen reduction is obtained. The best hydrodesulfurization catalysts are Harshaw HT 400, Shell 344 and Cyanamid HDS20A with about 90% of the sulfur removed. The program is now devoted to synthesizing new catalysts for this specific feed stock. Five Ketjen and one Norton supports impregnated with molybdenum, cobalt and nickel are being evaluated.

For PAMCO Solvent Refined Coal (SRC) Vacuum Flash Feed, the best commercially available denitrogenation catalyst is Harshaw Co-Mo-0401-T-1/8". The best desulfurization catalyst is Shell 324-E-1/16". Improved desulfurization was obtained with a catalyst fabricated here containing 0.2% NiO, 1.1% CoO, 15.5% MoO_3 on alumina and improved denitrogenation was accomplished with a catalyst comprising 0.26% NiO, 1.15% CoO, 13.1% MoO_3 on a Ketjen support.

For SYNTHOIL the best commercially available catalyst for desulfurization is Harshaw HT 500, for denitrogenation is Shell 324.

NUGGET

For SRC a catalyst synthesized here comprising a nickel - cobalt-molybdenum on a Ketjen alumina-silica support gives the greatest amount of denitrogenation.

COED PYROLYSIS OIL - S. Kujawa

SUMMARY OF TECHNICAL PROGRESS

During previous quarters, it was found that for hydrotreating COED Pyrolysis oil, nitrogen removal was best effected by the nickel-moly catalysts Cyanamid HDS9A and Harshaw HT500. Sulfur removal was best using the Cobalt-Moly catalysts Harshaw HT400, Shell 344, and Cyanamid HDS20A. Sulfur removal averaged over 90 percent and nitrogen removal averaged 30 percent in the better runs at 415^{o}C and 800 psig.

The intent of the work done for this report was to test the effects of the support on heteroaton removal. To accomplish this, five Ketjen and one Norton support were impregnated with Molybdenum, Cobalt and Nickel, the finished sulfided catalysts were then reacted with the feed.

The metal amounts on the supports varied greatly so that only two of the catalysts could be compared on an equal loading basis. One other catalyst was eliminated due to impregnation difficulty, and two others were of large diameter so the results of using them are clouded by film diffusion more than the smaller supports.

Two of the MSU catalysts, containing varying amounts of silica, and having different average unimpregnated pore sizes, were compared with the conclusion that nitrogen removal could be either a function of pore size or silica amount. Sulfur removal data was too scattered to conclude this however. Neither of the catalysts worked as well as the commercial catalysts.

It is apparent that closer control of catalysts makeup is necessary to determine support effects. To accomplish this, factorial catalyst tests will be run to determine metal content effect and then support effect.

OBJECTIVES DURING THIS QUARTER

The experimental work during this quarter attempted to establish the effects of the support on hydrotreating COED Pyrolysis Oil. To accomplish this objective, six catalysts were made that contained approximately the same amounts of metal oxides on one Norton and five Ketjen catalyst carriers. The feedstock was then reacted over these catalysts at the same conditions that had previously been used for the commercial catalyst screening tests. THe ranking of these catalysts was then determined by the heteroatom removal from the feed.

CATALYST PREPARATION

The catalysts were made by impregnating aqueous solutions of Ammonium Hepta Molybdate, Nickel Nitrate, and Cobalt Nitrate on the supports in separate steps. The catalyst was impregnated first with Ammonium Molybdate, air dried, oven dried, and then calcined to 450^{o}C. The catalyst was then weighed to determine the amount of M_0O_3 that was on it. Nickel and Cobalt were put on the catalyst in similar separate steps and weighed to determine the nickel oxide and cobalt oxide amounts. The catalysts were then sulfided in an H_2S-H_2 mixture and then loaded in the reactor prior to the experimental run. The supports and catalysts were described in Table I-1.

EXPERIMENTAL PROCEDURE

The experimental runs were made with a continuous reactor made from a 30" long piece of 1" Inconel schedule 80 pipe. TNe pressure was approximately 800 psig and the hydrogen feed rate was approximately 10,000 scf/bbl (1781 NL/L). The catalyst bed consisted of 80 ml. of catalyst mixed with 80 ml of inert

Denstone support and was preceeded in the reactor by inertsupport used as a preheating section. During the runs it was attempted to keep the top and bottom of the bed at 410°C; usually the middle of the bed temperature was such that the average of the three was approximately 415°C. Two to three reactor volumes of feed were run through the reactor between changes of variables to allow the reactor operation to steady out, usually three samples were taken during a run with the total amount of feed being between 1200 and 1700 ml. No attempt was made to check the initial activity decay of the catalyst.

TABLE I-1

SUPPORT PROPERTIES

Norton 6176:

Al_2O_3 (>99.85%)
NA_2O (<.014%)
SiO_2 (<.12%)
S.A. = 250 ± 20 m^2/g
P.V. = .8 - 1.1 cc/g
Avg. Pore Dia. ∿152 Å [1]

Ketjen Supports

Support No.	Weight Percent Al_2O_3	SiO_2	NA_2O	S.A.	P.V.	P.D.[1]
003-1.5E	bal.	1.33%	.01%	240	.7	117
006-1.5E	bal.	.37	.10	200	.73	146
005-2E	bal.	.55	.06	150	.64	171
000-3E	bal.	1.5	.13	230	.64	111
LA-3P	13.8	bal.	.13	410	.56	55

1. Avg. Pore Dia. = 40,000 X P.V. ÷ S.A. in Å

TABLE I-1 continued

CATALYST DESCRIPTION

Catalyst No.	Support No.	Weight Percent Mo[2]	Ni	Co
STK5-2-1	Norton 6176	23.9	.48	.75
STK5-2-2	Ketjen 003-1.5E	13.1	.26	1.15
STK5-2-3	Ketjen 000-3E	16.4	.5	1.1
STK5-2-4	KetjenLA-3P	5	1	.9
STK5-2-5	Ketjen 005-2E	14	.5	.8
STK5-2-6	Ketjen 006-1.5E	15.5	.2	1.1

2. Metal oxide weight percent

Shell 344	2.4% Co, 9.9% Mo, Alumina, 195 m^2/g, .6cc/g 123Å Avg. P.D.
Harshaw HT500	3.17% Ni, 15.5% Mo, Alumina, 210 m^2/g, .49 cc/gm, 93 Å Avg. P.D.

RESULTS AND DISCUSSION

CATALYST CHARACTERISTICS

The six supports described in Table I-1 varied mainly in silica content and average pore size. When the six were made into catalysts, the metal oxide amounts varied more than was wanted, so that the data from the runs using the catalysts cannot be interpreted only as due to support properties.

Of the six catalysts, one, STK5-2-4 on Ketjen LA-3P support, can be eliminated from consideration because of pore plugging during Molybdenum impregnation and the inability to impregnate it without agglomerating the particles.

The catalysts STK5-2-3 and STK5-2-5 are both of a diameter greater than 1/16", so when interpreting the results using these, it must be remembered that they will show external diffusion effects as compared to the other catalysts of 1/16" diameter, namely STK5-2-1, STK5-2-2, and STK5-2-6.

The three catalysts, STK5-2-1, 5-2-2, and 5-2-6 are of the same diameter but STK-5-2-1 was a much greater amount of Molybdenum oxide on it, which eliminates it from support properties comparison. Finally, STK-5-2-2 and 5-2-6 are the same diameter and approximately the same metals composition, therefore, of the six, the results of the runs using them can probably be used to interpret support effects.

RESULTS OF EXPERIMENTAL RUNS

NITROGEN REMOVAL

Figure I-1 plots the weight percent of Nitrogen in the product against space velocity for the three best MSU catalysts and one of the best commercial catalysts. The experimental results for all of the MSU catalysts is presented in Table I-2. None of the MSU catalysts performed as well as the Harshaw catalysts, however, the slightly better nitrogen removal by STK5-2-6 seems to imply that either a catalyst with larger average pore size or less silica improves nitrogen removal. (This assumes that the impregnated pore size stays larger when comparing STK5-2-6 with 5-2-2.) As was stated before, STK5-2-1 contained much more Molybdenum than the other catalysts and could not be compared with them. The poorer performance of STK5-2-1 could therefore be due to pore plugging.

SULFUR REMOVAL

Figure I-2 shows the sulfur removal effected by four of the MSU catalysts and one of the best commercial catalysts. Again, the commercial catalyst performed best. In this Figure, STK-5-2-2 and STK-5-2-6 performed equally well, the data for 5-2-6 having much scatter however. The two best MSU catalysts performed much closer to the commercial catalyst in sulfur removal than in nitrogen removal.

STK5-2-1, it is assumed, again probably had pores plugged by high molybdenum content. The performance of STK5-2-5 could possibly be explained by its larger diameter since it is believed that film diffusion is present to a great extent in this system.

CONCLUSION

From Figure I-2, and the data for STK5-2-2 and STK5-2-6, it appears that pore size effects do not have the influence on sulfur removal that they appear to have on nitrogen removal. More work will have to be done before this conclusion can be verified.

FORECAST

Eight catalysts are now being prepared on Ketjen 003-1.5E support. These will be used in a factorial experiment to determine the effects of cobalt, nickel, and molybdenum oxides on the heteroaton removal. This is necessary because of the apparent pore plugging that occurred in this quarters work. After these experiments are completed, the Norton 6176 and Ketjen 006-1.5E supports will be impregnated in an attempt to determine support effects in the reaction.

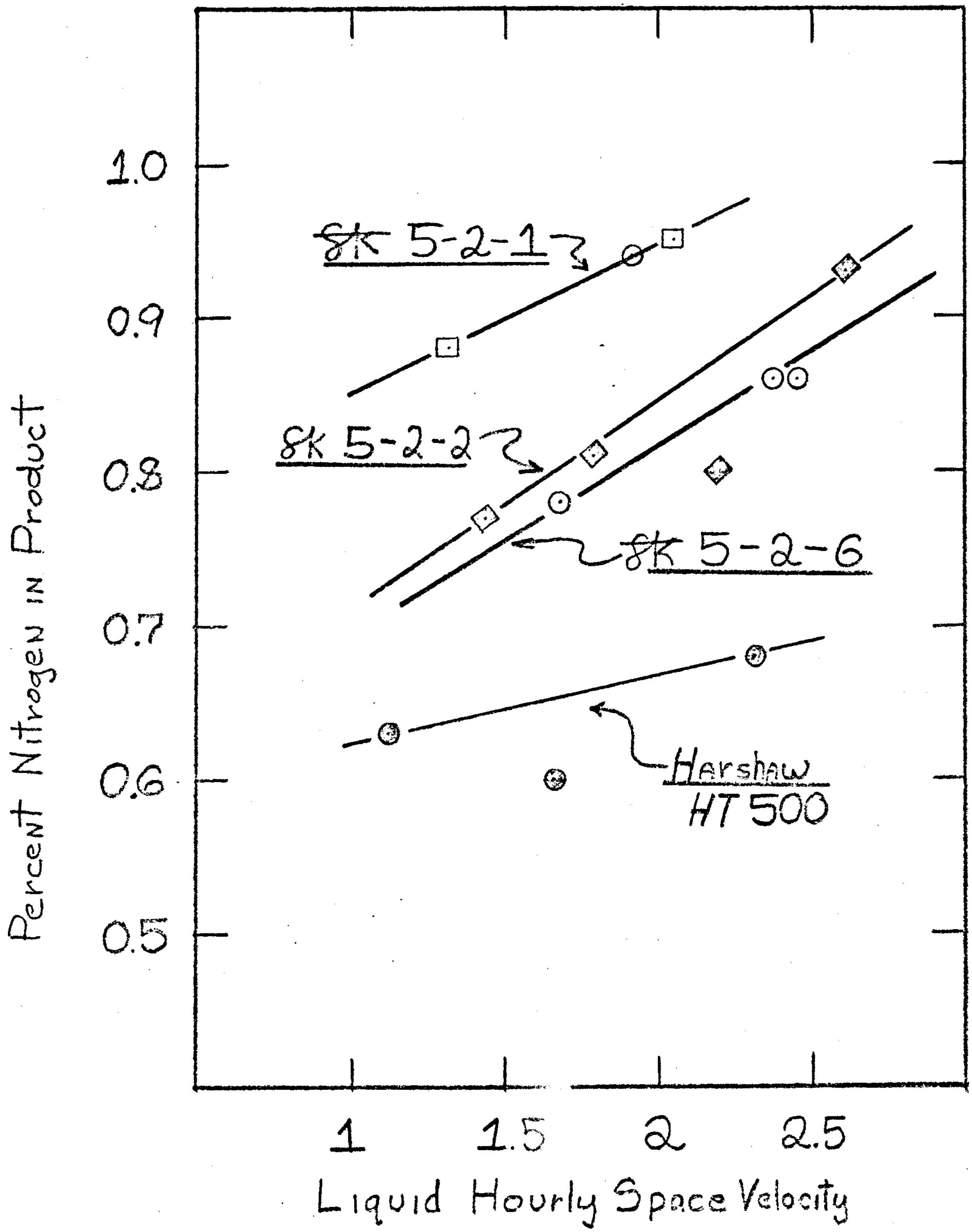
1.0
0.9
0.8
0.7
0.6
0.5
8K 5-2-1
8K 5-2-2
8K 5-2-6
Harshaw HT 500
Percent Nitrogen in Product
1
1.5
2
2.5
Liquid Hourly Space Velocity

FIGURE I-1

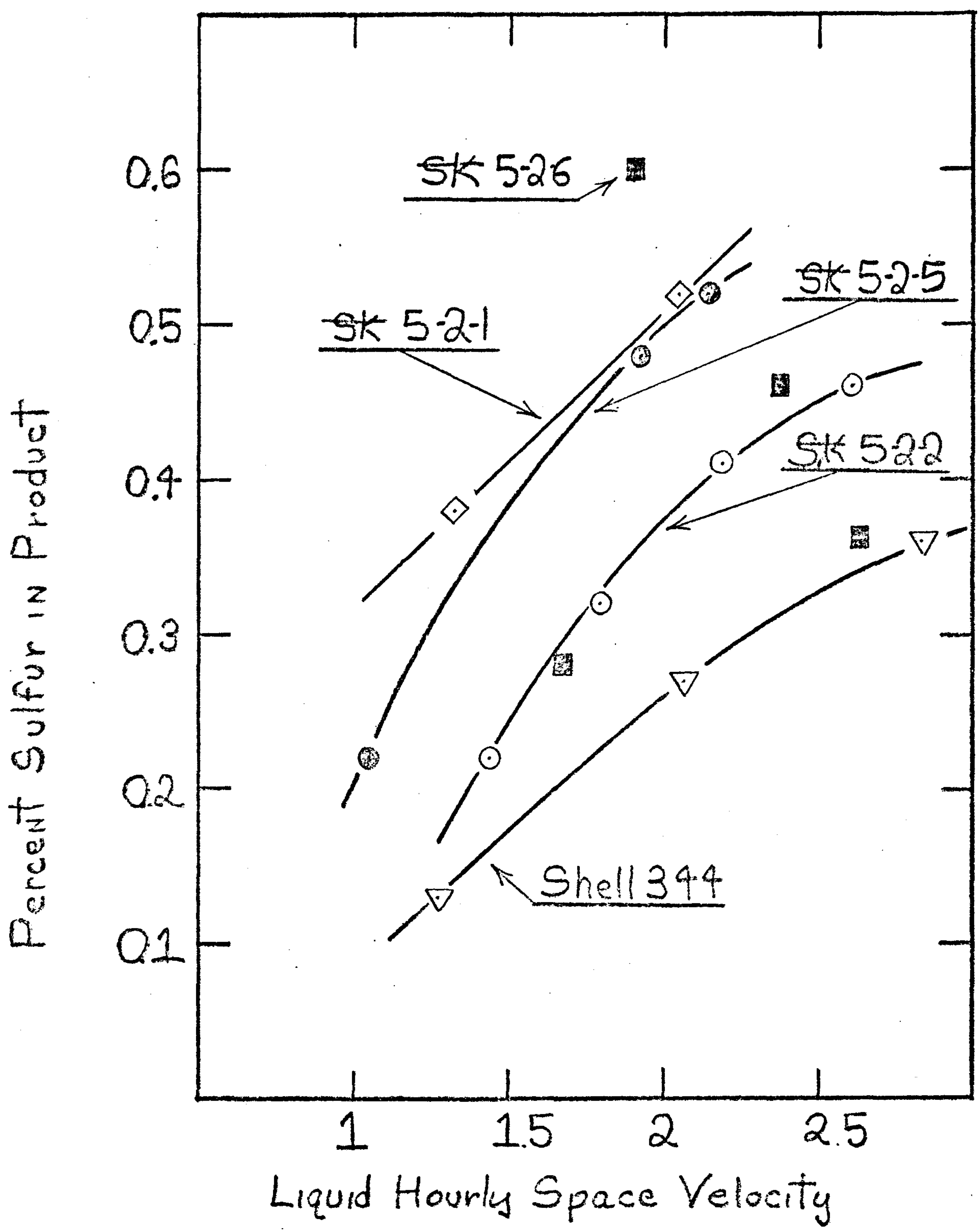
SK 5-26
SK 5-2-5
SK 5-2-1
SK 5-2-2
Shell 344
0.6
0.5
0.4
0.3
0.2
0.1
1
1.5
2
2.5
Percent Sulfur in Product
Liquid Hourly Space Velocity

FIGURE I-2

TABLE I-2

COBALT - NICKEL - MOLYBDATE CATALYST PERFORMANCE

Catalyst Avg. Bed Temp (^{o}C) H_2 Feed Rate (NL/L	Liquid Hourly Space Velocity	% S in Product	% Removal of S	% N in Product	% Removal of N	ASTM D86 Distillation of Liquid Product. Vol. % Boiling Below			
						425F	600F	700F	Recovery
STK 5-2-1	1.32	.38	83	.88	4.3	14	41	60	67
416	2.05	.52	77	.95	0	14	38	58	68
1811									
STK 5-2-2	1.44	.22	90	.77	17				
413	1.78	.32	86	.81	12	15	41	61	68
1831	2.19	.41	82	.80	13	15	42	61	70
	2.61	.46	80	.93	0				
STK 5-2-3	1.66	.57	75	.92	0				
415	1.81	.52	77	.90	2	14	40	57	64
1755	1.97	.57	75	1.04	0				
	2.36	.65	71	.93	0				
STK 5-2-4	1.23	1.19	48	.97	0	11	35	51	60
412	1.71	1.22	46	.94	0				
1792									
STK 5-2-5	1.05	.22	90	.97	0	15	43	60	66
413	1.93	.48	79	.91	1				
1843	2.24	.52	77	.91	1	13	35	53	65
STK 5-2-6	1.67	.28	88	.78	20				
413	1.91	.6	74	.94	0				
1699	2.37	.46	80	.86	7	14	43	68	76
	2.45	.36	84	.86	7	15	42	64	74

CONVERSION OF SOLVENT REFINED COAL TO DISTILLATE FUELS - G. R. Hass

SUMMARY OF BATCH CATALYST SCREENING TESTS

Table II-I appended to this report, summarizes heteroatom removal data and ASTM distillation data for all batch tests made with PAMCO's Solvent Refined Coal (SRC) Vacuum Flash Feed. All batch tests were made previous to this quarter but complete ASTM Distillation data has not been previously reported. Batch tests 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	= 420C $\pm$ 5^{o}C
Residence Time	= 1 hour at run temp.

From Table II-I it can be seen that Shell 324-E-1/16" catalyst (2.7% Ni, 13.2% Mo on alumina) and MSU STK-14-E-1/16" (17.4% MoO_3, 2.3% NiO, 1.8% CuO on alumina) gave the best desulfurization in a batch run. It can also be seen that Harshaw Co-Mo-0401-T-1/8" (3% CoO, 9% MoO_3 on alumina) and MSU STK-8-1-E-1/16" (8.6% MoO_3, 1.4% NiO, 11% WO_3 on alumina) gave the best denitrogenation in a batch run.

SUMMARY OF CONTINUOUS FIXED BED REACTOR TESTS

Table II-11 summarized heteroatom removal data and ASTM Distillation data for continuous fixed bed reactor tests made with PAMCO's SRC Vacuum Flash Feed. Runs numbered C-1 through C-19 were completed previous to this quarter and runs C-20 through C-28 were made during this quarter. These continuous fixed bed reactor runs were made at the following conditions unless specifically noted:

Pressure	= 1000 psig
Temperature	= 450°C ± 5°C
H_2 to oil ratio	= 10,000 SCF/BBL
Catalyst bed	= 60 ml catalyst diluted with 60 ml Denstone 1/8" support.
LHSV	= 1.0, 1.5, 2.0

From Table II-11, it can be seen that the best desulfurization averaged over the three space velocities tested was obtained with MSU-STK 5-2-6 (.2% NiO, 1.1% CoO, 15.5% MoO_3 on alumina). THe best denitrogentation, over the space velocities tested was obtained with MSU-STK 5-2-2 (.26% NiO, 1.15% CoO, 13.1% MoO_3 on Ketjen-00 -E 1/16" support which contains 1.33% SiO_2).

DETAILED RESULTS

During this quarter five catalysts fabricated at MSU were tested to determine support effects on heteroatom removal. Four supports from Ketjen and one Norton support were impregnated with nickel oxide, cobalt oxide, and molybdenum trioxide. The properties of these supports and catalysts are reported in Table II-4.

Figure II-1 shows percent sulfur in product versus space time ($LHSV^{-1}$) for these five catalysts. The best sulfur removal was obtained with MSU-STK 5-2-6. Figure II-3 shows percent nitrogen in product versus space time ($LHSV^{-1}$) for these five catalysts. The best nitrogen removal was obtained with MSU-STK 5-2-2. Also this quarter five catalysts were fabricated on Ketjen support 003-E 1/16" to determine optimum metal loadings of nickel oxide, cobalt oxide, and tungsten trioxide. The support was chosen from the test results of the five Ni-Co-Mo catalysts mentioned above. Ketjen 003-E1/16" support gave the best denitrogenation when loaded with NiO, CoO, and MoO_3. The properties of the five Ni-Co-W catalysts are reported on Table II-5.

Figure II-2 shows percent sulfur in product versus space time ($LHSV^{-1}$) for these five catalysts. These data are too similar to make any conclusions on the effects of metal loading on sulfur removal. Figure II-4 shows percent nitrogen versus space time ($LHSV^{-1}$) for these five catalysts. These data are too similar to make any conclusions on the effects of metal loading on nitrogen removal.

The data from the five Ni-Co-Mo catalysts seems to indicate pore volume and average pore diameter has some effect on nitrogen removal. This is also substantiated in the literature[1,2].

CONCLUSIONS FROM THIS QUARTER'S WORK

1. MSU-STK 5-2-2-E1/16" gave the best denitrogenation over the space velocities tested.
2. MSU-STK 5-2-6E1/16" gave the best desulfurization over the space velocities tested.
3. Pore volume distribution plays a very important role in denitrogenation.

FORECAST OF FUTURE WORK

Eight nickel oxide, cobalt oxide, and molybdenum trioxide catalysts are being fabricated on Ketjen 003-E1/16" support to further study the effects of metal

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[1] U.S. Patent 3,928,176 Exxon Research Co.

[2] U.S. Patent 3,891,539 Texaco, Inc.

loading on denitrogenation and desulfurization.

The gas chromatograph system has been set up and calibrated and is ready for mass balance studies around our reactors.

Temperature studies using the best catalysts will be completed.

TABLE II-I

DATA SUMMARY OF BATCH RUNS ON S R C VACUUM FLASH FEED

RUN	CATALYST	% DN*	% DS**	ASTM DISTILLATION D-86 (VOL %) IBP-425°F	425-600°F	600-700°F	YIELD
26B	Harshaw HT-400-E-1/8"	25.4	34.8	12.0	32.7	23.7	68.4
27B	Harshaw HT-500-E-1/8"	16.9	33.2	7.8	37.2	19.5	64.5
28B	Ketjen HC-5-E-1/16"	5.8	27.0	8.0	32.0	21.9	61.9
29B	Ketjen-330-E-3/32"	12.3	37.3	9.8	35.2	21.2	66.2
30B	Harshaw Co-Mo-0401-T-1/8"	29.5	36.0	9.5	34.0	24.2	67.9
31B	MSU-STK-6-E-1/16"	1.5	17.7	10.7	36.1	18.3	65.1
32B	Shell 324-E-1/16"	27.5	75.3	9.1	39.2	27.4	75.7
33B	Shell 344-E-1/16"	18.8	52.5	8.5	35.4	32.2	76.1
34B	MSU-STK-5-E-1/16"	20.2	44.1	8.7	35.8	29.2	73.7
35B	Harshaw Ni-4401-T-1/8"	20.4	35.7	12.0	28.8	25.0	65.8
36B	MSU-STK-8-2-E-1/16"	21.5	47.7	8.5	36.8	31.8	77.1
37B	MSU-STK-10-E-1/16"	12.0	28.3	9.4	32.9	26.8	69.1
38B	MSU-STK-11-E-1/16"	12.0	38.9	8.3	32.5	28.7	69.5
39B	Harshaw Ni-4303-1/8"	19.4	42.1	8.8	31.7	25.6	67.05
40B	MSU-STK-14-E-1/16"	10.2	50.8	8.0	34.0	34.2	76.2
41B	MSU-STK-9-E-1/16"	14.9	8.7	5.7	34.6	24.3	64.6
42B	MSU-STK-12-E-1/16"	16.1	46.7	8.7	34.3	24.7	67.7
43B	MSU-STK-13-E-1/16"	21.7	21.0	8.9	32.8	24.5	66.2
44B	MSU-STK-8-1-E-1/16"	29.4	15.7	8.1	36.5	25.9	70.5

* % DN - Weight Percent Denitrogenation

** % DS - Weight Percent Desulfurization

NOTE: This sample of S R C Vacuum Flash Feed contained .644% Sulfur and 1.30% Nitrogen.

TABLE II-II

DATA SUMMARY OF CONTINUOUS RUNS ON S R C VACUUM FLASH FEED

RUN	CATALYST	LHSV*	% DN**	% DS***	ASTM DISTILLATION D-86 (VOL %) IBP-425°F	425-600°F	600-700°F	YIELD
C-1	Shell 324-E-1/16"	1.0	38.8	70.5	13.6	41.2	22.1	76.9
		1.5	15.4	61.8	7.3	35.5	31.4	74.2
		2.0	8.5	49.5	7.8	33.8	27.3	68.9
C-3	Harshaw Co-Mo-0401-T-1/8"	1.0	19.2	54.2	8.3	41.5	26.6	76.4
		1.5	12.7	59.9	8.0	36.6	28.2	72.8
		2.0	3.8	38.8	7.9	35.4	31.2	74.5
C-4	Harshaw HT-400-E-1/16"	1.0	33.8	67.1	11.9	39.5	24.2	75.6
		1.5	32.3	53.9	8.5	41.6	28.0	78.1
		2.0	26.2	55.3	8.2	37.6	28.0	73.8
C-5	Harshaw HT-4-0-E-1/8"	1.0	18.8	62.3	8.3	38.4	30.5	77.2
		1.5	20.5	56.4	8.2	36.6	34.3	79.2
		2.0	10.1	34.3	5.6	33.0	29.0	67.6
C-6	Harshaw HT-500-E-1/8"	1.0	18.5	53.1	7.9	38.8	31.4	78.1
		1.5	20.0	58.8	7.9	37.5	26.3	71.7
		2.0	13.1	53.6	5.7	36.0	33.3	75.0
C-7	Shell 344-E-1/16"	1.0	31.1	73.9	12.4	38.9	23.3	74.6
		1.5	37.0	61.2	13.5	39.0	24.2	76.7
		2.0	17.7	65.2	8.0	38.3	28.9	75.2
C-8	Harshaw Ni-4401-T-1/8"	1.0	15.2	66.3	7.7	35.6	30.01	73.4
		1.5	17.8	38.2	8.1	34.6	31.5	74.2
		2.0	13.5	41.5	1.3	38.2	32.7	72.2
C-9	Cyanamid HDS-20A	1.0	18.4	62.5	10.2	47.0	26.7	83.9
		1.5	16.7	70.8	9.7	44.6	27.1	81.4
		2.0	11.0	69.4	9.0	44.5	23.8	77.3
C-10	Cyanamid HDS-9A	1.0	21.1	61.1	7.7	49.3	24.6	81.6
		1.5	26.3	62.5	12.5	51.0	17.7	81.2
		2.0	21.1	61.1	8.2	47.3	25.0	80.5

continued....

TABLE II-II - Continued

DATA SUMMARY OF CONTINUOUS RUNS ON S R C VACUUM FLASH FEED

RUN	CATALYST	LHSV*	% DN**	% DS***	ASTM DISTILLATION D-86 (VOL %)			
					IBP-425°F	425-600°F	600-700°F	YIELD
C-11	Harshaw Co-Mo-0603-T-1/8"	1.0	13.2	54.2	13.0	43.0	21.7	77.7
		1.5	15.4	45.8	12.4	46.7	21.8	80.9
		2.0	4.4	54.9	13.0	57.6	20.9	75.5
C-12	Harshaw Ni-4301-T-1/8"	1.0	9.6	61.1	12.0	39.6	23.0	74.6
		1.5	10.5	51.4	10.4	41.3	28.4	80.1
		2.0	2.2	48.6	9.9	40.5	22.1	72.5
C-13	Harshaw Ni-4303-T-1/8"	1.0	11.4	53.5	10.2	45.9	25.7	81.8
		1.5	15.8	55.6	10.2	44.7	24.9	79.8
		2.0	11.4	48.6	8.8	43.7	24.1	76.6
C-14	Harshaw HT-400-E-1/16"							
	C-14-1	2.0	20.2	54.9	4.7	42.7	22.3	69.7
	C-14-2	2.0	1.8	43.1	6.3	38.2	27.2	71.7
	C-14-3	2.0	-0-	47.2	9.5	38.5	24.8	72.8
	C-14-4	2.0	-0-	41.7	6.5	38.5	23.4	68.4
C-15	Harshaw HT-100-E-1/12"	1.0	17.1	56.2	10.1	45.3	23.3	78.7
		1.5	21.5	51.4	10.2	45.7	22.7	78.6
		2.0	6.0	54.2	7.5	43.2	21.3	72.0
C-16	Harshaw Ni-3250-T-1/8"	1.0	18.0	21.5	7.5	43.5	22.5	73.5
		1.5	14.5	16.0	5.1	47.5	21.2	73.8
		2.0	4.8	18.1	2.7	42.6	23.3	68.6
C-17	Harshaw Ni-1601-T-1/8"	1.0	30.3	20.1	5.6	44.0	25.3	74.9
		1.5	32.9	27.8	6.1	50.7	23.9	80.7
		2.0	24.1	4.2	7.1	40.5	28.5	76.1
C-18	MSU-STK-5-2-1-E-1/16"	1.0	32.9	47.9	11.8	42.8	22.6	77.2
		1.5	39.5	47.9	11.9	43.6	21.2	76.7
		2.0	29.8	39.6	10.0	40.7	24.9	75.6

continued...

TABLE II-II - Continued

DATA SUMMARY OF CONTINUOUS RUNS ON S R C VACUUM FLASH FEED

RUN	CATALYST	LHSV*	% DN**	% DS***	ASTM DISTILLATION D-86 (VOL %) IBP-425°F	425-600°F	600-700°F	YIELD
C-19	MSU-STK-5-2-2-E-1/16"	1.0	46.5	56.2	15.4	45.3	25.7	86.4
		1.5	54.8	65.3	14.8	45.6	27.2	88.6
		2.0	35.1	53.5	8.1	44.5	26.3	78.9
C-20	MSU-STK-5-2-3-E-1/16"	1.0	32.0	58.3	10.2	46.1	23.6	79.9
		1.5	36.8	54.9	10.1	43.1	14.1	67.7
		2.0	30.7	52.1	9.1	42.6	25.4	77.1
C-21	MSU-STK-5-2-5-E-1/16"	1.0	34.2	64.6	10.2	45.3	24.0	79.5
		1.5	37.7	61.1	10.2	44.4	27.6	82.2
		2.0	30.3	48.6	10.2	46.5	21.3	78.0
C-22	MSU-STK-5-2-6-E-1/16"	1.0	36.0	72.9	10.1	50.8	24.5	85.4
		1.5	39.0	74.3	10.2	47.2	25.7	83.1
		2.0	31.1	70.1	10.3	46.3	24.8	81.4
C-23	MSU-GRH-1-E-1/16"	1.0	18.2	72.2	10.1	50.7	26.2	87.0
		1.5	-	66.0	19.8	45.1	25.1	90.0
		2.0	5.7	47.9				
C-24	MSU-GRH-2-E-1/16"	1.0	15.6	59.7				
		1.5	-	63.9				
		2.0	4.9	66.7	8.5	48.1	24.5	81.1
C-25	MSU-GRH-3-E-1/16"	1.0	18.0	56.1				
		1.5	24.2	61.1				
		2.0	6.6	47.8				
C-26	MSU-GRH-4-E-1/16"	1.0	22.5	54.7				
		1.5	23.8	56.0				
		2.0	6.1	51.1				

continued.....

TABLE II-II - Continued

DATA SUMMARY OF CONTINUOUS RUNS ON S R C VACUUM FLASH FEED

RUN	CATALYST	LHSV*	% DN**	% DS***	ASTM DISTILLATION D-86 (VOL %) IBP-425°F	425-600°F	600-700°F	YIELD
C-27	MSU-GRH-5-E-1/16"	1.0	20.7	54.3				
		1.5	29.3	61.1				
		2.0	8.6	43.1				
C-28	KETJEN-330-3-E-1/16"	1.0	15.1	55.8				
		1.5	15.8	48.3				
		2.0	5.2	45.8				

* LHSV - Liquid Hourly Space Velocity
** % DN - Weight Percent Denitrogenation
*** % DS - Weight Percent Desulfurization

NOTES: Runs C-1 through C-8 Feedstock contained: .644% S and 1.30% N
Runs C-9 through C-22 Feedstock contained: .72% S and 1.14% N
Runs C-23 through C-28 Feedstock contained: .72% S and 1.22% N

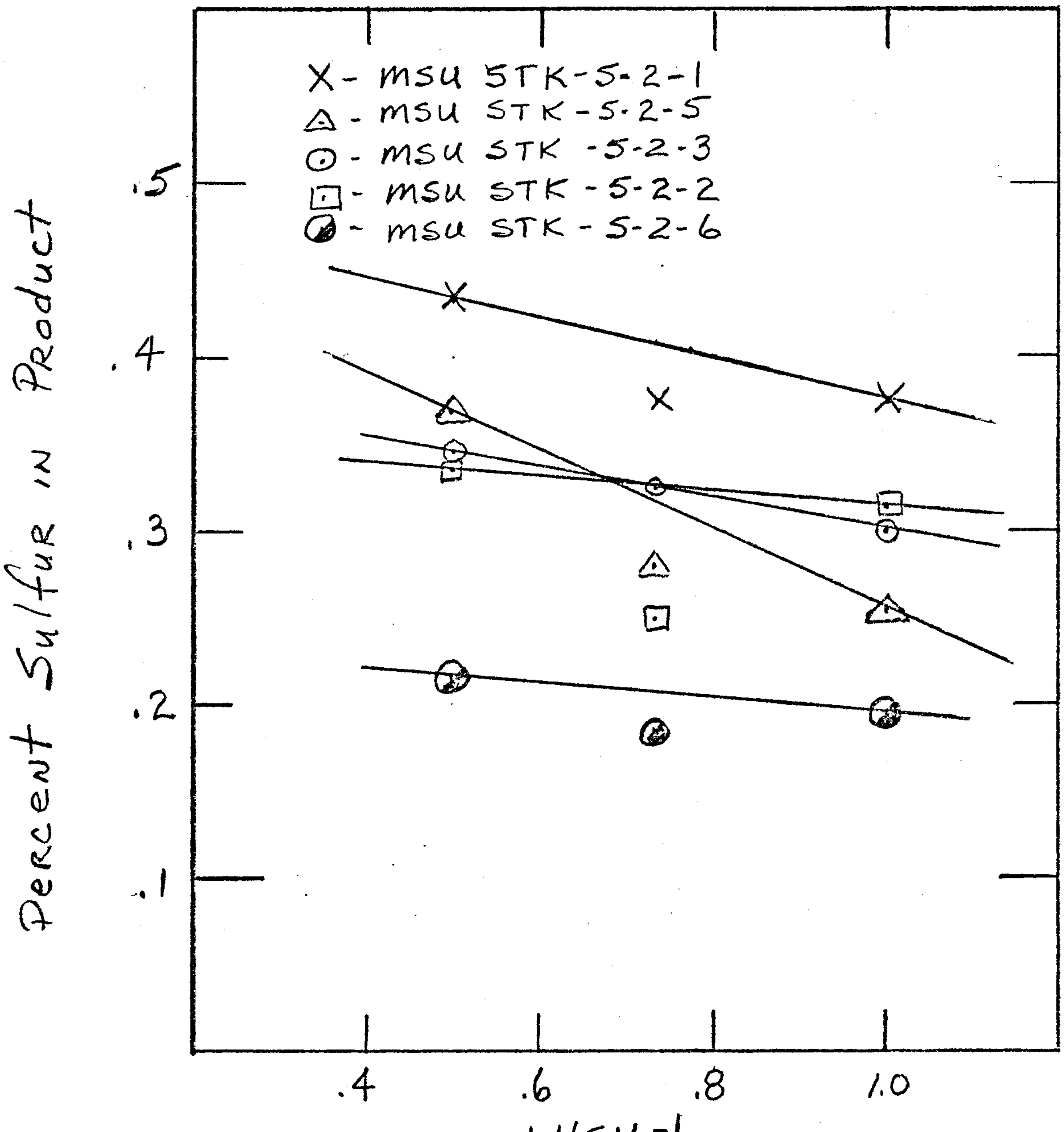


Figure II-1 MSU Ni-Co-Mo Catalysts

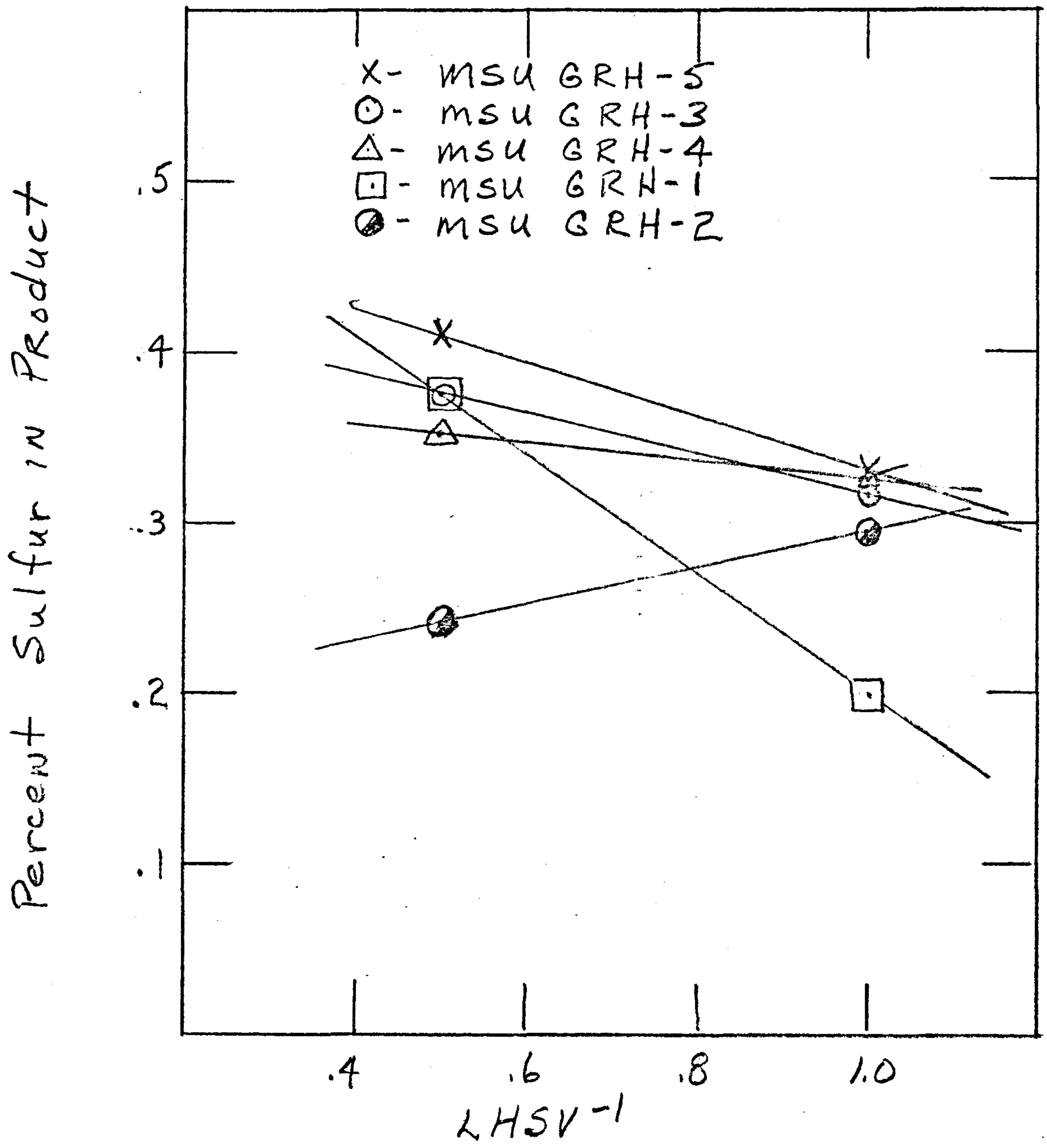


Figure II-2 MSU Ni-Co-W Catalysts

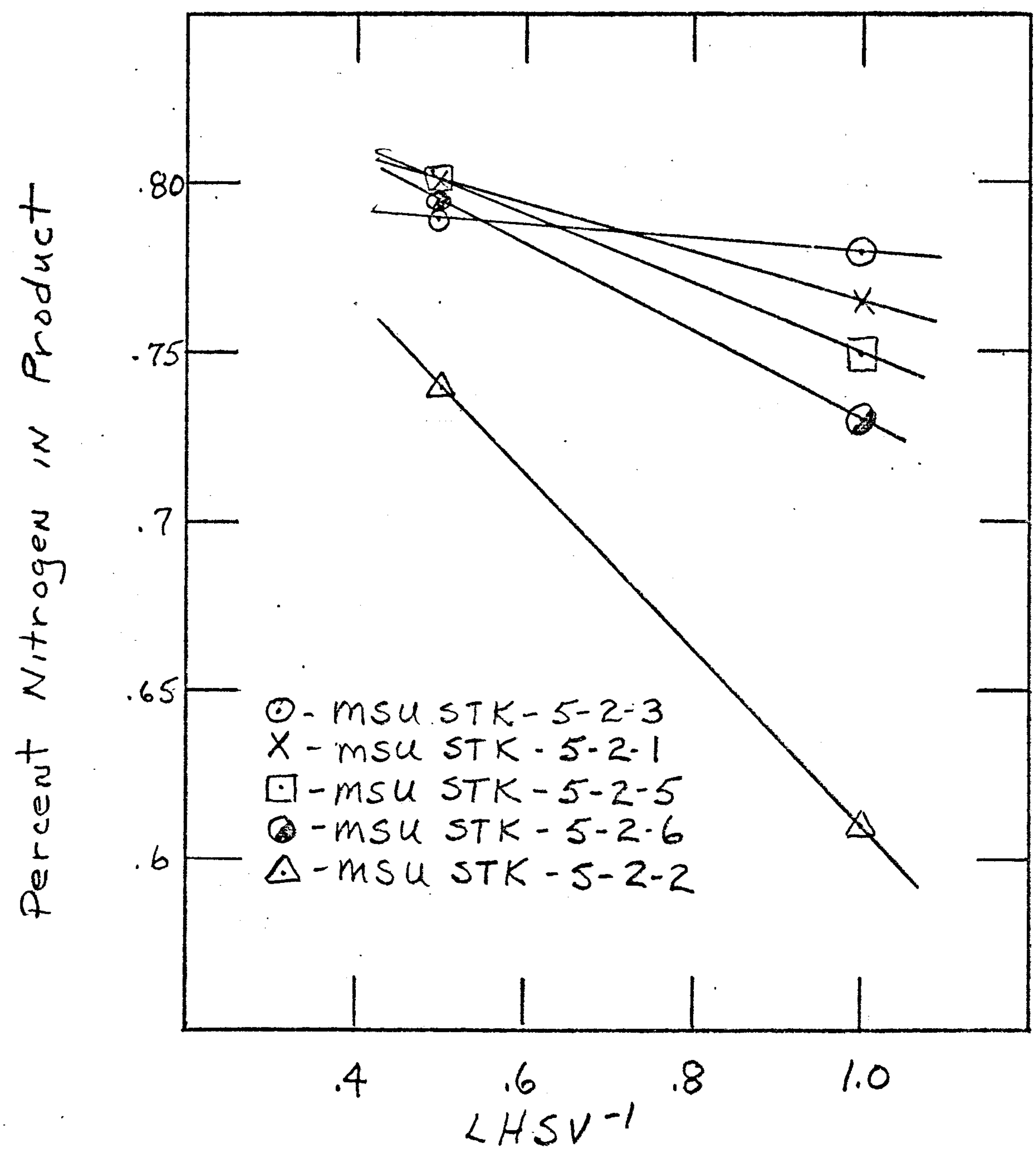


Figure II-3 MSU Ni-Co-Mo Catalysts

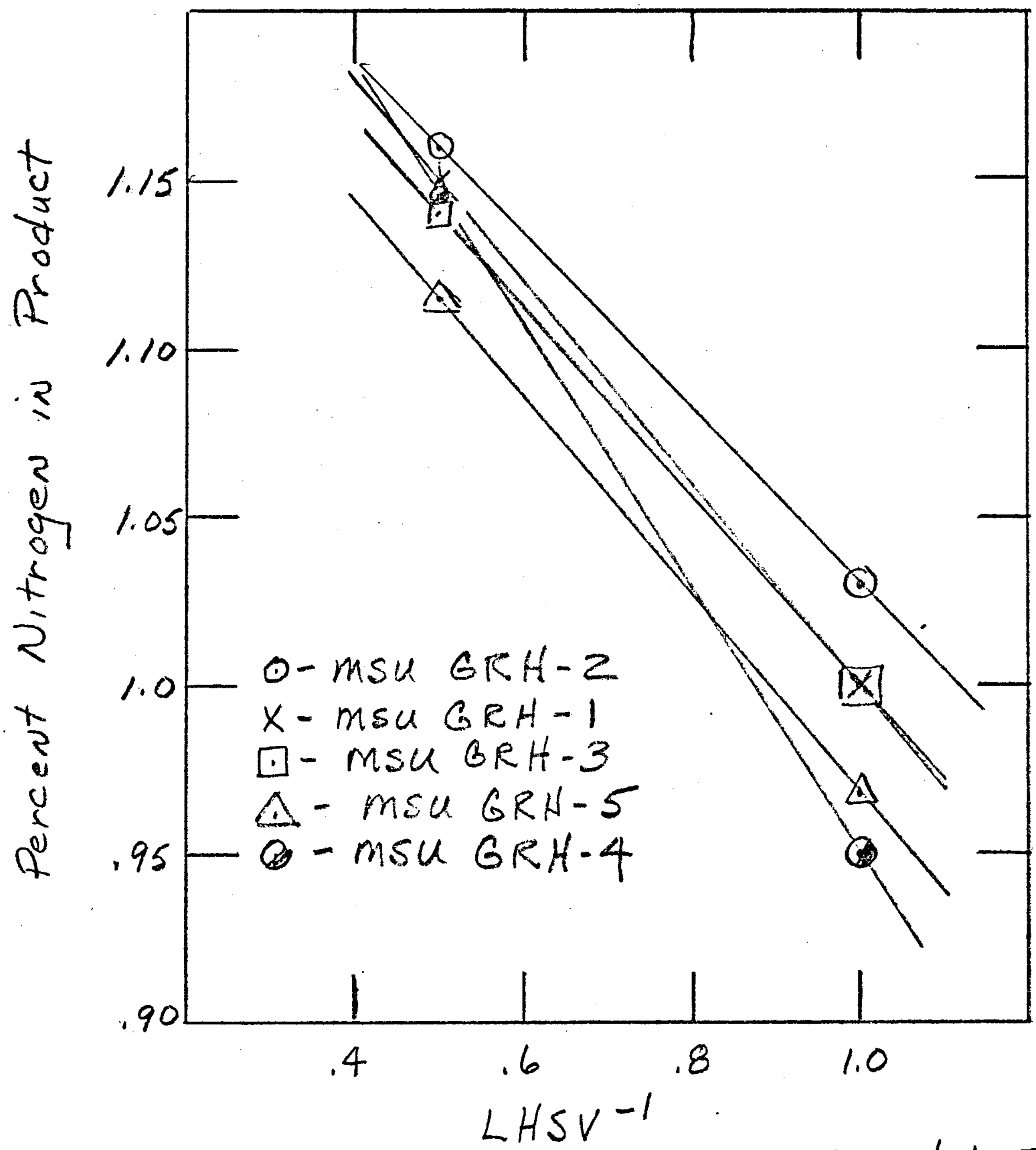


Figure II-4 MSU Ni-Co-W Catalysts

TABLE II-III

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.

continued...

TABLE II-III -continued

CATALYST DESCRIPTION

Cyanamid HDS-20A	5% CoO, 16.2% MoO_3 on alumina, 1/16" Tilobe S.A. = 230 m^2/g P.V. = .52 cc/g
Cyanamid HDS-9A	3.5% NiO, 18.0% MoO_3 on alumina, S.A. = 300 m^2/g, 1/8" extrudates
Houdry HR-811	3.0% NiO, 15.0% MoO_3 on alumina, S.A. = 300 m^2/g, 1/8" extrudates
Harshaw Co-Mo-0603	3% CoO, 12.0% MoO_3 on alumina
M.S.U.-STK-5-2-1	.48% NiO, 23.9% MoO_3, .75% CoO on Norton 6176 support.
M.S.U.-STKk-5-2-2	.26% NiO, 1.15% CoO, 13.1% MoO_3, on Ketjen-003-1.5E support which contains 1.33% SiO_2 .01% NA_2O, Balance Al_2O_3 S.A. = 240 m^2/g P.V. = .7 cc/g

TABLE II-4

Ni - Co - Mo CATALYSTS

Catalyst	Support	% MoO_3	% NiO	% CoO
MSU-STK-5-2-1	NORTON 6176	23.9	.48	.75
MSU-STK-5-2-2	KETJEN-003-1.5E	13.1	.26	1.15
MSU-STK-5-2-3	KETJEN-000-3E	16.4	.5	1.1
MSU-STK-5-2-5	KETJEN-005-2E	14.0	.5	.8
MSU-STK-5-2-6	KETJEN-006-1.5E	15.5	.2	1.1

SUPPORT PROPERTIES

Support	% Al_2O_3	% SiO_2	% NA_2O	S A m^2/g	P V cc/g	P.D.[1] Å
NORTON 6176	99.85	.12	.014	250	.9	152
KETJEN-003-1.5E	bal.	1.33	.01	240	.7	117
KETJEN-006-1.5E	bal.	.37	.10	200	.73	146
KETJEN-005-2E	bal.	.55	.06	150	.64	171
KETJEN-000-3E	bal.	1.5	.13	230	.64	111

1. Average Pore Diameter = 40,000 x P.V./S.A. in Å

TABLE II-5

KETJEN-003-E1/16" SUPPORT DATA

Al_2O_3	SiO_2	NA_2O	S A	P V	P.D.[1]
bal.	1.33%	.01%	240 m^2/g	.73 cc/g	146 Å

CATALYST DATA

Catalyst	NiO	CoO	Wo_3
MSU-GRH-1	6.10%	2.85%	19.91%
MSU-GRH-2	2.91%	2.91%	18.84%
MSU-GRH-3	6.06%	6.12%	18.53%
MSU-GRH-4	3.13%	5.90%	19.02%
MSU-GRH-5	5.88%	0	18.00%

1. Average Pore Diameter = 40,000 x P.V./S.A. in Å

CATALYTIC HYDROGENATION OF SYNTHOIL - M. D. Anderson

SUMMARY OF PREVIOUS WORK

To date, a total of 36 bomb runs have been made on SYNTHOIL using 27 commercially prepared catalysts and three M.S.U. catalysts. SYNTHOIL has been hydrotreated with twelve commercial catalysts in the continuous reactor. In the continuous reactor Harshaw HT-500 gave the best sulfur removal, and Shell 324 gave the best hydrocracking and nitrogen removal.

SUMMARY OF PROGRESS DURING THIS QUARTER

During this quarter, one bomb run and two continuous runs were made on SYNTHOIL. Cyanamid Catalyst HDS-20A (Co-Mo), was tested in the batch autoclave, and two nickel molybdate catalysts, Cyanamid HDS-9A and Houdry HR-811 were tested in the continuous reactor. Table III-1 gives the complete description of these catalysts. The analysis of products from these runs has not yet been completed.

DISCUSSION OF BOMB RUNS

Batch catalyst testing takes place in a 500 ml Parr rocking autoclave at the following conditions:

SYNTHOIL charged	= 150 ml.
Catalyst charged	= 25 ml.
Initial hydrogen pressure	= 2,000 psig
Run temperature	= 450°C $\pm$ 5°C
Run time	= 1 hour

The catalyst tested in run BR-1 was Cyanamid catalyst HDS-20A (5% Co, 16.2% Mo on alumina), which is loaded on a trilobe support. Due to a thermocouple malfunction, the actual temperature of the bomb during the run was between 500 and

550°C, instead of the usual 450°C. As a result of thse extreme conditions, approximately 50 percent of the SYNTHOIL charged was either converted to gas or deposited as coke in the bottom of the bomb. The remaining liquid product was very light and contained only 0.40 percent nitrogen. Although this is almost twice the denitrogenation that has been achieved at normal operating conditions, the extreme temperatures and loss of liquid product are obviously not desirable. The remaining analysis of this product has not yet been completed.

DISCUSSION OF CONTINUOUS RUNS

Two commercial catalysts were tested in the continuous fixed bed reactor at the following conditions. The products of these runs have not yet been analyzed.

Pressure	=	800 psig
Temperature	=	450°C ± 5°C
H_2:SYNTHOIL Ratio	=	10,000 scf/bbl
Catalyst Bed	=	70 ml. catalyst diluted with 70 ml. Denstone 1/8" inert support.
LHSV	=	1.0 - 2.0

Run CR-3 was made using Cyanamid HDS-9 (3.5% Ni, 18% Mo on alumina). The liquid hourly space velocity (LHSV) was varied from 1.0 to 1.6 at a H_2:Oil ratio of 10,000 scf/bbl.

Run CR-4 was made using Houdry HR-811 (3.0% Ni, 15.0% Mo on alumina) at the above conditions.

During preheating, the temperature of the reactor reached a maximum of 550°C before it was allowed to cool down to operating temperature. This excessive temperature may have had a tendency to deactivate the catalyst, but this will not be determined until the products are analyzed.

CONCLUSIONS FROM THIS QUARTER'S WORK

1. The severe cracking conditions that were experienced in run BR-1 resulted in high nitrogen removal at the cost of high conversion of SYNTHOIL to gas.

FORECAST OF FUTURE WORK

1. The analysis of the products from runs BR-1, CR-3, and CR-4 will be completed.
2. Five of the available commercial catalysts that have not yet been tested with SYNTHOIL will be tested in the continuous reactor.

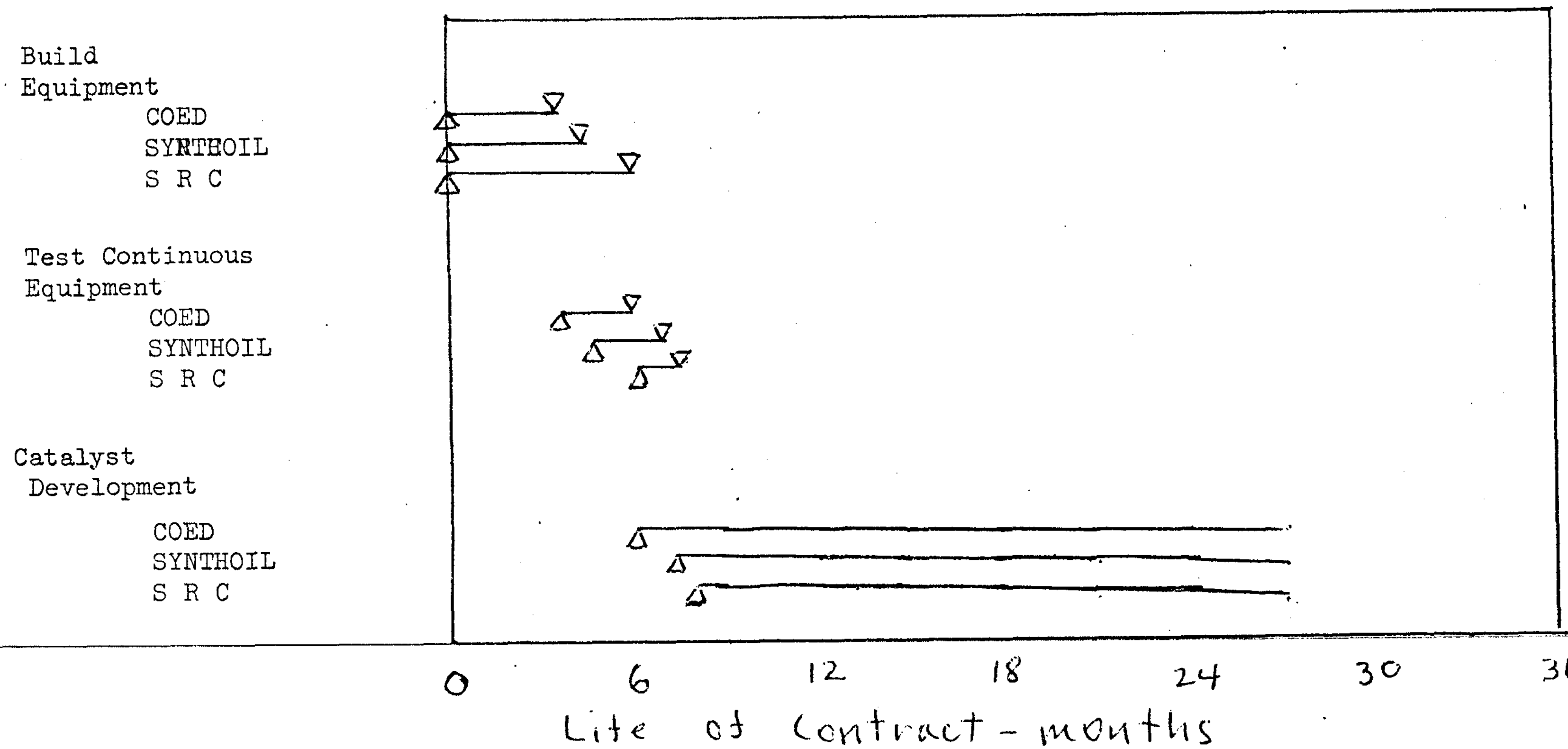
TABLE III-1

CATALYST DESCRIPTION

Cyanamid HDS-20A	5.0% CoO, 16.2% MoO_3 on alumina, 1/16" trilobe S.A. = 230 m^2/g P.V. = .52 cc/g
Cyanamid HDS-9A	3.5% NiO, 18.0% MoO_3 on alumina, 1/16" extrudates
Houdry HR-811	3% NiO, 15.0% MoO_3 on alumina, 1/16" extrudates, S.A. = 300 m^2/g

NOTE: All catalysts were sulfided prior to testing

PICTORIAL PROGRESS REPORT



G & C   PROJECT FINANCIAL REPORT   NO. 789   9/30/77

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

	CURRENT MO.	TOTAL TO DATE		AMT. AUTH.	
RECEIPTS	.00	90021.90		155932.00	

EXPENDITURES			ENCUMBRANCES	TOTAL COMMITTED	BUDGET
SALARY AND WAGES	2762.64	47386.32 ✓	16396.56	63782.88	68657.
BENEFITS	310.72	2087.99 ✓		2087.99	4255.
REP & MAINT		475.64		475.64	
TRAVEL	403.08	2147.37 ✓		2147.37	3000.
COMMUNICATIONS	22.11	300.43		300.43	
COMPUTER					3000.
SUPPLIES	1508.94	15273.62		15273.62	12750.
SUBCONTRACT		150.97		150.97	
EQUIPMENT	560.00	9033.11 ✓		9033.11	12700.
AWARDS	400.00	1850.15 ✓		1850.15	6000.
INDIRECT CHARGES	2102.49	33845.37 ✓	11724.63	45570.00	45570.
TOTAL	8069.98	112551.17	28121.19	140672.36	155932.

BALANCE   CASH -22529.27   FREE BALANCE 15259.64

33

DETAIL TRANSACTION	DATE	NUMBER	DESCRIPTION	AMOUNT	TOTAL
	- -7		TILLERY JAMES ROSS	271.59	
	- -7		HASS GARY P	658.00	
	- -7		CONRAD ELIZABETH A	364.50	
	- -7		KUJAWA STEPHAN T	635.00	
	- -7		HASS DANAE A	199.50	
	- -7		HASS DANAE A	376.80	
	- -7		BUSH SILAS A	257.25	
					2762.64
	09-14-77	J800190	AUG PERS	31.45	
	09-15-77	J800196	AUG MT IA	11.51	
	09-15-77	J800202	AUG FICA	132.63	
	09-14-77	J800208	AUG MT UCC	4.56	
	09-14-77	J800213	AUG TRS	110.57	
	09-23-77	J800263	AUG GRP MED	20.00	
					310.72
	09-01-77	J800159	SERVICE SHOP	10.40	
	09-09-77	8401762	VWR SCIENTIFIC INC	205.70	

DETAIL	DATE	NUMBER	DESCRIPTION	AMOUNT	TOTAL
TRANSACTION	09-16-77	8401916	IDAHO VALVE&FITTING	28.49	
	09-16-77	8401917	NORTON CO	78.01	
	09-16-77	8401918	H-P OXYGEN & SUPPLY	227.42	
	09-14-77	J800186	CHEM STORES	26.53	
	09-14-77	J800215	CHEM STORES	153.15	
	09-14-77	J800217	CHEM STORES	77.50	
	09-23-77	J800266	XEROX PE CH E	693.34	
	09-20-77	J800232	ART PHOTO	17.40	
					1508.94
	09-01-77	J800170	WATS JULY	22.11	
					22.11
	09-19-77	8402008	PHILLIP MCCANDLESS	8.04	
	09-19-77	8402009	LLOYD BERG	395.04	
					403.08
	09-07-77	8401608	SCIENTIFIC PRDCTS	560.00	
					560.00
	09-15-77	8401889	MARK D ANDERSON	400.00	
					400.00
ENCUMBRANCE	09-30-78		SALARY ENCUMBRANCE	2444.31	
	09-30-78		SALARY ENCUMBRANCE	11637.00	
	09-30-78		SALARY ENCUMBRANCE	2315.25	
					16396.56

G & C PROJECT FINANCIAL REPORT NO. 789 11/3/77

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

	CURRENT MO.	TOTAL TO DATE		AMT. AUTH.
RECEIPTS	.00	90021.90		155932.00

EXPENDITURES	CURRENT MO.	TOTAL TO DATE	ENCUMBRANCES	TOTAL COMMITTED	BUDGET
SALARY AND WAGES	2537.30	49923.62	19537.28	69460.90	63657.
BENEFITS	260.53	2348.52		2348.52	4255.
REP & MAINT		475.94		475.94	
TRAVEL		2147.37		2147.37	3000.
COMMUNICATIONS	6.17	306.60		306.60	
COMPUTER					3000.
SUPPLIES	715.18	15988.00		15988.00	12750.
SUBCONTRACT		150.97		150.97	
EQUIPMENT	169.65	9202.76		9202.76	12700.
AWARDS	450.80	2300.95		2300.95	6000.
INDIRECT CHARGES	1914.00	35759.37	9810.63	45570.00	45570.
TOTAL	6053.63	118604.80	29347.91	147952.71	155932.

BALANCE CASH -28582.90 FREE BALANCE 7979.29 35

DETAIL TRANSACTION	DATE	NUMBER	DESCRIPTION	AMOUNT	TOTAL
	- -7		BERG LLOYD	620.37	
	- -7		TILLERY JAMES ROSS	271.54	
	- -7		HASS GARY R	658.00	
	- -7		HARTZ ELIZABETH C	79.50	
	- -7		KUJAWA STEPHAN T	635.00	
	- -7		HUSO SILAS A	257.25	
	10-19-77	J800330	FIN AID WRK STUDY	15.64	
					2537.30
	10-19-77	J800355	SEPT MT UCC	3.64	
	10-19-77	J800359	SEPT MTRS	81.61	
	10-19-77	J800335	SEPT GRP MED	15.00	
	10-19-77	J800336	SEPT GRP MED	10.00	
	10-19-77	J800342	SEPT MT IA	11.36	
	10-19-77	J800347	SEPT SOC SEC	106.57	
	10-19-77	J800351	SEPT PERS	31.45	
	10-19-77	J800330	FIN AID WRK STUDY	.90	
					260.53

DETAIL	DATE	NUMBER	DESCRIPTION	AMOUNT	TOTAL
TRANSACTION	10-03-77	8402227	VAN WATERSOROGERS	10.81	
	10-17-77	8402677	MOUNTAIN SUPPLY CO	6.18	
	10-17-77	8402678	VWR SCIENTIFIC INC	58.32	
	10-17-77	8402679	H-R OXYGEN & SUPPLY	336.97	
	10-17-77	8402680	JANE CURTIS	5.88	
	10-20-77	8402789	MSU BOOKSTORE INC	7.75	
	10-03-77	J800294	TECHNICAL SERVICES	29.25	
	10-19-77	8402765	VALLEY MOTOR SUPPLY	4.00	
	10-19-77	J800361	CHEM STORES	219.56	
	10-21-77	J800405	LIBRARY XEROX	.18	
	10-06-77	J800304	CHEM STORES	9.54	
	10-10-77	J800310	ERL STOCKROOM	2.30	
	10-21-77	J900409	XEROX REVOL CH E	24.44	
					715.18
	10-19-77	J800362	WATS BILL AUGUST	6.17	
					6.17
	10-19-77	9402735	BROOKS INSTRUMENT DV	165.00	
	10-19-77	8402735	BROOKS INSTRUMENT DV	4.65	
					169.65
	10-11-77	8402506	MARK ANDERSON	400.00	
	10-17-77	J800292	BUS OFC-SUMMER DEFR	50.80	
					450.80
ENCUMBRANCE	10-31-71		SALARY ENCUMBRANCE	4962.96	
	10-31-71		SALARY ENCUMBRANCE	2172.32	
	10-31-71		SALARY ENCUMBRANCE	10344.00	
	10-31-71		SALARY ENCUMBRANCE	2058.00	
					19537.28

G & C PROJECT FINANCIAL REPORT NO. 789 N/V /0,

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

	CURRENT MO.	TOTAL TO DATE		AMT. AUTH.	
RECEIPTS	.00	90021.90		155932.00	

EXPENDITURES			ENCUMBRANCES	TOTAL COMMITTED	BUDGET
SALARY AND WAGES	3286.75	53210.37	17095.12	70305.49	68657.
BENEFITS	317.29	2665.81		2665.81	4255.
REP & MAINT		475.84		475.84	
TRAVEL		2147.37		2147.37	3000.
COMMUNICATIONS		306.60		306.60	
COMPUTER					3000.
SUPPLIES	1075.70	17064.50		17064.50	12750.
SUBCONTRACT	15.00	165.97		165.97	
EQUIPMENT	776.50	9979.26		9979.26	12700.
AWARDS	585.95	2886.90		2886.90	6000.
INDIRECT CHARGES	2465.52	38224.89	7345.11	45570.00	45570.
TOTAL	8522.71	127127.51	24440.23	151567.74	155932.

BALANCE CASH -37105.61 FREE BALANCE 4364.26

DETAIL TRANSACTION	DATE	NUMBER	DESCRIPTION	AMOUNT	TOTAL
	- -7		BERG LLOYD	620.37	
	- -7		TILLERY JAMES ROSS	271.54	
	- -7		HASS GARY P	658.00	
	- -7		HARTZ ELIZABETH C	175.00	
	- -7		KUJAWA STEPHAN T	635.00	
	- -7		HUSO SILAS A	257.25	
	11-08-77	J800487	FIN AID WRK STUDY	23.46	
	11-22-77	J800529	FIN AID WRK STUDY	25.76	
	11-18-77	J800506	P/R CORR-L BERG	620.37	
					3286.75
	11-10-77	J800466	OCT SOC SEC	106.57	
	11-10-77	J800473	OCT MT IA	5.84	
	11-10-77	J800477	OCT MTRS	120.76	
	11-10-77	J800480	OCT PERS	31.47	
	11-01-77	J800485	OCT UCC	4.88	
	11-08-77	J800487	FIN AID WRK STUDY	1.35	
	11-22-77	J800529	FIN AID WRK STUDY	1.48	

DETAIL TRANSACTION	DATE	NUMBER	DESCRIPTION	AMOUNT	TOTAL
	11-18-77	J800503	P/R CORR-L BERG	4.40	
	11-18-77	J800506	P/R CORR-L BERG	38.77	
	11-18-77	J800506	P/R CORR-L BERG	.54	
	11-18-77	J800506	P/R CORR-L BERG	1.23	
					317.29
	11-01-77	8403044	IDAHO VALVE & FITTNG	63.79	
	11-07-77	J800457	CHEM STORES	70.78	
	11-10-77	8403238	COLE-PARMER	72.79	
	11-18-77	8403393	H-R OXYGEN & SUPPLY	310.28	
	11-18-77	8403394	VAN WATERS & ROGERS	78.87	
	11-18-77	8403395	COLE-PARMER	82.28	
	11-18-77	8403396	MATHESON	112.50	
	11-25-77	8403536	SALT CREEK FRGHTWYS	17.48	
	11-22-77	J800525	XEROX REVOL CH E	266.93	
					1075.70
	11-17-77	J800502	TECHNICAL SERVICES	15.00	
					15.00
	11-15-77	8403264	VWR SCIENTIFIC	776.50	
					776.50
	11-15-77	8403266	MARK ANDERSON	400.00	
	11-17-77	J800499	AUT OST DEFERRMENTS	185.95	
					585.95
ENCUMBRANCE	11-30-71		SALARY ENCUMBRANCE	4342.59	
	11-30-71		SALARY ENCUMBRANCE	1900.78	
	11-30-71		SALARY ENCUMBRANCE	9051.00	
	11-30-71		SALARY ENCUMBRANCE	1800.75	
					17095.12