FE-2034-21
Dist. Category UC-90d

CATALYTIC HYDROGENATION OF COAL-DERIVED LIQUIDS

Interim Report for the Period

Sept. 1980 - Nov. 1980

Lloyd Berg & F. P. McCandless

MONTANA STATE UNIVERSITY

Bozeman, Montana 59717

Date Published - December 1980

PREPARED FOR THE UNITED STATES
DEPARTMENT OF ENERGY
Under Contract No. EX-76-C-01-2034
AC01-76ET10495

FE-2034-21
Dist. Category UC-90d

December 31, 1980

PRINCIPAL INVESTIGATORS: Lloyd Berg & F. P. McCandless

AFFILIATION/ADDRESS: Montana State University, Bozeman, MT. 59717

TELEPHONE NO. 406-994-2222

PROJECT TITLE: CATALYTIC HYDROGENATION OF COAL-DERIVED LIQUIDS
Contract No. EX-76-C-01-2034

SUMMARY

It is the objective of this research to convert coal to clean distillate fuels. This program will be limited to research on the product of PAMCO's solvent refined coal (SRC-II). The SRC 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 and 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.

The analyses and data evaluation from the runs on the sixteen catalysts comprising each possible four metal combination of 2 and 4% CoO, 2 and 8% MoO_3, 1 and 4% NiO and 2 and 8% WO_3 were completed The statistical analysis of the results was repeated at the 90% confidence level. At this level, the concentration of CoO, MoO_3 and WO_3 were significant. The carbon laid down on the catalyst and supports during a run is in the range of 9.9% - 12.5% of the feed. This carbon laydown contains about 1% nitrogen. Two runs were made with NALCO 477 cobalt molybdate catalyst under hydrotreating-hydrocracking conditions. Seven catalyst base materials have been obtained which possess the pore diameter range desired as well as adequate surface area and pore volume. These will be loaded with the optimum quantity of CoO, MoO_3 and WO_3 and evaluated under hydrotreating-hydrocracking conditions. Electron photomicrographs of one of our catalysts indicate that it possesses the proper pore diameter for SRC processing.

OBJECTIVE

It is the objective of this research to convert coal to clean distillate fuels. This program will be limited to research on theproduct of PAMCO's solvent refined coal (SRC-II). The SRC 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 and the 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

The work on the development of catalysts capable of converting solvent refined coal (SRC-II), into a feedstock suitable for a conventional petroleum refinery was continued. This requires a process which reduces the nitrogen content from the 1.17% in SRC-II to at least as low as 0.3%.

During the quarter a statistical analysis of sixteen combinations of CoO, MoO_3, NiO and WO_3 catalysts was completed. The amount of carbon laydown during the hydrotreating-hydrocracking cycle was determined as well as the nitrogen included in that carbon. A commercial cobalt molybdate was evaluated under the hydrotreating-hydrocracking conditions. Several catalyst base materials were obtained to determine the effect of the properties of the base on this process. An electron photomicrograph was prepared on one of our successful catalysts.

CONVERSION OF SOLVENT REFINED COAL, SRC-II, TO DISTILLATE FUELS, BY An-gong Yeh

The purpose of the research is to develop new catalysts capable of converting PAMCO's Solvent Refined Coal, SRC-II, into clean distillate fuels and/or a feed stock acceptable to a conventional petroleum refinery. The nitrogen and sulfur contents of the SRC-II which are 1.17 wt% and 0.72 wt%, respectively, must be reduced as much as possible and the distillation yield of the SRC-II, 55 vol.% at 650°F, is to be upgraded. To accomplish these, the catalyst with a combination of hydrotreating and hydrocracking activities is required. But the denitrogenation is considered by us to be the major problem, the nitrogen content of the SRC-II is to be reduced at least as low as 0.3 wt%.

The equipment shown in Figure 1 was designed to catalytically hydrotreat the SRC-II. Hydrogen and SRC-II were fed at the top of the trickle bed reactor. The reactor was made by a one-inch I.D. 40 inches long schedule 80 Inconel pipe. Starting from the top, the reactor was loaded with 175 ml. of 1/4" Denstone inert support, 25 ml. of 1/8" Denstone inert support, followed by a mixture of 60 ml. of catalyst and 60 ml. of 1/8" Denstone inert support. The remaining spaces at the bottom of the reactor was filled with 1/8" Denstone inert support. The reactor was heated with three heating wires wrapped on an aluminum block. A catch-pot was attached to the bottom of the reactor to receive the liquid product. Gases flowed from the reactor through the back-pressure regular, the absorber, and the scrubber, then to the vent. The absorber was filled with 30 ml. of concentrated sulfuric acid to absorb the soluble nitrogen compounds of gas stream. Operating conditions usually were 425°C, 1,000 psig, liquid hourly space velocity of 1.0, hydrogen flow rate of 10,000 scf/bbl of oil, and SRC-II feed temperature of 85°C.

During the past quarters, the non-metal-loaded base material, Nalco-78-6008C-1/32", possessing a surface area of 214.6 m^2/gram, a pore volume of 0.839 ml./gram, a pore diameter of 156.5 Å and a median pore diameter of 161 Å was tested in Runs A-31 and A-34. The results are summarized in Tables I and II. A sixteen experiment 2^4 full two level metal-loading factorial design was performed on the same base material to determine the metal effects. The catalysts designated from C-41 to C-56 comprising every combination of 2 and 4% CoO, 2 and 8% MoO_3, 1 and 4% Ni, and 2 and 8% WO_3 were evaluated in Runs A-41 to A-51 shown in Appendix A. Tables I and II summarize the results in which the ASTM D-86 distillation yield of Run A-46 was not obtained due to the equipment was out of order when the analysis proceeded.

The denitrogenation for Run A-41 to A-56 was correlated with the running time and the metal composition of catalyst by the forward stepwise regression. The main effects of CoO, MoO_3, and WO_3 were found to be significant and no significant interaction between metal oxides has been found. The analysis of variance shown in Appendix B indicates the denitrogenation is expected to increase 3.4% by increasing 1 wt% of CoO and to increase 0.5% by increasing 1 wt% of MoO_3 or WO_3.Figure 2 plots the experimental data and fitted regression line with a R-square of 0.85 for 2 and 4 wt% CoO. The variances of MoO_3 and WO_3 are plotted in Figures 3 and 4.

The effect of metal oxides on desulfurization was analyzed by regressing the average weight percent of desulfurization on the composition of catalyst by using a confidence coefficient of 90 percent. The average desulfurization is expected to decrease by 8.5% when the amount of CoO increases by 1 wt%, to increase by 3.5% when the amount of MoO_3 increases by 1 wt%, and to increase by 1.6% when the amount of WO_3 increases by 1 wt%. Figures 6, 7, and 8 plot the variances between two levels for CoO, MoO_3, and WO_3. The effect of NiO and the interactions between metal oxides are found to be insignificant. The ANOVA table is shown in Appendix C and the R-square of the regression equation is 0.81.

The relation between oil product yield and metal oxides was also studied through the regression technique. The result in Appendix D shows the yield is expected to decrease 1 vol.% when the amount of WO_3 on the catalyst increases by 1 wt%. None of other metals effects was found to be significant.

Catalyst C-54 possessing the activity to reduce the nitrogen content of the SRC-II to an average of 0.22 wt% in Run A-54 was retested in Run A-59. The data is shown in Table III but the analysis has not been completed. The nitrogen and carbon laid-down on the spent catalyst and inert supports have been analyzed by coworkers. Table IV shows the nitrogen content of 1/4" inert support in the preheat section and catalyst and 1/8" inert support in the catalyst section at different locations for Run A-59. The amount of nitrogen for each section is simply obtained by the product of average nitrogen weight percent and the weight of material for each section. The results are shown as followings:

	Average N_2, wt%	Volume of material loaded, ml	Weight of material, gram	Amount of Nitrogen, gram
1/4" inert support	0.036	175	207	0.075
1/8" inert support	0.34	115	19	0.065
Catalyst	0.14	60	22	0.031
Total				0.171

The total amount of nitrogen laid-down with carbon, 0.171 grams, is the sum of nitrogen contained in each portion. The SRC-II fed in Run A-59 was 135 ml. or 142 grams within 135 minutes at the liquid hourly space velocity of 1.0 and feed temperature of 85^{o}F. The percent of nitrogen laid-down with carbon of the SRC-II feed is to be 0.171/142 x 100% which is 0.12%. The average percent of carbon laid-down of the SRC-II feed was 12% presented by the coworker, therefore the nitrogen laid-down with carbon is to be 1% of carbon laid-down.

The results of statistical study demonstrated the change in the concentration of CoO significantly affect the activity of catalyst on both denitrogenation and desulfurization. The effects of MoO_3 and WO_3 on both denitrogenation and desulfurization are positive but relatively small. The performance of nitrogen mass balance will be possible when the nitrogen analysis is completed.

TABLE I

DENITROGENATION FOR BLANK AND METAL-LOADED CATALYSTS
USING NALCO-78-6008C-1/32" AS BASE MATERIAL

Run	Catalyst	%DN* time, minutes 45	60	75	90	105	120	150	%DN Avg.	Metal Oxides on the Catalyst, wt% CoO	MoO_3	NiO	WO_3
A-31	Base	65.4	39.7	35.9	27.4	26.6	18.8	-	35.6	0	0	0	0
A-34	Base	40.2	27.8	25.6	27.4	23.5	23.5	-	28	0	0	0	0
A-41	C-41	92.0	89.3	85.5	77.8	72.6	61.5	50.0	75.5	2	8	1	8
A-42	C-42	85.5	92.8	69.2	61.5	48.7	44.0	35.9	62.5	2	8	1	2
A-43	C-43	97.0	96.2	91.0	80.3	65.4	56.4	51.7	76.8	2	8	4	8
A-44	C-44	98.6	92.2	80.8	68.8	51.3	42.7	43.6	68.3	2	8	4	2
A-45	C-45	98.3	87.2	79.5	62.8	56.4	45.3	30.3	65.7	2	2	1	8
A-46	C-46	93.8	79.5	65.8	57.7	49.1	44.9	42.3	61.9	2	2	1	2
A-47	C-47	95.5	89.7	81.6	66.7	58.5	52.1	35.9	68.6	2	2	4	8
A-48	C-48	93.2	80.0	70.5	64.1	57.7	54.3	48.7	67.0	2	2	4	2
A-49	C-49	98.6	93.8	88.9	80.3	66.7	60.7	56.8	77.9	4	8	1	8
A-50	C-50	97.3	91.7	84.6	78.6	69.7	60.3	57.3	77.1	4	8	1	2
A-51	C-51	97.9	92.1	81.2	70.9	62.0	55.6	57.3	73.8	4	8	4	8
A-52	C-52	89.7	87.2	82.0	72.2	68.4	66.7	50.8	73.8	4	8	4	2
A-53	C-53	95.1	88.9	79.1	70.1	57.7	52.6	57.3	71.5	4	2	1	8
A-54	C-54	92.3	99.1	97.4	73.5	71.8	70.1	63.2	81.1	4	2	1	2
A-55	C-55	97.4	88.6	70.1	75.2	72.6	68.4	57.3	75.6	4	2	4	8
A-56	C-56	94.9	91.4	79.5	58.1	91.4	47.0	28.2	70.1	4	2	4	2

* Nitrogen content of SRC-II is 1.17 wt%

TABLE II

DESULFURIZATION, DISTILLATION YIELD, AND PRODUCT OIL FRACTION OF BLANK AND METAL-LOADED CATALYSTS USING NALCO-78-6008C-1/32" AS BASE MATERIAL

Run	Catalyst	Avg. %DS @	ASTM D-86 Yield at 650°F, vol.% @	Yield of Oil Product, vol%	Metal Oxides on Catalyst, wt% CoO	MoO_3	NiO	WO_3
A-31	Base	22	66	45	0	0	0	0
A-34	Base	28	66	44	0	0	0	0
A-41	C-41	77	77	72	2	8	1	8
A-42	C-42	64	75	77	2	8	1	2
A-43	C-43	67	82	62	2	8	4	8
A-44	C-44	71	80	70	2	8	4	2
A-45	C-45	65	80	64	2	2	1	8
A-46	C-46	34	--*	76	2	2	1	2
A-47	C-47	46	74	76	2	2	4	8
A-48	C-48	42	82	75	2	2	4	2
A-49	C-49	48	85	76	4	8	1	8
A-50	C-50	43	80	74	4	8	1	2
A-51	C-51	56	83	79	4	8	4	8
A-52	C-52	56	81	84	4	8	4	2
A-53	C-53	41	76	75	4	2	1	8
A-54	C-54	35	77	76	4	2	1	2
A-55	C-55	37	76	58	4	2	4	8
A-56	C-56	15	80	77	4	2	4	2

@ Sulfur content of SRC-II feed is 0.72 wt%, distillation yield at 650°F for SRC-II is 55 vol%.

* Data missed.

TABLE III

Run No. A-59

Catalyst No. C-54

Catalyst Composition

Metals : 4%CoO 2%MoO_3 1%NiO 2%WO_3

Base : Nalco-78-6008C-1/32"

Base Surface Area, m^2/g : 214.57
Base Pore Volume, ml/g : .8397
Base Pore Diameter (4V/A), Å : 156.5
Base Median Pore Diameter, Å : 161

Run Temperature, °C : 417 SRC-II Feed Temperature, °C : 85

Run Pressure, psig : 1,000

Liquid Hourly Space Velocity : 1.0

H_2 : oil Ratio, scf/bbl : 10,000

Yield of Oil, Volume % (balance is gas, coke & holdup) : 70

Total run time, min : 135

TABLE IV

Nitrogen content in the used catalyst & inert supports

Sample	Wt %				
	TOP	MID	BTM1	BTM2	AVG.
Inert support section, 1/4"	.01	.05	.05	--	.036
Inert support section, 1/8"	.55	.36	.31	.15	.34
Catalyst section	.20	.03	.19	--	.14

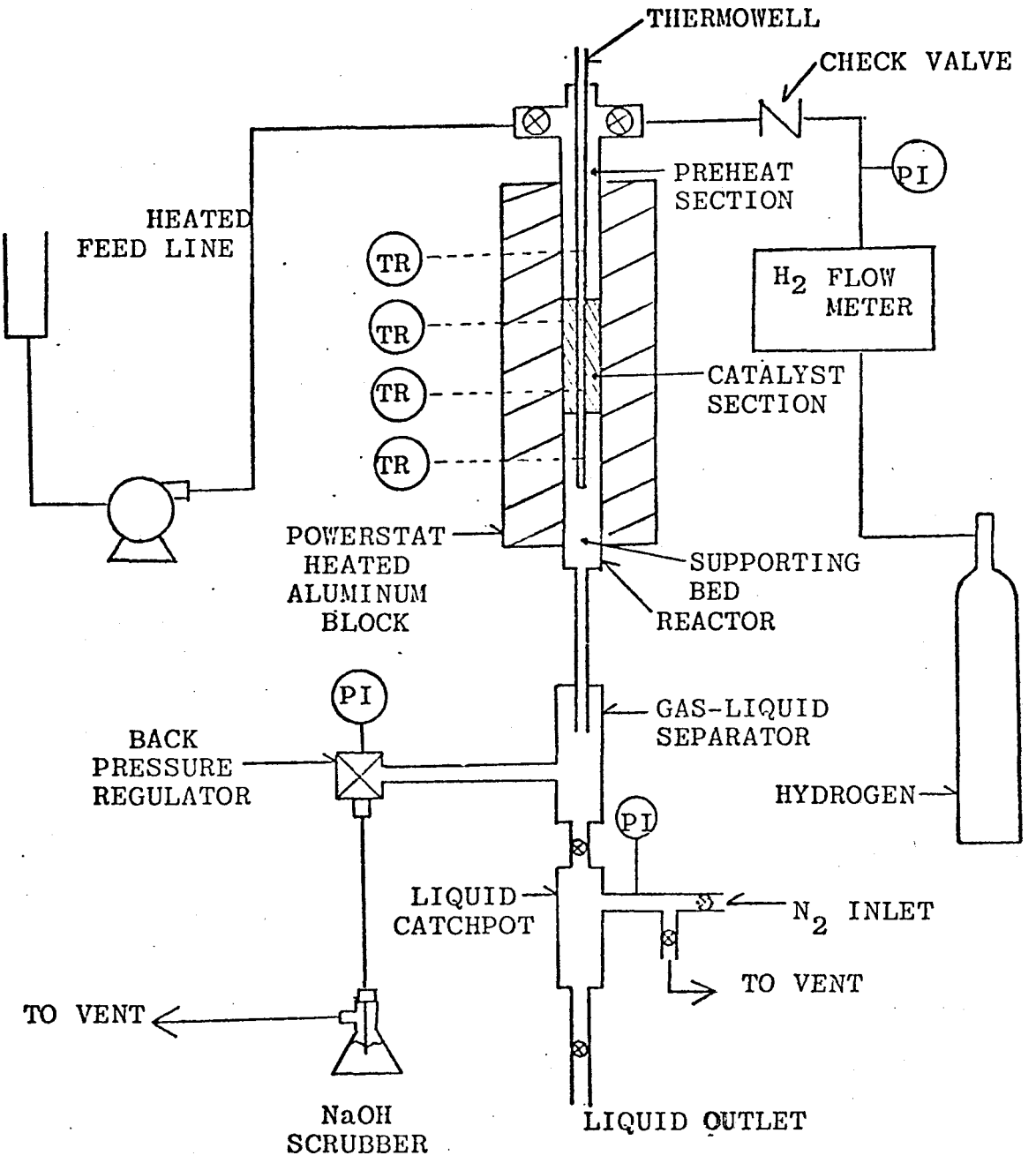


FIGURE 1. TRICKLE BED REACTOR

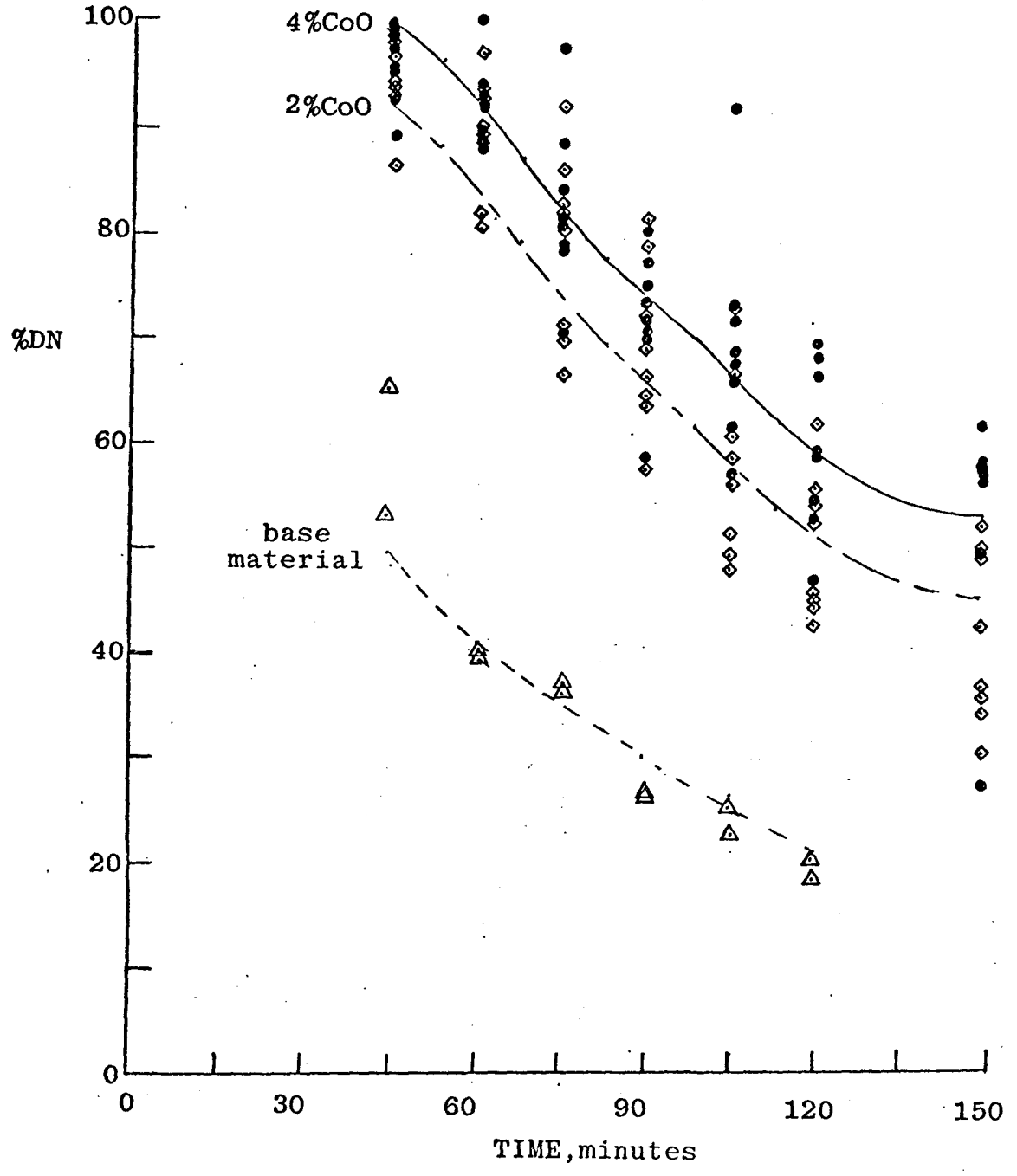


Figure 2. Nitrogen removal as a function of running time and CoO concentration.

- ● 4%CoO
- ◇ 2%CoO
- △ base material Nalco-78-6008C-1/32"

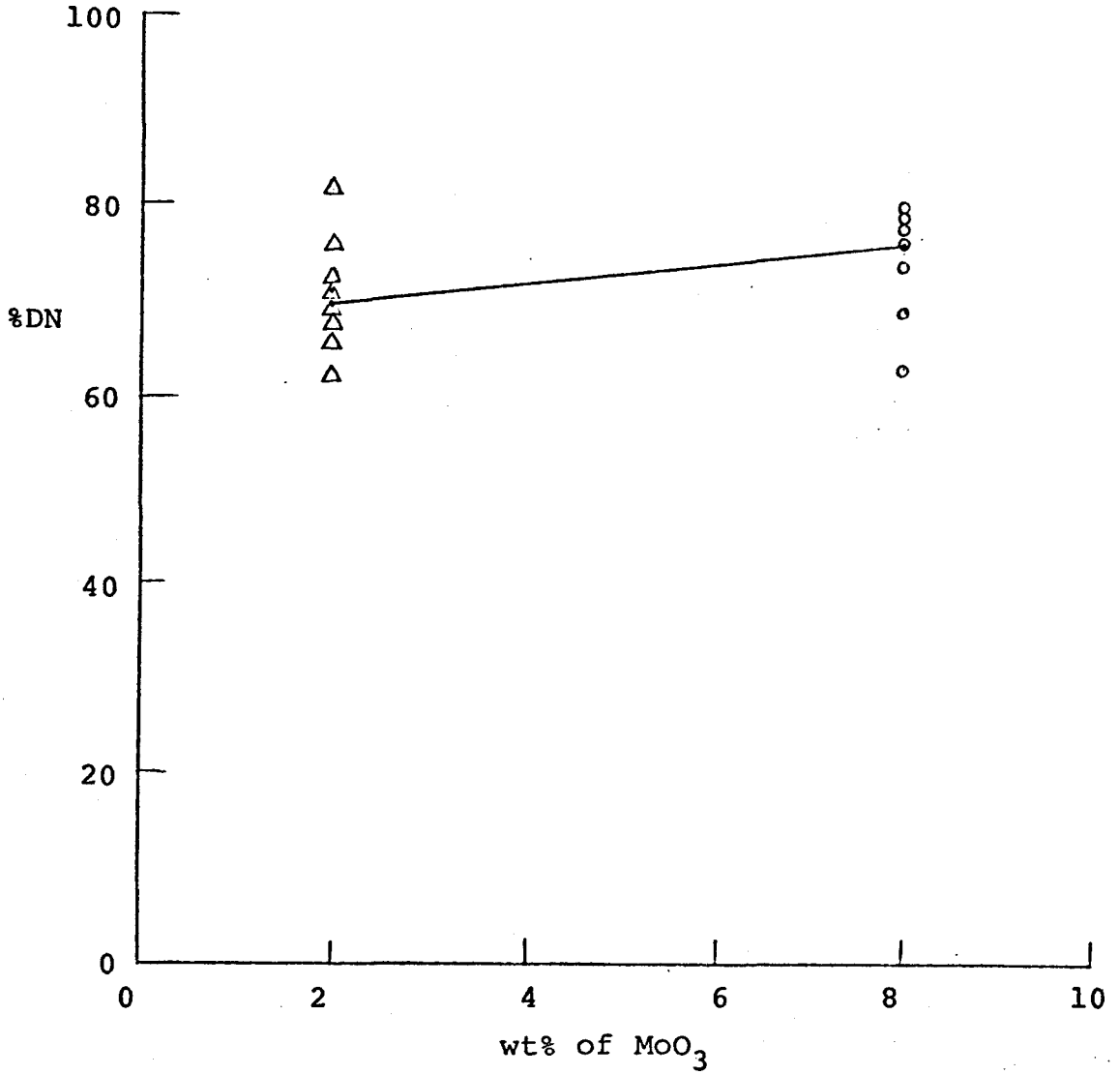


Figure 3. The effect of MoO_3 concentration on denitrogenation.

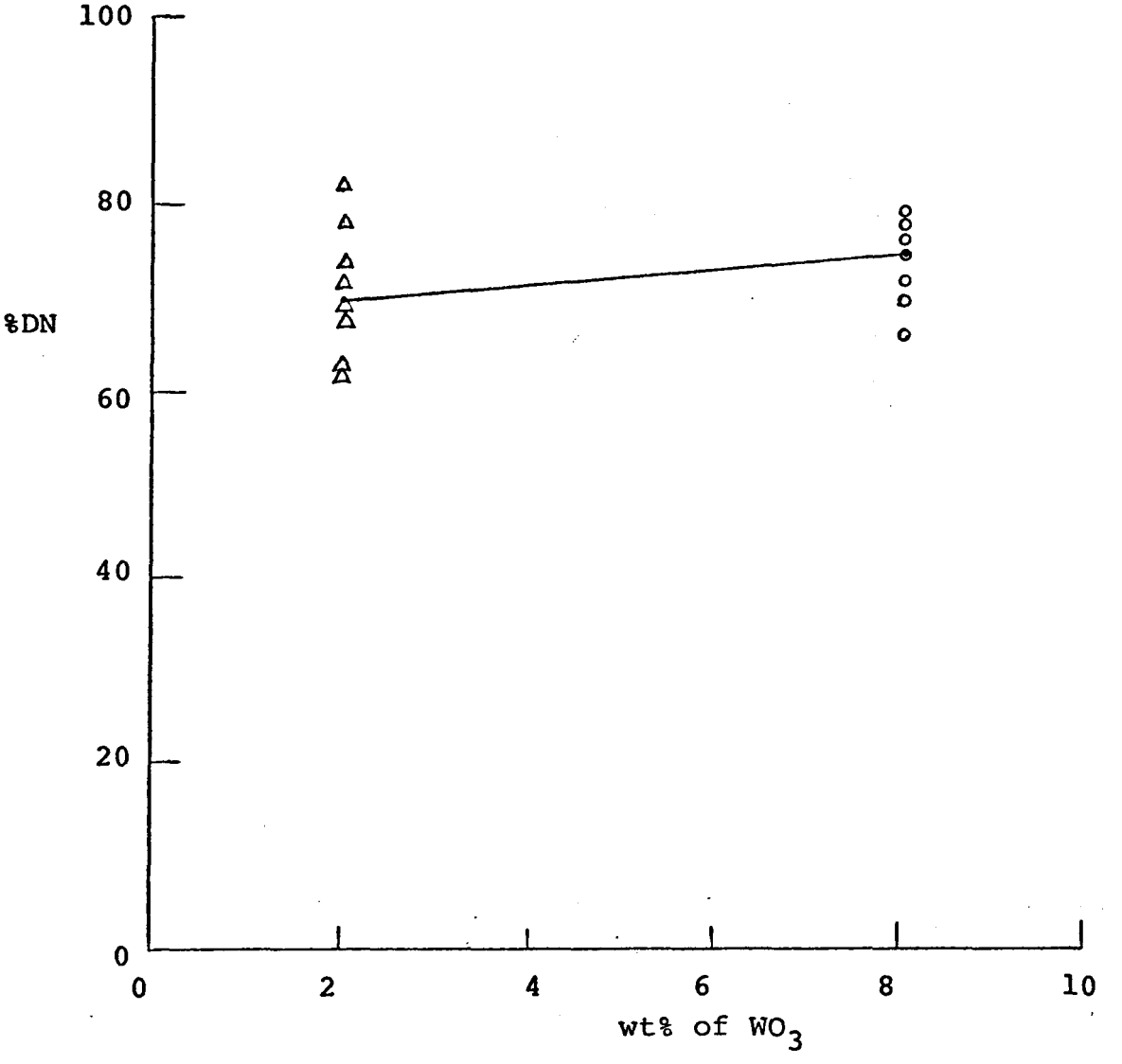


Figure 4. The effect of WO_3 concentration on denitrogenation.

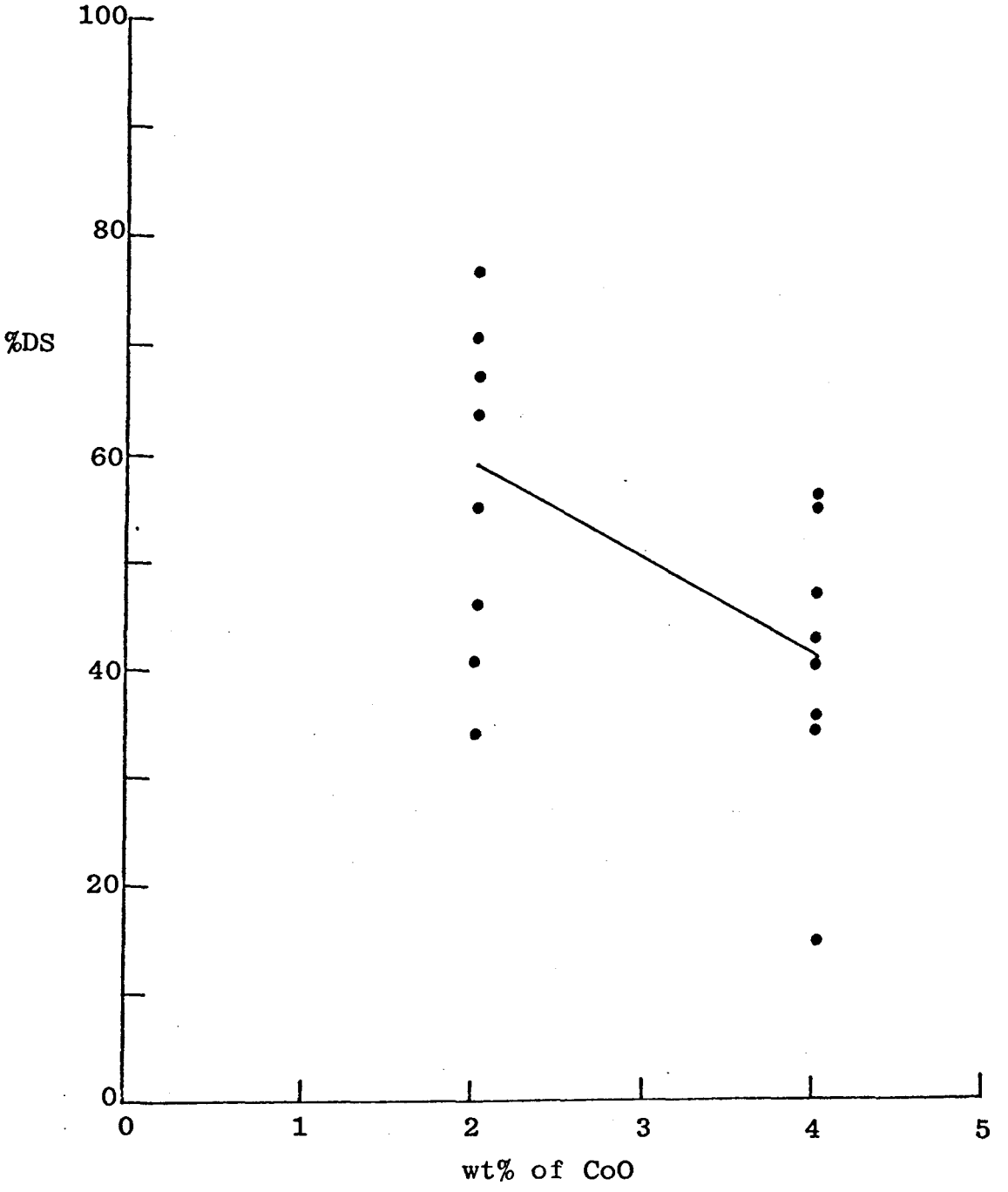


Figure 5. The effect of CoO concentration on desulfurization.

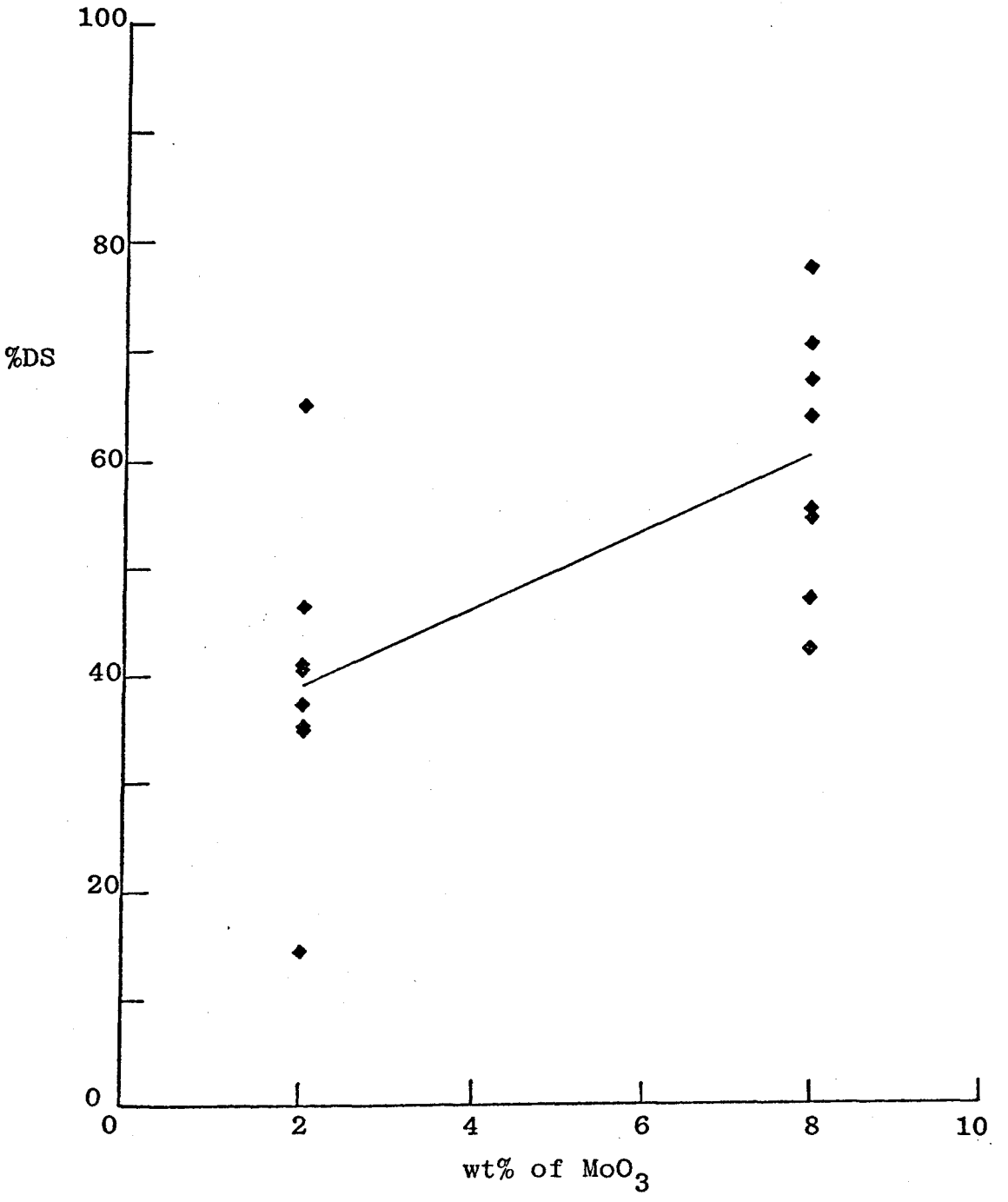


Figure 6. The effect of MoO_3 concentration on desulfurization.

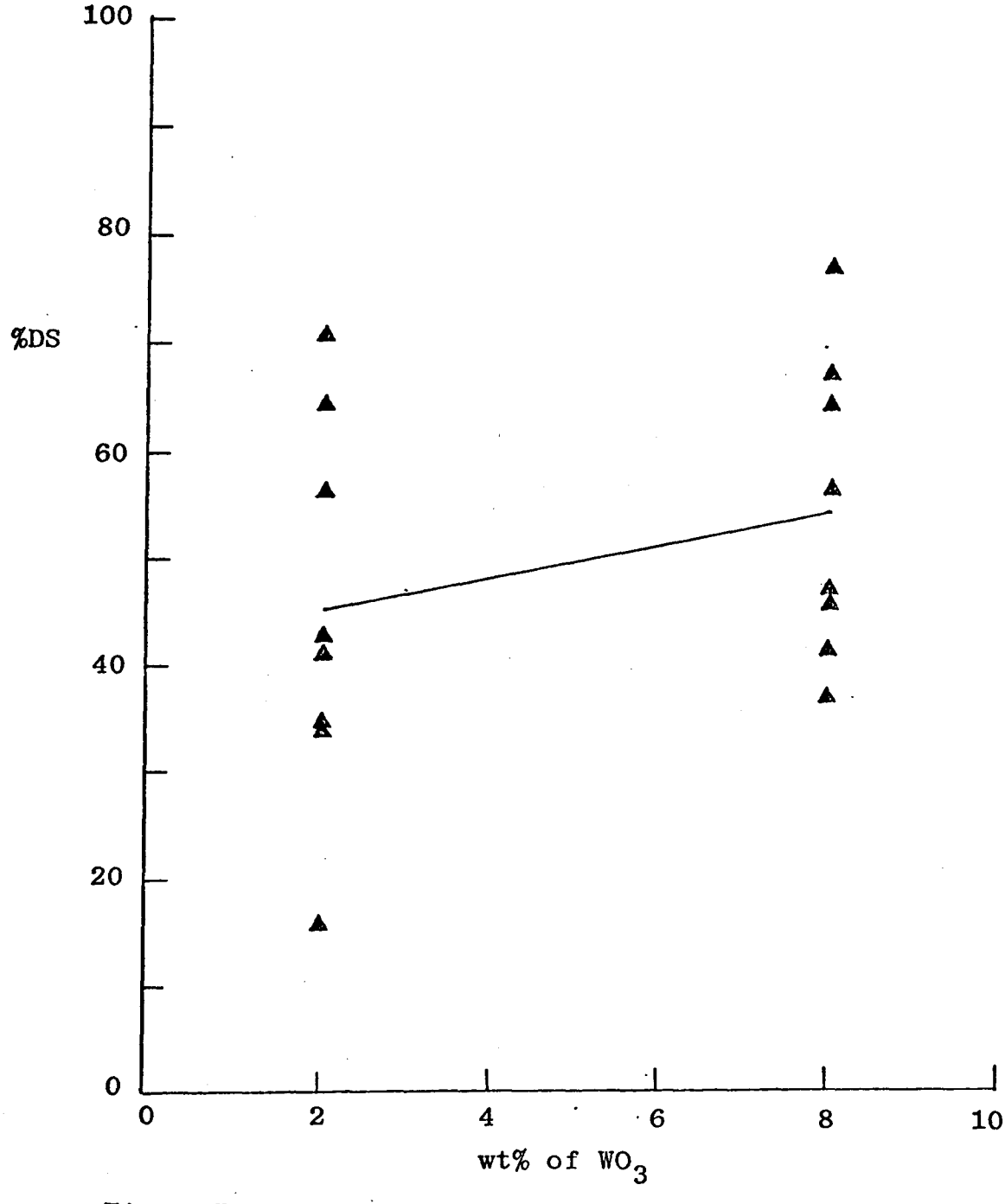


Figure 7 . The effect of WO_3 concentration on desulfurization.

APPENDIX A

Run No. A-31

Catalyst No. NALCO-78-6008C-1/32"

Catalyst Composition

Metals : None

Base : NALCO-78-6008C-1/32"

Base Surface Area, m^2/g : 214.57
Base Pore Volume, ml/g : .8397
Base Pore Diameter (4V/A), Å : 156.5
Base Median Pore Diameter, Å : 161

Run Temperature, °C : 425±5 SRC-II Feed Temperature, °C :85

Run Pressure, psig : 1,025

Liquid Hourly Space Velocity :1.1

H_2: Oil Ratio, scf/bbl : 10,000

Yield of Oil, Volume % (balance is gas, coke & holdup) : 5%

Time, min:	30	45	60	75	90	105	120	150
wt% N_2 :	.46	.405	.705	.75	.85	.86	.95	
wt% S :	-	-	-	-	.635	-	.485	

ASTM Distillation

Volume of Charge: 30.0 ml Final Volume: 18.0 ml

Volume, ml. :	0	5	10	15	18	25	30	35	40
°F :	387	450	492	550	639				

wt% N_2 in Outlet Gas Absorber:
wt. of Sulfuric Acid Absorption Solution, gram:

Run No. A-34

Catalyst No. NALCO-78-6008C-1/32"

Catalyst Composition

Metals : None

Base : NALCO-78-6008C-1/32"

Base Surface Area, m^2/g	: 214.57
Base Pore Volume, ml/g	: .8397
Base Pore Diameter (4V/A), Å	: 156.5
Base Median Pore Diameter, Å	: 161

Run Temperature, °C : 425 ± 5 SRC-II Feed Temperature, °C : 85

Run Pressure, psig : 1,000

Liquid Hourly Space Velocity : 1.0

H_2: Oil Ratio, scf/bbl : 10,000

Yield of Oil, Volume % (balance is gas, coke & holdup) : 44%

Time, min:	30	45	60	75	90	105	120	150
wt% N_2 :	.355	.70	.845	.87	.85	.895	.895	
wt% S :	-	-	-	-	.545	-	.496	

ASTM Distillation

Volume of Charge: 18.0 ml Final Volume: 9.0 ml

Volume, ml. :	0	5	10	15	20	25	30	35	40
°F :	406	494	556						

wt% N_2 in Outlet Gas Absorber:
wt. of Sulfuric Acid Absorption Solution, gram:

Run No. A-41

Catalyst No. C-41

Catalyst Composition

Metals : CoO 2% MoO_3 8% NiO 1% WO_3 8%

Base : Nalco-78-6008C-1/32"

Base Surface Area, m^2/g : 214.57
Base Pore Volume, ml/g : .8397
Base Pore Diameter (4V/A), Å : 156.5
Base Median Pore Diameter, Å : 161

Run Temperature, °C : 428 SRC-II Feed Temperature, °C : 90

Run Pressure, psig : 1,000

Liquid Hourly Space Velocity : .92

H_2: Oil Ratio, scf/bbl : 10,000

Yield of Oil, Volume % (balance is gas, coke & holdup) : 72

Time, min:	30	45	60	75	90	105	120	150
wt% N_2 :	-	.093	.125	.170	.260	.320	.450	.585
wt% S :	-	-	-	-	.110	-	-	.215

ASTM Distillation

Volume of Charge: 35.0 ml Final Volume: 28.0 ml

Volume, ml. :	0	5	10	15	20	25	28	35	40
°F :	354	425	474	519	578	615	676		

wt% N_2 in Outlet Gas Absorber: 0.053
wt. of Sulfuric Acid Absorption Solution, gram: 48.6

Run No.A-42

Catalyst No.C-42

Catalyst Composition

Metals : 2%CoO 8%MoO_3 1%NiO 2%WO_3

Base : Nalco-78-6008C-1/32"

Base Surface Area, m^2/g : 214.57
Base Pore Volume, ml/g : .8397
Base Pore Diameter (4V/A), Å : 156.5
Base Median Pore Diameter, Å : 161

Run Temperature, °C : 428 SRC-II Feed Temperature, °C : 92

Run Pressure, psig : 1,000

Liquid Hourly Space Velocity : .99

H_2: Oil Ratio, scf/bbl : 10,000

Yield of Oil, Volume % (balance is gas, coke & holdup) : 77

Time, min:	30	45	60	75	90	105	120	150
wt% N_2 :	-	.170	.084	.360	.450	.600	.655	.750
wt% S :	-	-	-	-	.290	-	-	.230

ASTM Distillation

Volume of Charge: 25.0 ml Final Volume: 18.5 ml

Volume, ml. :	0	5	10	15	19	25	30	35	40
°F :	329	443	511	587	647				

wt% N_2 in Outlet Gas Absorber: 0.015
wt. of Sulfuric Acid Absorption Solution, gram: 50.2

Run No. A-43

Catalyst No. C-43

Catalyst Composition

Metals : 2%CoO 8%MoO_3 4%NiO 8%WO_3

Base : Nalco-78-6008C-1/32"

Base Surface Area, m^2/g : 214.57
Base Pore Volume, ml/g : .8397
Base Pore Diameter (4V/A), Å : 156.5
Base Median Pore Diameter, Å : 161

Run Temperature, °C :427 SRC-II Feed Temperature, °C : 92

Run Pressure, psig :1,000

Liquid Hourly Space Velocity : 1.0

H_2: Oil Ratio, scf/bbl : 10,000

Yield of Oil, Volume % (balance is gas, coke & holdup) : 62

Time, min:	30	45	60	75	90	105	120	150
wt% N_2 :	-	.035	.044	.105	.230	.405	.510	.565
wt% S :	-	-	-	-	.255	-	-	.215

ASTM Distillation

Volume of Charge: 30.0 ml Final Volume: 24.0 ml

Volume, ml. :	0	5	10	15	20	24	30	35	40
°F :	317	418	476	531	585	644			

wt% N_2 in Outlet Gas Absorber: 0.053
wt. of Sulfuric Acid Absorption Solution, gram: 55.8

Run No. A-44

Catalyst No. C-44

Catalyst Composition

Metals : 2%CoO 8%MoO_3 4%NiO 2%WO_3

Base : Nalco-78-6008C-1/32"

Base Surface Area, m^2/g	: 214.57
Base Pore Volume, ml/g	: .8397
Base Pore Diameter (4V/A), Å	: 156.5
Base Median Pore Diameter, Å	: 161

Run Temperature, °C :434 SRC-II Feed Temperature, °C : 88

Run Pressure, psig : 1,000

Liquid Hourly Space Velocity : 1.1

H_2: Oil Ratio, scf/bbl : 10,000

Yield of Oil, Volume % (balance is gas, coke & holdup) :70

Time, min:	30	45	60	75	90	105	120	150
wt% N_2 :	-	.016	.091	.225	.365	.570	.670	.660
wt% S :	-	-	-	-	.190	-	-	.230

ASTM Distillation

Volume of Charge: 35.0 ml Final Volume: 25.1 ml

Volume, ml. :	0	5	10	15	20	25	30	35	40
°F :	332	422	468	516	566	610			

wt% N_2 in Outlet Gas Absorber: 0.113
wt. of Sulfuric Acid Absorption Solution, gram: 48.5

Run No.A-45

Catalyst No. C-45

Catalyst Composition

Metals : 2%CoO 2%MoO_3 1%NiO 8%WO_3

Base : Nalco-78-6008C-1/32"

Base Surface Area, m^2/g : 214.57
Base Pore Volume, ml/g : .8397
Base Pore Diameter (4V/A), Å : 156.5
Base Median Pore Diameter, Å : 161

Run Temperature, °C :422 SRC-II Feed Temperature, °C : 80

Run Pressure, psig :1,000

Liquid Hourly Space Velocity : 1.0

H_2: Oil Ratio, scf/bbl : 10,000

Yield of Oil, Volume % (balance is gas, coke & holdup) : 64

Time, min:	30	45	60	75	90	105	120	150
wt% N_2 :	-	.020	.150	.240	.435	.510	.640	.815
wt% S :	-	-	-	-	.275	-	-	.230

ASTM Distillation

Volume of Charge: 35.0 ml Final Volume: 26.0 ml

Volume, ml. :	0	5	10	15	20	25	26	35	40
°F :	356	423	469	513	565	615	635		

wt% N_2 in Outlet Gas Absorber: 0.056
wt. of Sulfuric Acid Absorption Solution, gram: 52.4

Run No. A-46

Catalyst No. C-46

Catalyst Composition

Metals : 2% CoO 2%MoO_3 1%NiO 2%WO_3

Base : Nalco-78-6008C-1/32"

Base Surface Area, m^2/g : 214.57
Base Pore Volume, ml/g : .8397
Base Pore Diameter (4V/A), Å : 156.5
Base Median Pore Diameter, Å : 161

Run Temperature, °C : 425 SRC-II Feed Temperature, °C : 88

Run Pressure, psig : 1,000

Liquid Hourly Space Velocity : .83

H_2: Oil Ratio, scf/bbl : 10,000

Yield of Oil, Volume % (balance is gas, coke & holdup) : 76

Time, min:	30	45	60	75	90	105	120	150
wt% N_2 :	-	.072	.240	.400	.495	.595	.645	.675
wt% S :	-	-	-	-	.720	-	-	.225

ASTM Distillation

Volume of Charge: Final Volume:

Volume, ml. :	0	5	10	15	20	25	30	35	40
°F :	--	--	--	--	--	--			

wt% N_2 in Outlet Gas Absorber: 0.062
wt. of Sulfuric Acid Absorption Solution, gram: 50.8

Run No. A-47

Catalyst No. C-47

Catalyst Composition

Metals : 2%CoO 2%MoO_3 4%NiO 8%WO_3

Base : Nalco-78-6008C-1/32"

Base Surface Area, m^2/g : 214.57
Base Pore Volume, ml/g : .8397
Base Pore Diameter (4V/A), Å : 156.5
Base Median Pore Diameter, Å : 161

Run Temperature, °C :429 SRC-II Feed Temperature, °C : 88

Run Pressure, psig :1,000

Liquid Hourly Space Velocity : 1.0

H_2: Oil Ratio, scf/bbl : 10,000

Yield of Oil, Volume % (balance is gas, coke & holdup) : 76

Time, min:	30	45	60	75	90	105	120	150
wt% N_2 :	-	.053	.120	.215	.390	.485	.560	.750
wt% S :	-	-	-	-	.470	-	-	.300

ASTM Distillation

Volume of Charge: 35.0 ml Final Volume: 25.5 ml

Volume, ml. :	0	5	10	15	20	25	26	35	40
°F :	277	416	458	512	567	630	670		

wt% N_2 in Outlet Gas Absorber: 0.058
wt. of Sulfuric Acid Absorption Solution, gram: 55.0

Run No. A-48

Catalyst No.C-48

Catalyst Composition

Metals : 2%CoO 2%MoO_3 4%NiO 2%WO_3

Base : Nalco-78-6008C-1/32"

Base Surface Area, m^2/g	: 214.57
Base Pore Volume, ml/g	: .8397
Base Pore Diameter (4V/A), Å	: 156.5
Base Median Pore Diameter, Å	: 161

Run Temperature, °C :424 SRC-II Feed Temperature, °C : 80

Run Pressure, psig : 1,000

Liquid Hourly Space Velocity : .93

H_2: Oil Ratio, scf/bbl : 10,000

Yield of Oil, Volume % (balance is gas, coke & holdup) : 75

Time, min:	30	45	60	75	90	105	120	150
wt% N_2 :	-	.080	.225	.345	.420	.495	.535	.600
wt% S :	-	-	-	-	.593	-	-	.245

ASTM Distillation

Volume of Charge: 35.0 ml Final Volume: 27.5 ml

Volume, ml. :	0	5	10	15	20	25	28	35	40
°F :	247	399	446	490	541	593	645		

wt% N_2 in Outlet Gas Absorber: 0.052
wt. of Sulfuric Acid Absorption Solution, gram: 55.3

Run No. A-49

Catalyst No. C-49

Catalyst Composition

Metals : 4%CoO 8%MoO_3 1%NiO 8%WO_3

Base : Nalco-78-6008C-1/32"

Base Surface Area, m^2/g	: 214.57
Base Pore Volume, ml/g	: .8397
Base Pore Diameter (4V/A), Å	: 156.5
Base Median Pore Diameter, Å	: 161

Run Temperature, °C : 425 SRC-II Feed Temperature, °C : 90

Run Pressure, psig : 1,000

Liquid Hourly Space Velocity : 1.0

H_2: Oil Ratio, scf/bbl : 10,000

Yield of Oil, Volume % (balance is gas, coke & holdup) : 76

Time, min:	30	45	60	75	90	105	120	150
wt% N_2 :	-	.016	.073	.130	.230	.390	.460	.505
wt% S :	-	-	-	-	.495	-	-	.260

ASTM Distillation

Volume of Charge: 35.0 ml Final Volume: 29.0 ml

Volume, ml. :	0	5	10	15	20	25	29	35	40
°F :	236	308	432	467	511	578	621		

wt% N_2 in Outlet Gas Absorber: 0.069
wt. of Sulfuric Acid Absorption Solution, gram: 47.9

Run No. A-50

Catalyst No. C-50

Catalyst Composition

Metals : 4%CoO 8%MoO_3 1%NiO 2%WO_3

Base : Nalco-78-6008C-1/32"

Base Surface Area, m^2/g : 214.57
Base Pore Volume, ml/g : .8397
Base Pore Diameter (4V/A), Å : 156.5
Base Median Pore Diameter, Å : 161

Run Temperature, °C : 422 SRC-II Feed Temperature, °C : 82

Run Pressure, psig : 1,000

Liquid Hourly Space Velocity : .88

H_2: Oil Ratio, scf/bbl : 10,000

Yield of Oil, Volume % (balance is gas, coke & holdup) : 74

Time, min:	30	45	60	75	90	105	120	150
wt% N_2 :	-	.032	.097	.180	.250	.355	.465	.500
wt% S :	-	-	-	-	.420	-	-	.400

ASTM Distillation

Volume of Charge: 29.75 ml Final Volume: 23.0 ml

Volume, ml. :	0	5	10	15	20	23	30	35	40
°F :	289	426	470	540	589	643			

wt% N_2 in Outlet Gas Absorber: 0.085
wt. of Sulfuric Acid Absorption Solution, gram: 49.7

Run No. A-51

Catalyst No. C-51

Catalyst Composition

Metals : 4%CoO 8%MoO_3 4%NiO 8%WO_3

Base : Nalco-78-6008C-1/32"

Base Surface Area, m^2/g : 214.57
Base Pore Volume, ml/g : .8397
Base Pore Diameter (4V/A), Å : 156.5
Base Median Pore Diameter, Å : 161

Run Temperature, °C : 420 SRC-II Feed Temperature, °C : 85

Run Pressure, psig : 1,000

Liquid Hourly Space Velocity : .97

H_2: Oil Ratio, scf/bbl : 10,000

Yield of Oil, Volume % (balance is gas, coke & holdup) : 79

Time, min:	30	45	60	75	90	105	120	150
wt% N_2 :	-	.024	.092	.220	.340	.445	.420	.500
wt% S :	-	-	-	-	.385	-	-	.245

ASTM Distillation

Volume of Charge: 35.0 ml Final Volume: 27.0 ml

Volume, ml. :	0	5	10	15	20	25	27	35	40
°F :	361	414	451	491	547	597	632		

wt% N_2 in Outlet Gas Absorber: 0.053
wt. of Sulfuric Acid Absorption Solution, gram: 50.7

Run No. A-52

Catalyst No. C-52

Catalyst Composition

Metals : 4%CoO 8%MoO_3 4%NiO 2%WO_3

Base : Nalco-78-6008C-1/32"

Base Surface Area, m^2/g	: 214.57
Base Pore Volume, ml/g	: .8397
Base Pore Diameter (4V/A), Å	: 156.5
Base Median Pore Diameter, Å	: 161

Run Temperature, °C : 420 SRC-II Feed Temperature, °C : 85

Run Pressure, psig : 1,000

Liquid Hourly Space Velocity : .90

H_2: Oil Ratio, scf/bbl : 10,000

Yield of Oil, Volume % (balance is gas, coke & holdup) : 84

Time, min:	30	45	60	75	90	105	120	150
wt% N_2 :	-	.120	.150	.210	.325	.370	.390	.575
wt% S :	-	-	-	-	.390	-	-	.245

ASTM Distillation

Volume of Charge: 29.8 ml Final Volume: 23.0 ml

Volume, ml. :	0	5	10	15	20	23	30	35	40
°F :	319	425	470	524	588	643			

wt% N_2 in Outlet Gas Absorber: 0.036
wt. of Sulfuric Acid Absorption Solution, gram: 49.8

Run No. A-53

Catalyst No. C-53

Catalyst Composition

Metals : 4%CoO 2%MoO_3 1%NiO 8%WO_3

Base : Nalco-78-6008C-1/32"

Base Surface Area, m^2/g	: 214.57
Base Pore Volume, ml/g	: .8397
Base Pore Diameter (4V/A), Å	: 156.5
Base Median Pore Diameter, Å	: 161

Run Temperature, °C : 420 SRC-II Feed Temperature, °C : 85

Run Pressure, psig : 1,000

Liquid Hourly Space Velocity : .91

H_2: Oil Ratio, scf/bbl : 10,000

Yield of Oil, Volume % (balance is gas, coke & holdup) : 75

Time, min:	30	45	60	75	90	105	120	150
wt% N_2 :	-	.057	.130	.245	.350	.495	.555	.500
wt% S :	-	-	-	-	.600	-	-	.250

ASTM Distillation

Volume of Charge: 23.5 ml Final Volume: 17.0 ml

Volume, ml. :	0	5	10	15	17	25	30	35	40
°F :	377	455	537	600	635				

wt% N_2 in Outlet Gas Absorber: 0.096
wt. of Sulfuric Acid Absorption Solution, gram: 53.2

Run No. A-54

Catalyst No. C-54

Catalyst Composition

Metals : 4%CoO 2%MoO_3 1%NiO 2%WO_3

Base : Nalco-78-6008C-1/32"

Base Surface Area, m^2/g : 214.57
Base Pore Volume, ml/g : .8397
Base Pore Diameter (4V/A), Å : 156.5
Base Median Pore Diameter, Å : 161

Run Temperature, °C : 428 SRC-II Feed Temperature, °C : 85

Run Pressure, psig : 1,000

Liquid Hourly Space Velocity : .87

H_2: Oil Ratio, scf/bbl : 10,000

Yield of Oil, Volume % (balance is gas, coke & holdup) : 76

Time, min:	30	45	60	75	90	105	120	150
wt% N_2 :	-	.090	.010	.030	.310	.330	.350	.430
wt% S :	-	-	-	-	.600	-	-	.340

ASTM Distillation

Volume of Charge: 30.5 ml Final Volume: 21.5 ml

Volume, ml. :	0	5	10	15	20	22	30	35	40
°F :	367	441	478	534	599	633			

wt% N_2 in Outlet Gas Absorber: 0.073
wt. of Sulfuric Acid Absorption Solution, gram: 50.7

Run No. A-55

Catalyst No. C-55

Catalyst Composition

Metals : 4%CoO 2%MoO_3 4%NiO 8%WO_3

Base : Nalco-78-6008C-1/32"

Base Surface Area, m^2/g : 214.57
Base Pore Volume, ml/g : .8397
Base Pore Diameter (4V/A), Å : 156.5
Base Median Pore Diameter, Å : 161

Run Temperature, °C : 420 SRC-II Feed Temperature, °C : 80

Run Pressure, psig : 1,000

Liquid Hourly Space Velocity : .96

H_2: Oil Ratio, scf/bbl : 10,000

Yield of Oil, Volume % (balance is gas, coke & holdup) : 58

Time, min:	30	45	60	75	90	105	120	150
wt% N_2 :	-	.030	.140	.350	.290	.320	.370	.500
wt% S :	-	-	-	-	.625	-	-	.285

ASTM Distillation

Volume of Charge: 30.0 ml Final Volume: 21.0 ml

Volume, ml. :	0	5	10	15	20	21	30	35	40
°F :	367	442	480	538	607	639			

wt% N_2 in Outlet Gas Absorber: 0.035
wt. of Sulfuric Acid Absorption Solution, gram: 51.0

Run No. A-56

Catalyst No. C-56

Catalyst Composition

Metals : 4%CoO 2%MoO_3 4%NiO 2%WO_3

Base : Nalco-78-6008C-1/32"

Base Surface Area, m^2/g	: 214.57
Base Pore Volume, ml/g	: .8397
Base Pore Diameter (4V/A), Å	: 156.5
Base Median Pore Diameter, Å	: 161

Run Temperature, °C : 420 SRC-II Feed Temperature, °C : 85

Run Pressure, psig : 1,000

Liquid Hourly Space Velocity : .96

H_2: Oil Ratio, scf/bbl : 10,000

Yield of Oil, Volume % (balance is gas, coke & holdup) : 77

Time, min:	30	45	60	75	90	105	120	150
wt% N_2 :	-	.060	.100	.240	.490	.010	.620	.840
wt% S :	-	-	-	-	.720	-	-	.505

ASTM Distillation

Volume of Charge: 24.0 ml Final Volume: 17.5 ml

Volume, ml. :	0	5	10	15	18	25	30	35	40
°F :	325	427	484	567	627				

wt% N_2 in Outlet Gas Absorber: 0.026
wt. of Sulfuric Acid Absorption Solution, gram: 50.9

APPENDIX B

VARIABLE		1	2	3	4	5
		6	7	8		
MEAN (112)=		71.71	92.14	3.000	5.000	2.500
		5.000	9611.	.1356E 09		
STD DEV	=	18.22	33.62	1.004	3.013	1.307
		3.013	6608.	.1658E 09		
SKEWNESS	=	-.2316	.2834	.0000	.0000	.0000
		.0000	.7696	1.451		
KURTOSIS	=	2.065	2.040	1.000	1.000	1.000
		1.000	2.518	3.762		
MAXIMUM	=	99.10	150.0	4.000	8.000	4.000
		8.000	.2250E 05	.5062E 09		
MINIMUM	=	28.20	45.00	2.000	2.000	1.000
		2.000	2025.	.4101E 07		

DEPENDENT VARIABLE = 1

INDEPENDENT VARIABLES= 2,3,4,6,8

FIT:	VAR	R-PART	B	SE(B)	T	P-VALUE
	2	-.7667	-.6224	.5062E-01	-12.29	.0000
	3	.4343	3.421	.8891	4.964	.0000
	4	.2105	.5052	.2297	2.217	.2878E-01
	6	.2030	.4879	.2297	2.186	.3244E-01
	8	.2868	.3161E-07	.1028E-07	3.080	.2648E-02

INTERCEPT	=	109.5
R-SQUARED	=	.8471

ANALYSIS OF VARIANCE:

SOURCE	DF	S.S.	M.S.	F-VALUE	P-VALUE
REGRESS	5	.3123E 05	6246.	117.4	.0000
RESIDUAL	106	5638.	53.19		
TOTAL	111	.3687E 05			

VARIABLES DESCRIPTION:

1 = %DN

2 = running time, t, in minutes

3 = wt% CoO

4 = wt% MoO3

5 = wt% NiO

6 = wt% WO_3

7 = t^2

8 = t^4

APPENDIX C

VARIABLE	1	2	3	4	5
	6	7			
MEAN (16)=	38.04	61.64	49.80	3.000	5.000
	2.500	5.000			
STD DEV =	26.10	10.93	16.49	1.033	3.098
	1.549	3.098			
SKEWNESS =	.1411	-1.856	-.1684	.0000	.0000
	.0000	.0000			
KURTOSIS =	1.921	5.636	2.498	1.000	1.000
	1.000	1.000			
MAXIMUM =	84.70	70.10	77.40	4.000	8.000
	4.000	8.000			
MINIMUM =	.0000	29.90	14.90	2.000	2.000
	1.000	2.000			

DEPENDENT VARIABLE = 3
INDEPENDENT VARIABLES= 4, 5, 7

FIT:	VAR	R-PART	B	SE(B)	T	P-VALUE
	4	-.7758	-8.525	2.002	-4.259	.1112E-02
	5	.8342	3.496	.6672	5.239	.0000
	7	.5791	1.642	.6672	2.460	.3002E-01

INTERCEPT = 49.69
R-SQUARED = .8114

ANALYSIS OF VARIANCE:

SOURCE	DF	S.S.	M.S.	F-VALUE	P-VALUE
REGRESS	3	3311.	1104.	17.21	.0000
RESIDUAL	12	769.3	64.11		
TOTAL	15	4080.			

VARIABLES DESCRIPTION:

1 = %DS in 90 minutes
2 = %DS in 150 minutes
3 = average of variables 1 and 2
4 = wt% CoO
5 = wt% MoO_3
6 = wt% NiO
7 = wt% WO_3

APPENDIX D

VARIABLE	1	2	3	4	5
	6	7	8		
MEAN (16)=	71.70	48.83	67.38	73.19	3.000
	5.000	2.500	5.000		
STD DEV =	5.674	16.48	3.982	6.685	1.033
	3.098	1.549	3.098		
SKEWNESS =	-.2341	-.1732	.6850	-.9309	.0000
	.0000	.0000	.0000		
KURTOSIS =	2.037	2.508	2.822	3.261	1.000
	1.000	1.000	1.000		
MAXIMUM =	81.10	77.40	76.70	84.00	4.000
	8.000	4.000	8.000		
MINIMUM =	61.90	14.30	62.40	58.00	2.000
	2.000	1.000	2.000		

DEPENDENT VARIABLE = 4
INDEPENDENT VARIABLES= 8

FIT: VAR	R-PART	B	SE(B)	T	P-VALUE
8	-.4538	-.9792	.5139	-1.905	.7747E-01

INTERCEPT = 78.08
R-SQUARED = .2059

ANALYSIS OF VARIANCE:

SOURCE	DF	S.S.	M.S.	F-VALUE	P-VALUE
REGRESS	1	136.1	136.1	3.631	.7747E-01
RESIDUAL	14	532.4	38.03		
TOTAL	15	670.4			

VARIABLE DESCRIPTION:

4 = Oil product yield, vol.%

8 = wt% of WO_3

Mass balance of nitrogen in the trickle bed reactor

By HUO -YEN HSIEH

The conversion of Solvent Refined Coal, SRC-II, to distillate fuels has been carried out in a trickle bed reactor by hydrogenation at MSU. The purpose of this research is to determine the amount of nitrogen absorbed by the packings in the trickle bed reactor.

During the quarter, catalyst designated C-54 was tested under the operation contion of 425°C, 1,000 psig, liquid hourly velocity of 1.0, hydrogen feed rate of 10,000 scf/bbl of oil, and SRC-II feed temperature of 85°C. Hydrogen and SRC-II were fed at the top of reactor. Starting from the top, the reactor was loaded with 175ml. of 1/4" Denstone inert support,25ml. of 1/8" Denstone inert support, followed by a mixture of 60 ml. of catalyst and 60 ml. of 1/8" Denstone inert support. The remaining space at the bottom of the reactor was filled with 2/8" Denstone inert support.

The detailed data is listed in the TABLEIV. The amount of nitrogen was analyzed on the packings of the reactor, for the run performed. To accomplish this, the following samples were taken

3 samples from 3 locations of the inert 1/4" support section, 3 samples from 3 locations of catalyst section and 4 samples from 4 locations of inert 1/8" support section.

TABLE V shows the nitrogen content of inert supports and catalyst. The total amount of nitrogen absorbed by the packings is 0.1g, which is 6.67% Wt. of the nitrogen content in the SRC II feed nitrogen absorbed by the catalyst is 2.08% Wt. of the nitrogen content in the SRC II feed, which is relatively small.

TABLE IV

Run No. A-59

Catalyst No. C-54

Catalyst Composition

Metals : 4%CoO 2%MoO_3 1%NiO 2%WO_3

Base : Nalco-78-6008C-1/32"

Base Surface Area, m^2/g : 214.57
Base Pore Volume, ml/g : .8397
Base Pore Diameter (4V/A), Å : 156.5
Base Median Pore Diameter, Å : 161

Run Temperature, °C : 417 SRC-II Feed Temperature, °C : 85

Run Pressure, psig : 1,000

Liquid Hourly Space Velocity : 1.0

H_2 : oil Ratio, scf/bbl : 10,000

Yield of Oil, Volume % (balance is gas, coke & holdup) : 70

Total run time, min : 135

TABLE V

Nitrogen content in the used catalyst & inert supports

Sample	Wt %					* Wt.	** %
	TOP	MID	BTM1	BTM2	AVG.		
Inert support section, 1/4"	.01	.05	.05	--	.036	.059	3.93
Inert support section, 1/8"	.55	.36	.31	.15	.34	.010	.66
Catalyst section	.20	.03	.19	--	.14	.031	2.08

* (Avg. nitrogen Wt%)(total amount of Wt. in the section) = Wt. of nitrogen in the section.

** % = Wt. of nitrogen in the Feed / Wt. of nitrogen in the catalyst or in the inert supports.

DETERMINATION OF CARBON LAYDOWN ON CATALYSTS DEVELOPED AND TESTED AT M.S.U.

by M.Rameswaran.

Catalysts have been developed at MSU, which will convert the Solvent Refined Coal (SRC-II) of PAMCO into a clean distillate fuel and/or a feedstock acceptable to a conventional refinary.

During the previous quarter 2^4 (Sixteen) cataysts have been developed by impregnating the base material, NALCO-78-6008-1/32" with oxides of Co, Mo, Ni and W.

These catalysts appear to be a combination of hydrotreating-hydrocracking. Considerable amount of carbonaceous laydown occurs on the inert Denstone supports, especially that portion above the catalysts, which receives the feedstock before the catalysts and catalysts themselves. This carbon laydown isolates the catalysts from the feed, making the conversion poor and enables pressure build up in the reactor.

In this research, a study is to be performed on the used catalysts to correlate the amount of carbon laydown on them with %DS,%DN and their pore diameters.

As the first step in this research, catalysts from 16 runs performed by Angong Yeh in the previous quarter and some random samples of inert Denstone supports from those runs were analysed.

After each run was performed, Angong Yeh drained the entire contents of the reactor on the countertop, in the same order in which the reactor was loaded. Approximately one gram of catalysts sample from three different locations in the catalyst section, of the contents drained out after each run,were dried at 100°C,until constant weight is attained.2 hours of drying time was found to be optimum. These dried samples were then calcined, to determine the loss on ignition.Calcining was done at different tempratures in order to get a complete burnoff of carbon, in a reasonable amount of time. One hour and 10 minutes at 750°C was found to be reasonable.

Under the above conditions, catalyst samples and some random inert Denstone supports were analysed, and the results are presented in the following tables.

Results :

Table VI gives the wt.percent of carbon laydown on 3 locations of catalysts section of runs A-41 to A-56. Carbon laydown varied from 23% to 32%. Attempts were made to correlate these results with diffe--rent metal loadings on the catalysts, which showed no significance.

TableVII gives % wt.loss on ignition of sulfided,unsulfided and blank catalysts. This wt.loss is assumed to be constant for all the cases.

Table VIII gives % wt.loss of inert supports. 1/8" supports which are below the catalyst section seem to have absorbed considerable amount of carbon.

Table IX gives the summery of the above listed results in terms of % of feed laid down as carbon on different locations of the reactor. From this table we find that, 9.9-12.7 wt. % of the feed is deposited as carbon on the reactor.

TABLE VI

Run No.	@Zone	*Average Wt. dry sample (gms.)	Average Wt. of sample after burnig (gms.)	% Wt.loss
	Top	1.0165	0.7362	27.38
A-41	Middle	1.0115	0.7708	23.80
	Bottom	1.2272	0.9438	22.97
	Top	1.1224	0.8289	26.15
A-42	Middle	1.2299	0.9306	24.33
	Bottom	1.0016	0.7538	24.74
	Top	0.9976	0.7349	26.33
A-43	Middle	1.0093	0.6994	30.73
	Bottom	1.0043	0.7212	28.19
	Top	1.0025	0.6820	31.97
A-44	Middle	1.0141	0.6881	32.15
	Bottom	0.9975	0.6295	30.58
	Top	0.9974	0.6846	31.37
A-45	Middle	1.0003	0.7072	29.31
	Bottom	1.0070	0.7125	29.25
	Top	1.0058	0.7105	29.36
A-46	Middle	0.9991	0.7144	28.50
	Bottom	0.9973	0.7315	26.66

TABLE VI (cont.)

Run No.	@ Zone	* Average Wt. dry sample (gms.)	Average Wt. of sample after burning (gms.)	% wt.loss
	Top	1.0036	0.7315	27.12
A-47	Middle	1.0002	0.7413	25.88
	Bottom	0.9955	0.7415	25.52
	Top	0.9986	0.7225	27.65
A-48	Middle	0.9969	0.7429	25.48
	Bottom	0.9978	0.7086	28.98
	Top	0.9993	0.6709	32.86
A-49	Middle	1.0018	0.6803	32.09
	Bottom	1.0118	0.7052	30.31
	Top	1.0026	0.7644	23.76
A-50	Middle	1.0067	0.7730	23.21
	Bottom	0.9958	0.7804	21.62
	Top	1.0070	0.7362	26.89
A-51	Middle	1.0147	0.7604	25.06
	Bottom	1.0020	0.7534	24.81
	Top	1.0035	0.7489	25.35
A-52	Middle	1.0000	0.7541	24.60
	Bottom	1.0181	0.7798	23.41

TABLE VI (cont.)

Run No.	@Zone	Average Wt. dry sample (gms.)	*Average Wt. of sample after burning (gms.)	%Wt.loss
	Top	1.0260	0.6848	33.25
A-53	Middle	1.0165	0.6848	32.63
	Bottom	1.0146	0.7084	30.18
	Top	1.0140	0.6963	31.33
A-54	Middle	1.0141	0.7303	27.99
	Bottom	1.0134	0.7421	26.68
	Top	1.0075	0.7493	25.63
A-55	Middle	1.0101	0.7468	26.07
	Bottom	1.0576	0.7563	28.49
	Top	1.0250	0.6976	31.94
A-56	Middle	1.0170	0.6890	32.31
	BOttom	0.9992	0.6990	30.04

@ Catalyst zone in the reactor.

* Samples are placed in the oven for 1 hr. and 10 mins.,at a temprature between 730-760° c.

TABLE VII

SAMPLE	A-50 SULFIDED	A-50 UNSULFIDED	BLANK
Wt.of Sample (gms.)	3.0910	3.0587	3.0514
Wt.after drying (gms.)	3.1049	3.0697	2.9190
Wt. after burning (gms.)	2.8946	3.0420	2.8608
*% Wt.loss	6.78	0.902	1.994

$$\left(*\%\ \text{Wt.loss} = \frac{(\text{Wt. after drying} - \text{Wt. after burning.})}{\text{Wt.after drying}} \times 100\right)$$

TABLE VIII

Sample	A-41		A-50		Unused	
	*Top	*Bottom	*Top	*Bottom	*Top	*Bottom
Wt.of Sample (gms.)	3.0055	1.1145	2.5095	1.0728	2.4827	1.3666
Wt. after drying (gms.)	3.0049	1.0984	2.5092	1.0658	2.4827	1.2633
Wt.after burning (gms.)	2.9721	0.8112	2.4849	0.7851	2.4778	1.1761
**% Wt.loss	1.09	26.15	0.97	26.34	0.197	6.90

* Top- 1/4" Denstone support above the catalst section
Btm.- 1/8" Inert support below the catalyst section.

** $\%Wt\ loss = \frac{Wt.after\ drying - Wt.\ after\ burning}{Wt.\ after\ drying} \times 100$

Table IX

Run No.	Wt.of feed (gms.)	wt.% of carbon laydown on					% wt. laydown as Carbon
		Inert supports		Catalysts			
		Top	Bottom	Top	Middle	Bottom	
A-41	151.62	1.403	4.614	1.744	1.442	1.372	10.576
A-42	163.157	1.304	4.288	1.524	1.382	1.414	9.911
A-43	164.805	1.291	4.245	1.523	1.864	1.667	10.589
A-44	181.285	1.174	3.859	1.782	1.794	1.684	10.292
A-45	164.805	1.291	4.245	1.913	1.754	1.749	10.952
A-46	136.788	1.555	5.114	2.117	2.037	1.865	12.690
A-47	164.805	1.291	4.245	1.584	1.488	1.460	10.068
A-48	153.269	1.388	4.564	1.747	1.567	1.858	11.125
A-49	164.805	1.291	4.245	2.029	1.969	1.831	11.365
A-50	145.028	1.467	4.824	1.504	1.465	1.316	10.567
A-51	159.861	1.331	4.376	1.615	1.468	1.449	10.239
A-52	148.324	1.434	4.717	1.608	1.543	1.441	10.743
A-53	149.972	1.419	4.665	2.262	2.210	2.001	12.557
A-54	143.380	1.484	4.879	2.196	1.898	1.782	12.238
A-55	158.213	1.345	4.422	1.530	1.565	1.761	10.622
A-56	158.213	1.345	4.422	2.039	2,069	1.886	11.760

CONVERSION OF SOLVENT REFINED COAL,SRC-II,TO DISTILLATE FUELS

By Turgut Sahin

During this quarter,work done on finding commercial catalysts capable of converting PAMCO's Solvent Refined Coal,SRC-II,to a substitute for petroleum.The aim of research has been to produce a material from SRC-II which can be used in conventional petroleum refineries as an acceptable feedstack. Since it is known that a feedstack to conventional refineries must have a nitrogen content of,at least, less than 0.3 percent;However,the SRC-II has 1.17%nitrogen.Commercial hydrotreating-hydrocracking catalysts,which have large surface area and large pore diameter for free passage of the liquified coal molecules,are selected to perform this objecktive.

The SRC-II contains 0.72% sulfur as well as 1.17% nitrogen.Since nitrogen removal is main purpose of this project,the sulfur content remained as a minor problem;However,it should be removed as much as possible.

The trickle bed reactor,shown in Figure 1,is made by a one-inch I.D. 40 inches long schedule 80 Inconel pipe,has been used in this research.Starting from the top,the reactor is loaded with 175 ml of 1/4" spherical Denstone inert support,25 ml of 1/8"cylindirical Denstone inert support,followed by a mixture of 60 ml of catalyst and 1/8"cylinderical Denstone inert support .The remaining space at the bottom of the reactor is filled with 1/8" cylindrical Denstone inert support.

The operating conditions are 425°C ,1000 psig,hydrogen feed rate of 10,000 scf/bbl of oil,Liquid Hourly Space Velocity of 1.0,and SRC-II feed temparature of 80°C.

In this quarter Nalcomo 477(#78-5973-B) which possesses a surface area of 250 m^2/gram,a pore diameter of 88 ^{o}A,a pore volume of 0.55 ml/gram,and a metal load of 3.3% CoO and 14%MoO_3,has been tested. The first run,T-1A,is made with unsulfided catalyst at the LHSV of 1.0 Table 1 summarizes the results.This catalist shows a considerable potantial for denitrogenation.After 2.5 hours of running time it was still active,and nitrogen % in the product samples was lower than 0.3%.

Two more runs are made with the same catalyst by sulfiding the catalyst.The first one,T-2A,is made by changing LHSV to 1.9.Table 2 shows the results.It is seen that LHSV effected denitrogenation too much,and catalyst deactivated whithin a short period of time.The second run with sulfided catalyst,T-3A,is made with the LHSV of 1.0 and very clean product samples are obtained for three hours of running time, but the lab analysis were'nt ready when this report written.The results will be reported the next quarter.Couple of more runs are planed with this catalyst ,especially,to test the catalyst life and regenaration properties.

Since the lab analysis for sulfur weren't ready until reporting time the sulfur results are not given.They will be in the next quarter's report.

The denitrogenation results for two runs are plotted on Figures 7 and 8 as a function of time respectively.Fig.8 shows that LHSV causes a sharp decrease on catalist activity.

RUN T-1A

CATALYST NALCOMO 477 1/16" #78-5973-B

Properties

Metal Load 14% MoO_3

3.3% CoO

Surface Area, m^2/gram =250

pore volume, ml/gram =.55

Pore Diametr, ^oA =88'

CONDITIONS

Temperature , ^oC $\pm 425 \pm 20$

Feed temperature, ^oC= 80 ± 5

Pressure ,psig =1000

Liquid Hourly Space Velocity=1.0

H_2:oil ratio, scf/bbl =10,000

Yield of oil, volume % =

Time min.	Density g/ml	% N wt %	% S wt%	% DN wt%	% DS wt%
40	0.908	0.17		86	
56	0.891	0.20		83	
81	0.867	0.17		86	
96	0.853	0.15		87	
111	0.859	0.18		85	
126	0.878	0.15		87	
141	0.905	0.21		83	
156	0.878	0.23		80	

RUN T-2A

CATALYST NACOMO 477 1/16" #78-5973-B

Properties

Metal Load 14 %MoO_3

3.3 % CoO

Surface Area, m^2/gram =250

Pore Volume, ml/gram =.55

Pore Diameter, ^oA =88

CONDITIONS

Temperature, ^oC =425$\bar{+}$20

Feed Temperature, ^oC =80$\bar{+}$5

Pressure , psig =1000

Liquid Hourly Space Velocity =1.9

H_2:oil ratio ,scf/bbl of oil =10,000

yield of oil, volume % =

Time	Density	% N	%S	% DN	% DS
min.	g/ml	wt %	wt %	wt %	wt %
30	0.53	0.01		99	
45	0.87	0.13		89	
60	0.92	0.87		26	
75	0.90	0.53		55	
90	0.98	0.67		48	
105	0.99	0.71		39	
120	0.91	0.51		66	

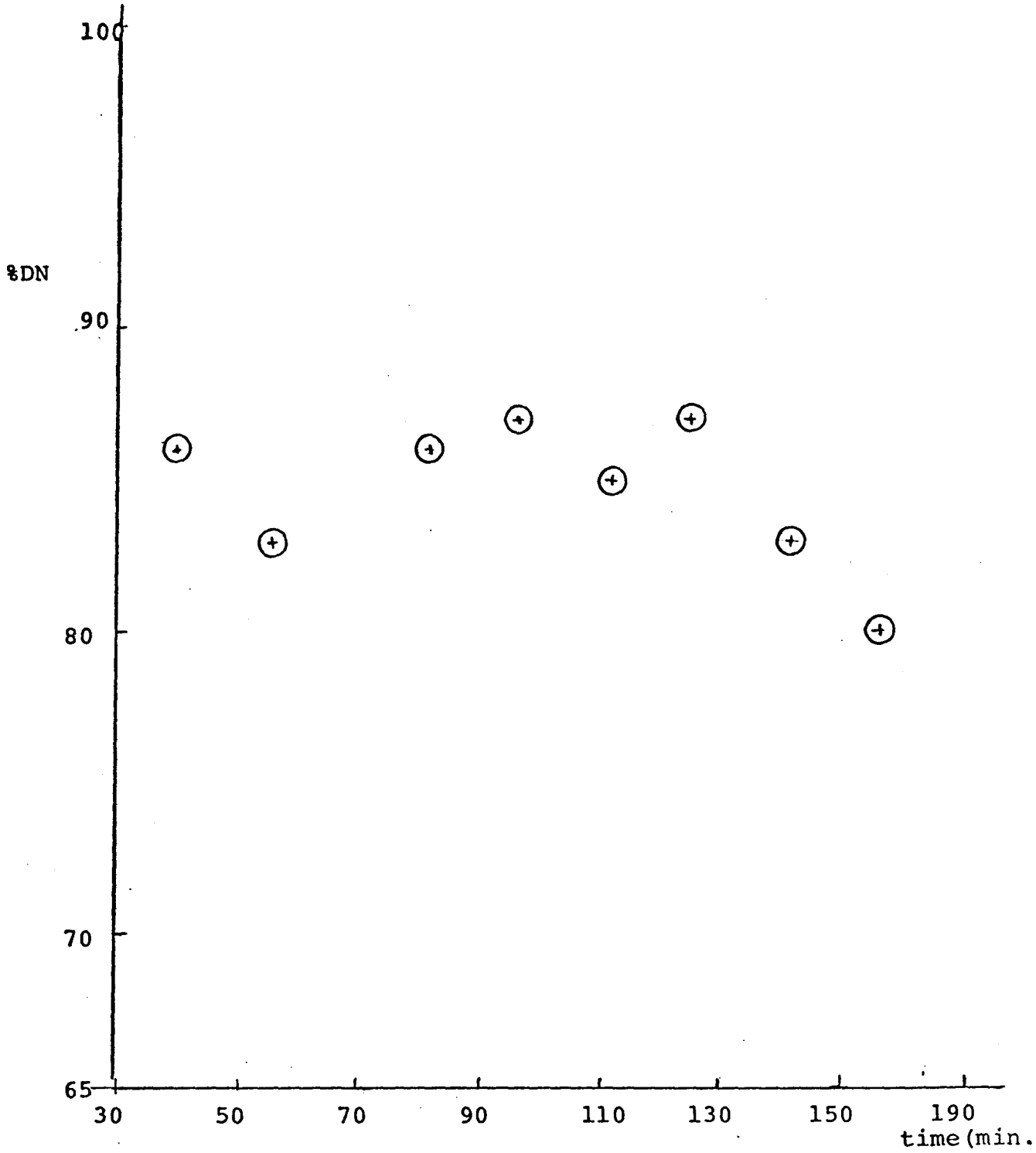


FIGURE 7 % DN vs. time for catalyst Nalcomo 477 (unsulfided)

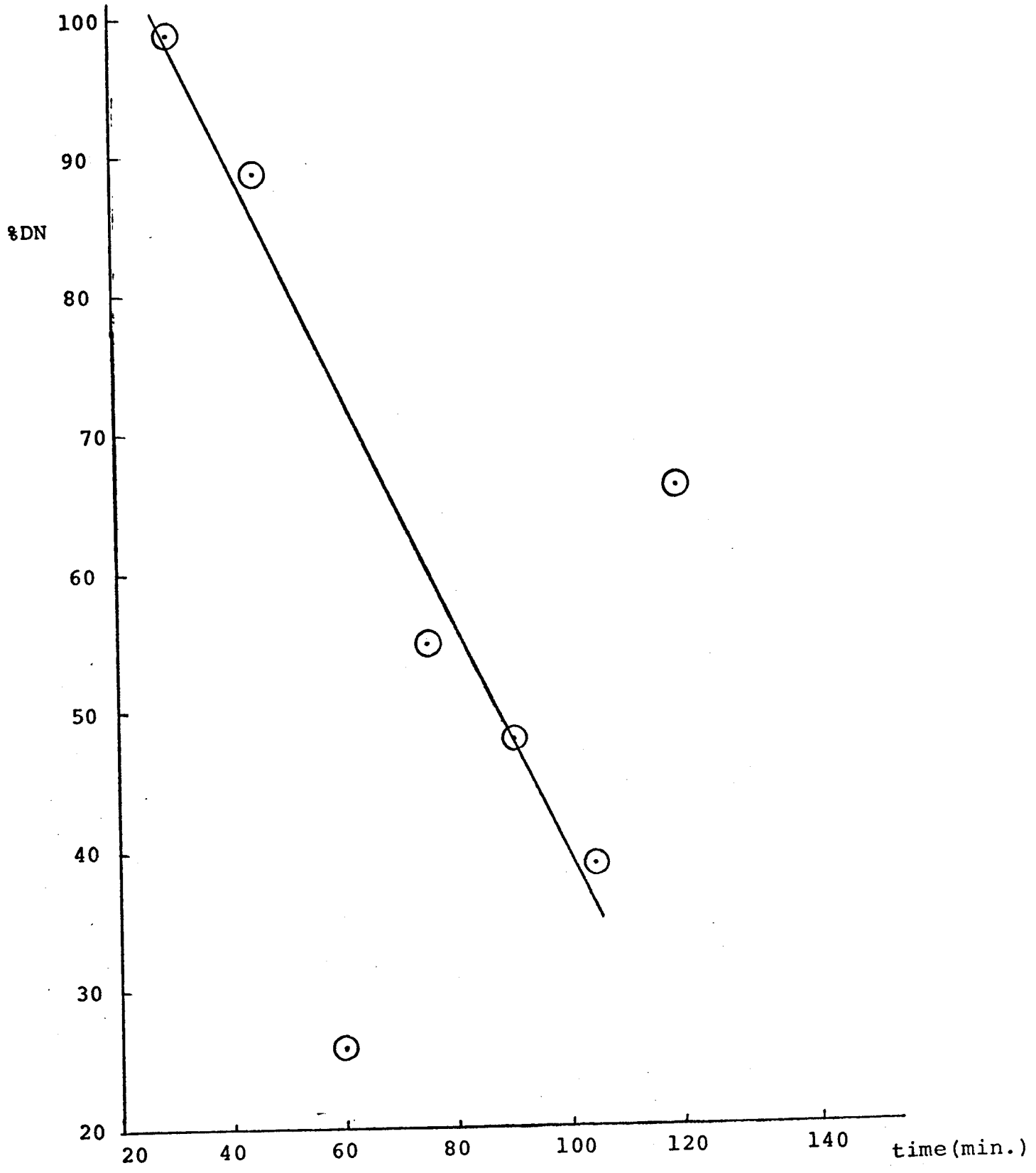


FIGURE 8 % DN vs. time for catalyst Nalcomo 477 (sulfided)

THE ROLE OF CATALYST PORE SIZE IN THE UPGRADING OF PAMCO SOLVENT REFINED COAL, SRC II.

By Tom Insley

In the upgrading of Pittsburg & Midway Coal Mining Company's solvent refined coal, SRC II, the objective of primary importance is to keep to a minimum the hydrogen consumption necessary to adjust the H/C ratio and to remove the nitrogen compounds (in our case 10,000 scf H_2/bbl of oil), while maintaining moderate operating conditions (425°C, 1,000-1,300 psig, and a LHSV of one). In order to enhance the economic competitiveness of the process, development of more active, longer life cycle catalysts is required.

In coal hydroliquefaction processes the structural properties of the catalyst carrier involved, in particular surface area and pore diameter, play a paramount role in upgrading. In the upgrading of SRC II, ready access to the active sites of the catalyst must be provided for the large asphaltenic molecules.

In SRC upgrading work carried out by the Chemical Engineering Department here at Montana State University there is an indication of the desirability of an active catalyst containing a major amount of pores larger than 60 Å in diameter (which would admit the larger asphaltene molecules) but not so large (> 1,000 Å) to reduce the effective surface area below a limiting amount. It is not clear, however, where the optimum effects of upgrading would be achieved in relation to median pore diameter and pore size distribution of the catalyst, within the desired pore diameter range.

It is, therefore, the intent of this facet of the research to develop a corrolation between the median pore diameter and pore size distribution, and the degree of hydrocracking, hydrodenitrogination, and to a lesser extent hydrodesulfuration of SRC II.

Experimental Section

Hydrogenation of SRC II. The degree of hydrogenation of an SRC II feed will be evaluated for various catalysts in a single pass, trickle bed reactor. The reactor in all cases will be charged, from top to bottom, in the following manner:

1. 175 cm^3, 1/4 in. Denstone support
2. 25 cm^3, 1/8 in. Denstone support
3. Mixture of 60 cm^3, 1/8 in. Denstone support + 60 cm^3, activated catalyst
4. Remaining volume filled with 1/8 in Denstone support

Evaluation conditions are to be maintained at 1100 psig, 420°C-430°C, LHSV of one, and a hydrogen input of 10,000 scf/bbl of oil. Duration of each catalyst evaluation will be for 3.0 h.

Catalysts. The catalyst carriers to be evaluated in the study[1] will be impregnated in as uniform a manner as possible so that a consistent metal loading can be maintained. The procedure for the incipient wetness impregnation will be to first load Molybdenum (its salt dissolved in aqueous ammoniun hydroxide) then a combination of Tungsten and Cobalt (their salts dissolved in distilled water) onto the carriers. Each wet preparation will be oven dried at 110°C for 8 h after which it will be calcined for 8 h at 450°C. As a final step the catalyst will be sulfided by passing 60 ml/h of an 10% hydrogen sulfide in hydrogen blend at 325°C for 12 h.

---

[1]See Table x

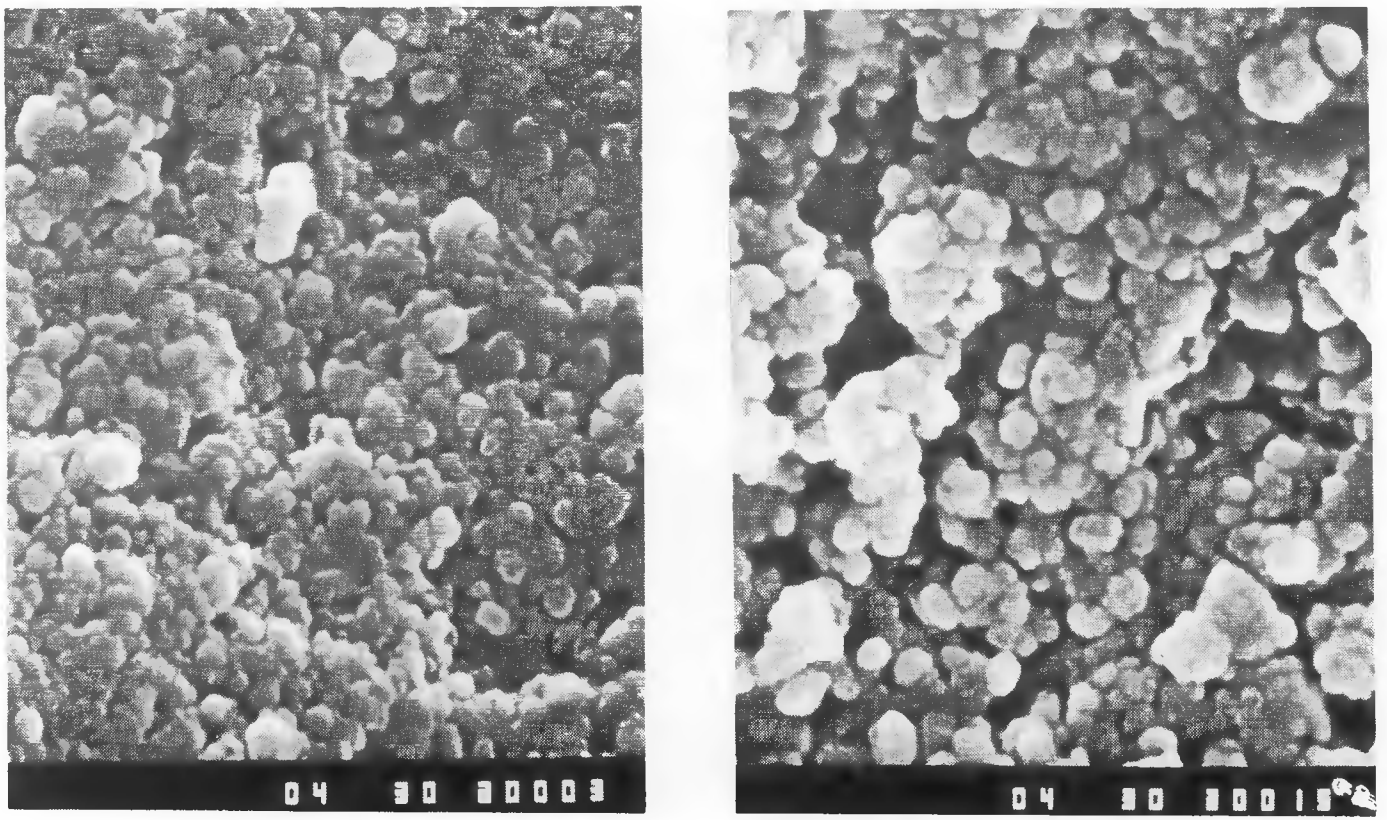
TABLE X

CATALYST CARRIER PROPERTIES

Carrier	Composition	Surface Area m^2/g	Pore Vol. ml/g	Pore Diameter Median Å	Pore Diameter Average Å
Katalco					
78-6008A	4% SiO_2 96% Al_2O_3	323.2	.7183	90.2	88.9
80-6476	2% SiO_2 98% Al_2O_3	238.1	.6918	93.6	116.2
80-6477	9% P_2O_5 91% Al_2O_3	280.6	.9313	220.4	132.8
78-6008D	9% P_2O_5 91% Al_2O_3	211.39	.7943	190.0	150.3
78-6008C	2% SiO_2 98% Al_2O_3	214.57	.8397	161	156.5
78-6008E	17% P_2O_5 83% Al_2O_3	146.95	.6841	420.2	186.2
W.R. Grace & Co.					
Gamma Spheres	100% Al_2O_3	250.0	1.2	90.0	-

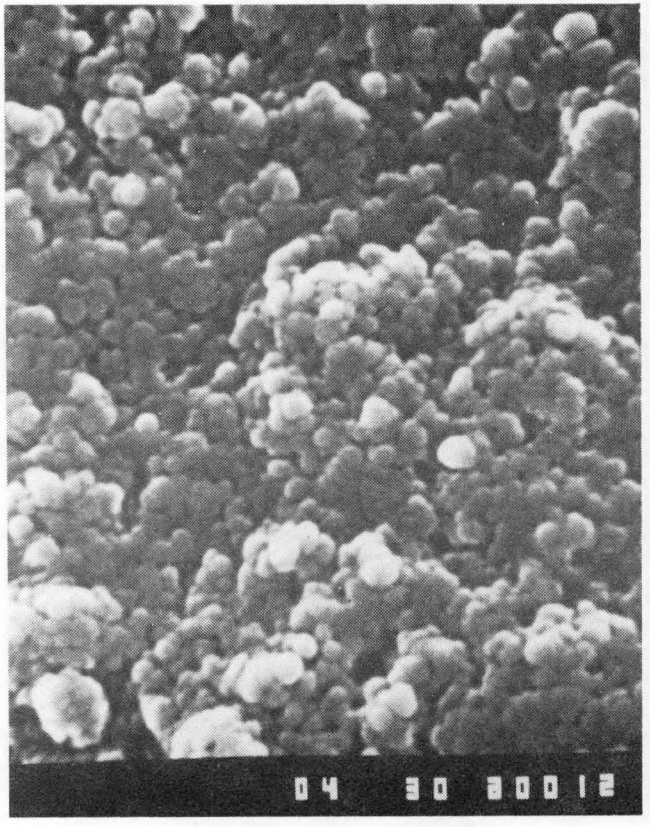
Electron Microscopic Investigation of Catalyst Pore Diameter.
By Nam Kim

The results of an electron microscopic investigation of two of our catalysts are shown in Figure XI. Figure XI-A shows NALCO base C with no metals impregnated upon it. Measurements have indicated a pore diameter of 161Å for this base. Inspection of the photomicrograph indicates that the space between particles is about 100 - 150Å. Figure XI-B shows the same base with 10% MoO_3, 1.1% NiO, 5.1% CoO and 10.8% WO_3 impregnated on it. The distance between the particles is still in the 100 - 150Å range according to inspection of the photomicrograph. This result adds credence to our theory that a successful catalyst for SRC-II processing must possess a pore diameter greater than 50Å.

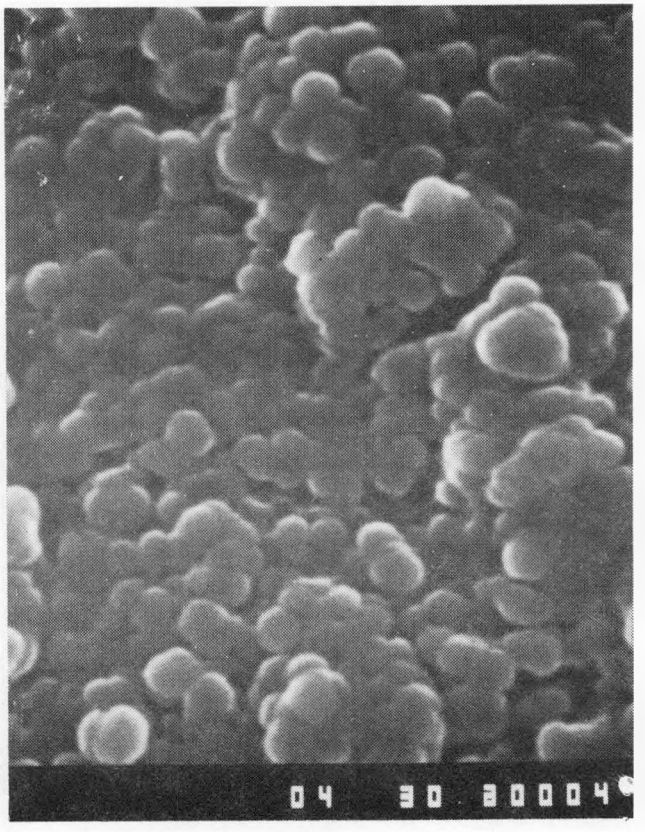


(A) (B)

FIGURE X/ . SCANNING ELECTRON PHOTOMICROGRAPHS:
(A) NALCO BASE C, 2%SiO_2;98%Al_2O_3 (B) MSU KN C8 CATALYST WITH 10.02% MoO_3, 1.13%NiO, 5.12%CoO, and 10.82%WO_3 on NALCO BASE C.
(C) MSU KN C5 CATALYST WITH 12.08%MoO_3 ON NALCO BASE C
(D) MSU KN C5 CATALYST AFTER SECOND REGENERATION

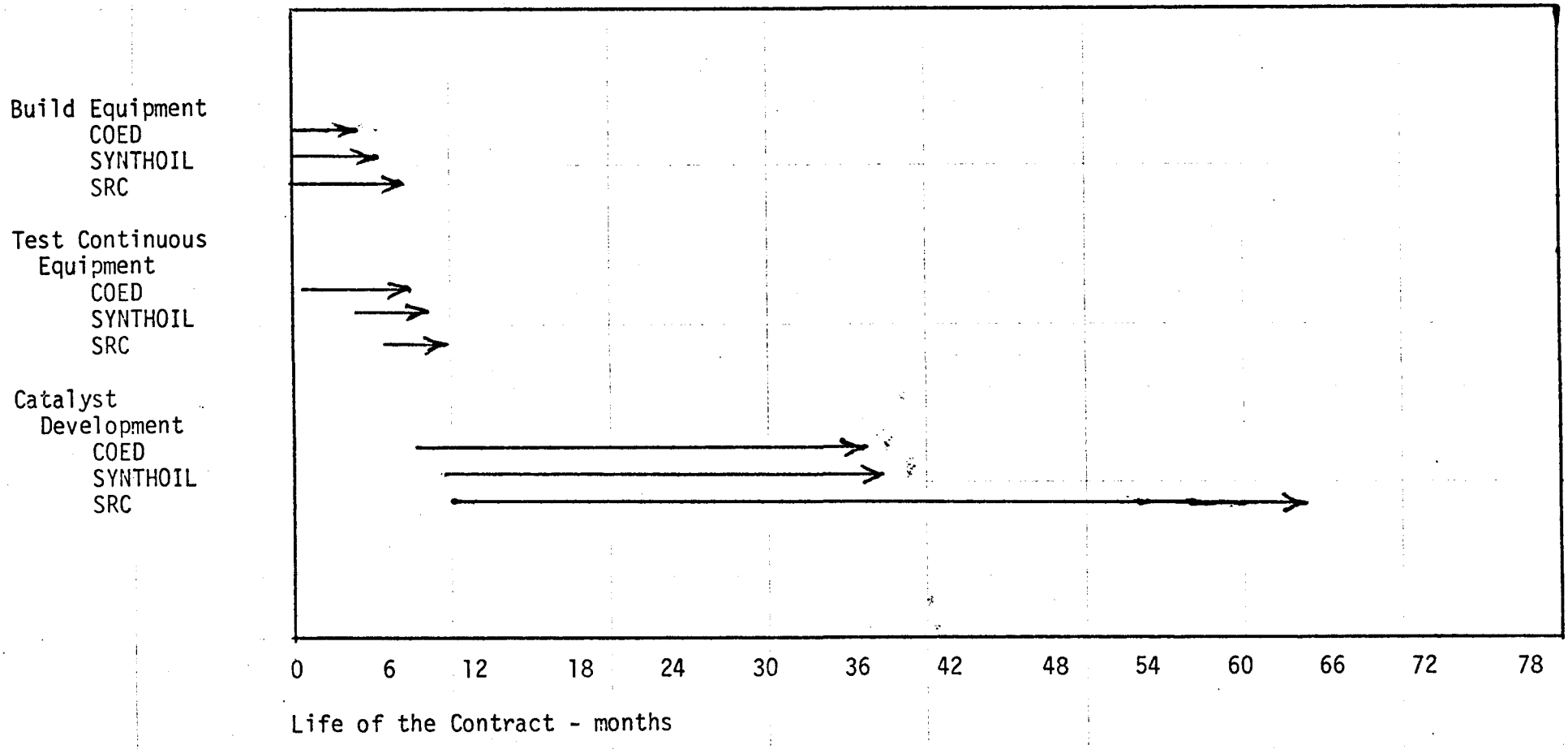


(C)



(D)

PICTORIAL PROGRESS REPORT



Standard Form 1034
September 1973
4 Treasury FRM 2000
1034-115

PUBLIC VOUCHER FOR PURCHASES AND SERVICES OTHER THAN PERSONAL

VOUCHER NO. 38

SCHEDULE NO.

PAID BY

U.S. DEPARTMENT, BUREAU, OR ESTABLISHMENT AND LOCATION

U. S. Energy Research and Development Administration
Office of Procurement Operations
2100 M Street N. W.
Washington, D.C. 20545

DATE VOUCHER PREPARED: October 17, 1980

CONTRACT NUMBER AND DATE: EX-76-C-01-2034

REQUISITION NUMBER AND DATE

PAYEE'S NAME AND ADDRESS

Montana State University
Grants & Contracts
Bozeman, Montana 59717

DATE INVOICE RECEIVED

DISCOUNT TERMS

PAYEE'S ACCOUNT NUMBER: 26000789

SHIPPED FROM | TO | WEIGHT

GOVERNMENT B/L NUMBER

NUMBER AND DATE OF ORDER	DATE OF DELIVERY OR SERVICE	ARTICLES OR SERVICES (Enter description, item number of contract or Federal supply schedule, and other information deemed necessary)	QUANTITY	UNIT PRICE COST	PER	AMOUNT (1)
		For reimbursement of Costs incurred under contract #E-49-(18)-0234, per attached 1035 for the period: September 1, 1980 through September 30, 1980				$ 8,486.85

I certify that all expenditures reported, or payments requested are for appropriate purposes ... set forth in the ...

(Use continuation sheet(s) if necessary) (Payee must NOT use the space below) TOTAL $ 8,486.85

PAYMENT:
- [ ] COMPLETE
- [ ] PARTIAL
- [ ] FINAL
- [ ] PROGRESS
- [ ] ADVANCE

APPROVED FOR =$

EXCHANGE RATE =$1.00

DIFFERENCES

BY [2]

TITLE

Amount verified; correct for

(Signature or initials)

Pursuant to authority vested in me, I certify that this voucher is correct and proper for payment.

(Date) (Authorized Certifying Officer) [2] (Title)

ACCOUNTING CLASSIFICATION

PAID BY

CHECK NUMBER | ON TREASURER OF THE UNITED STATES | CHECK NUMBER | ON (Name of bank)

CASH $ | DATE | PAYEE [3] Office of Grants & Contracts, Montana State University, Bozeman, Montana 59717

PER Lawrence T. Kain

TITLE Grant & Contract Administrator

[1] When stated in foreign currency, insert name of currency.
[2] If the ability to certify and authority to approve are combined in one person, one signature only is necessary; otherwise the approving officer will sign in the space provided, over his official title.
[3] When a voucher is receipted in the name of a company or corporation, the name of the person writing the company or corporate name, as well as the capacity in which he signs, must appear. For example: "John Doe Company, per John Smith, Secretary", or "Treasurer", as the case may be.

☆U.S.GPO.1978-0-261-647 3997

Standard Form 1035
September 1974
4 Treasury FRM 2000
1035-110

PUBLIC VOUCHER FOR PURCHASES AND SERVICES OTHER THAN PERSONAL

CONTINUATION SHEET

VOUCHER NO. 38
SCHEDULE NO.
SHEET NO. 2

U.S. DEPARTMENT, BUREAU, OR ESTABLISHMENT
U. S. Energy Research and Development Admin.

NUMBER AND DATE OF ORDER	DATE OF DELIVERY OR SERVICE	ARTICLES OR SERVICES (Enter description, item number of contract or Federal supply schedule, and other information deemed necessary)	QUANTITY	UNIT PRICE COST	UNIT PRICE PER	AMOUNT
		Montana State University Bozeman, Montana 59717 G&C 26000789		Contract No. EX-76-C-01-2034 "Catalytic Hydrogenation of Coal Derived Liquids", principal investigator Dr. Lloyd Berg		
		For the period of September 1, 1980 through September 30, 1980				
				CURRENT PERIOD		CUMULATIVE TO DATE
		Salaries & Wages		4,622	50	112,563.21
		Benefits		490	25	7,100.44
		Supplies & Materials		434	27	35,533.66
		Travel				3,978.91
		Equipment				12,625.85
		Awards (Tuition & Fees)				5,755.30
		Indirect Costs		2,939	83	66,928.47
		Subtotal		8,486	85	244,485.84
		Cost Sharing		1,381	58	41,078.13
		Total		9,868	43	285,563.97

*U.S.Government Printing Office: 1977 – 241-630/3284

Standard Form 1034
September 1973
4 Treasury FRM 2000
1033-115

PUBLIC VOUCHER FOR PURCHASES AND SERVICES OTHER THAN PERSONAL

VOUCHER NO. 39

U.S. DEPARTMENT, BUREAU, OR ESTABLISHMENT AND LOCATION

U. S. Energy Research and Development Administration
Office of Procurement Operations
[redacted] M Street NW
~~Washington, D.C. 20545~~

DATE VOUCHER PREPARED: October 17, 1980

CONTRACT NUMBER AND DATE: EX-76-C-01-2034

REQUISITION NUMBER AND DATE:

SCHEDULE NO.

PAID BY

DATE INVOICE RECEIVED

DISCOUNT TERMS

PAYEE'S ACCOUNT NUMBER: 789

GOVERNMENT B/L NUMBER

PAYEE'S NAME AND ADDRESS

Montana State University
Grants & Contracts
Bozeman, Montana 59717

SHIPPED FROM | TO | WEIGHT

NUMBER AND DATE OF ORDER	DATE OF DELIVERY OR SERVICE	ARTICLES OR SERVICES (Enter description, item number of contract or Federal supply schedule, and other information deemed necessary)	QUANTITY	UNIT PRICE COST	UNIT PRICE PER	AMOUNT (1)
		For reimbursement of Costs incurred under contract E-49-(18)-0234, per attached 1035 for the period: October 1, 1980 through November 30, 1980				$ 4,691.33

I certify that all expenditures reported, or payments requested are for appropriate purposes in accordance with the terms set forth in the contract documents.

[signature]
[illegible] Administrative Assistant to the [illegible] for Research

(Use continuation sheet(s) if necessary) (Payee must NOT use the space below) TOTAL $ 4,691.33

PAYMENT:
- ☐ COMPLETE
- ☐ PARTIAL
- ☐ FINAL
- ☐ PROGRESS
- ☐ ADVANCE

APPROVED FOR ... =$ | EXCHANGE RATE =$1.00

BY [2]

TITLE

DIFFERENCES

Amount verified; correct for

(Signature or initials)

Pursuant to authority vested in me, I certify that this voucher is correct and proper for payment.

(Date) (Authorized Certifying Officer) [1] (Title)

ACCOUNTING CLASSIFICATION

CHECK NUMBER	ON TREASURER OF THE UNITED STATES	CHECK NUMBER	ON (Name of bank)
CASH $	DATE	PAYEE [3] Office of Grants & Contracts, Montana State University, Bozeman, Montana 59717	

PER [signature]
Lawrence F. Kain
TITLE Grant & Contract Administrator

When stated in foreign currency, insert name of currency.
If the [illegible] to certify and authority to approve are combined in one person, one signature only is necessary, otherwise the approving officer will sign in the space provided, over his official title
When a voucher is receipted in the name of a company or corporation, the name of the person writing the company or corporate name, as well as the capacity in which he signs, must appear. For example "John Doe Company, per John Smith Secretary", or "Treasurer", as the case may be

[illegible]

Standard Form 1035
September 1975
4 Treasury FRM 2000
1035-110

PUBLIC VOUCHER FOR PURCHASES AND SERVICES OTHER THAN PERSONAL

CONTINUATION SHEET

VOUCHER NO. 39
SCHEDULE NO.
SHEET NO. 2

DEPARTMENT, BUREAU, OR ESTABLISHMENT: U. S. Energy Research and Development Admin.

NUMBER AND DATE OF ORDER	DATE OF DELIVERY OR SERVICE	ARTICLES OR SERVICES (Enter description, item number, contract or Federal supply schedule, and other information deemed necessary)	QUANTITY	UNIT PRICE COST	UNIT PRICE PER	AMOUNT
Montana State University Bozeman, Montana 59717 789		Contract NO. EX-76-C-01-2034 "Catalytic Hydrogenation of Coal Derived Liquids", principal investigator Dr. Lloyd Berg				
				Current Period		Cumulative to Date
Salaries & Wages				1,868	00	114,431.21
Benefits				13	37	7,113.81
Supplies & Materials				1,728	17	37,261.83
Travel						3,978.91
Equipment						12,625.85
Awards (Tuition & Fees)						5,755.30
Indirect Costs				1,081	79	68,010.26
SubTotal				4,691	33	249,177.17
Cost Sharing				763	70	41,841.83
Total				5,455	03	291,019.00

*U.S.Government Printing Office:1977-241 630/3284