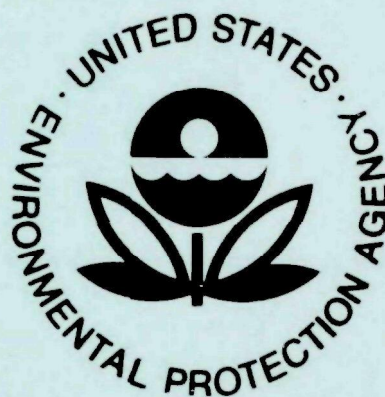


**EPA-600/2-76-165**  
**June 1976**

**Environmental Protection Technology Series**

# **DEMETALLIZATION OF HEAVY RESIDUAL OILS**

## **Phase III**



**Industrial Environmental Research Laboratory  
Office of Research and Development  
U.S. Environmental Protection Agency  
Research Triangle Park, North Carolina 27711**

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June 1976

DEMETALLIZATION  
OF HEAVY RESIDUAL OILS  
PHASE III

by

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Contract No. 68-02-0293  
ROAP No. 21ADD-050  
Program Element No. 1AB013

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## ABSTRACT

Under Phase I work of Contract No. 68-02-0293 funded by the Environmental Protection Agency, a new low cost demetallization catalyst for heavy petroleum residual oils was developed at the Trenton laboratory of Hydrocarbon Research, Inc., a subsidiary of Dynalectron Corp. Work under Phase II optimized promoter metal on the support, commercial production capabilities were demonstrated by the production of a 10,000 pound batch by Minerals and Chemicals Division of Engelhard Corporation, and activity and aging characteristics were tested on two vacuum residua. The demetallized products from these two residua were desulfurized over commercial HDS beads and costs were calculated to produce low sulfur fuel oil and compared against costs using unpromoted activated bauxite.

The present Phase III work optimized operating conditions in the demetallization step for overall desulfurization. Bachaquero Export and Lloydminster vacuum residua were demetallized to different levels of vanadium removal, the products desulfurized over commercial HDS catalyst at various operating conditions and minimum operating costs were calculated to produce low sulfur fuel oil.

Descriptions of test units, operating conditions and procedures are given, including run summaries, and tables of feedstock, product and catalyst inspections. Graphs and tables depicting operating costs for producing 0.3, 0.5 and 1.0 weight percent (W %) sulfur fuel oil are given, along with various correlations among demetallization levels, catalyst deactivation, demetallization rate constant and contaminant metals deposited on catalyst.

Conclusions based on experimental results are given.



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## GLOSSARY

MM	Millions
1 Angstrom ( $\text{\AA}$ )	$10^{-8}$ Centimeters
g/cc	Grams/cubic centimeter
$\text{M}^2/\text{g}$	Square meters/gram
Mesh Sizes	Mesh sizes are all United States Standard Sieve Series
psig	Pounds per square inch, gauge
SCF/Bbl	Standard cubic feet of gas per barrel of oil (60°F, 1 Atm.)
L.S.V.	Liquid Space Velocity, Volume of Oil/Hour/ Volume of Reactor
Vo/Hr/Vr	Volumes of Oil/Hour/Volume of Reactor
MMB	Million Barrels
Bbl/D/Lb	Barrels of Oil/Day/Pound of Catalyst
BPSD	Barrels per Stream Day
ppm	Parts per million
SFS	Saybolt Furol Seconds
SUS	Saybolt Universal Seconds
VB	Vacuum Bottoms = Vacuum Residuum



## 1. CONCLUSIONS

The newly developed demetallization catalyst, granular 20 x 50 mesh activated bauxite impregnated with 1.0 weight percent molybdenum, when used in the first stage of a two-stage demetallization desulfurization process, offers a substantial operating cost advantage over a direct desulfurization process in the production of low sulfur fuel oil from high metals petroleum vacuum residua.

For a typical case on Bachaquero Export vacuum residuum, a high metals stock from Venezuela, the saving in operating cost to produce 0.3 weight percent fuel oil was \$1.15/Bbl, to produce 0.5 weight percent sulfur fuel oil the saving was \$0.78/Bbl, and a saving of \$0.44/Bbl was realized to produce 1.0 weight percent sulfur fuel oil. Similar cost advantages were realized in the production of low sulfur fuel oils from Lloydminster vacuum residuum, a high sulfur Canadian stock.

These cost calculations were based on a 20,000 barrels per day plant, which is perhaps the minimum size plant a refiner would build. Operating costs would be lowered as the size of the plant is increased resulting in increased savings.

The optimum demetallization level to achieve minimum overall operating costs from Bachaquero Export to produce 1.0 weight percent sulfur fuel oil was about 45 percent vanadium removal. To produce 0.5 weight percent sulfur fuel oil to optimum demetallization level was about 55 percent vanadium removal. For the production of 0.3 weight percent sulfur fuel oil the operating costs decreased with increasing levels of vanadium removal. However, levels above 80 percent vanadium removal were difficult to achieve because of the rapid rate of catalyst deactivation, but removal of metals above this level are believed to be of dubious economic value, since these metal compounds are difficult to remove by the demetallization catalyst, they would also be difficult to remove by the commercial desulfurization catalyst.

For Lloydminster vacuum residuum, the optimum demetallization level to produce 1.0 weight percent sulfur fuel oil was about 65 percent vanadium removal. To produce 0.5 weight percent sulfur fuel oil the level was 75 percent and for 0.3 weight percent sulfur fuel oil the optimum level was about 85 percent vanadium removal.



## 2. INTRODUCTION

Because of more stringent federal environmental pollution standards along with the increased demands for energy in the 1970's, the need for and value of clean low sulfur fuel oil has been well established and documented. Given the finite nature of fossil fuels, full and best use of all petroleum fractions is not only desirable but imperative if we are to meet the energy demand before alternative sources are developed.

There are substantial reserves of high sulfur petroleum resids, foreign and domestic, containing contaminant metals vanadium and nickel, which rapidly poison HDS catalysts and render the overall processing of these resids economically unattractive. In order to improve removal of contaminants from these fuels while economically producing low sulfur fuel oil from petroleum resids, HRI undertook a project funded by the Environmental Protection Agency, under Contract No. 68-02-0293, to develop a low cost scavenger catalyst to remove contaminant metals from petroleum resids prior to desulfurization over commercial HDS catalysts.

In Phase I work of the present contract, a literature review was made for guidance in choosing catalyst supports and promoter metals for possible development. After evaluating catalyst supports, alumina, silica-alumina, bauxites, clays and solid carbons, activated bauxite was found to be the best support of those tested in terms of availability, low cost and relatively high demetallization activity. To further improve activity, activated bauxite was impregnated with promoter metals, V, Cr, Mo, W, Fe, Co, Ni, B, Mn, and Zn. It was found that low levels of molybdenum on activated bauxite was most effective in terms of demetallization activity, aging characteristics and surprisingly high desulfurization activity considering the low molybdenum loading.

Under Phase II work, optimization of molybdenum loading on activated bauxite was found to be 1.0 weight percent and particle size for fixed bed operations to be 20 x 50 mesh. To demonstrate commercial production capability, Minerals and Chemicals Division of Engelhard Corporation produced a 10,000 pound batch on commercial production equipment. The newly developed commercially produced catalyst was tested for activity and aging characteristics followed by desulfurization of the demetallized products over a commercial HDS catalyst. Preliminary costs to produce low sulfur fuel oil from Tia Juana and Gach Saran vacuum residua were calculated and found to offer substantial cost advantages

over unpromoted bauxite in the demetallization step of a two stage system.

The objectives under the present Phase III work were to optimize operating conditions in the demetallization and desulfurization steps in order to obtain more accurate cost figures to produce low sulfur fuel oil. The oils used for this phase were Bachaquero Export and Lloydminster vacuum residua. Bachaquero Export vacuum residuum, a high metals Venezuelan stock, was demetallized to three levels of vanadium removal (45, 65 and 83%), the blended products desulfurized over commercial HDS beads, and operating costs were calculated to produce 1.0, 0.5, and 0.3 weight percent sulfur fuel oils. Lloydminster vacuum residuum, a high sulfur medium metals stock from Canada, was demetallized to two levels of vanadium removal (63 and 85%), desulfurized over commercial HDS beads and costs calculated to produce low sulfur fuel oil.

The operating costs and plant investment for producing low sulfur fuel oil from Bachaquero Export and Lloydminster vacuum residua were compared to costs using a direct desulfurization process.

### 3. EXPERIMENTAL; DEMETALLIZATION

#### 3.1 Apparatus and Procedures

All demetallization operations were carried out in a continuous downflow, fixed bed reactor system. Figure 1 shows a schematic diagram of Unit 115 having two reactors connected in series contained in a single lead bath. Each reactor shown in Figure 2 was fabricated from  $1\frac{1}{2}$ " O.D. by 1" I.D. stainless steel tubing, and has a catalyst bed length of approximately 16". The volume of catalyst charged to each reactor was approximately 200 cc (loose). Temperatures were continuously recorded by means of a thermocouple situated at the center of each catalyst bed. Heat was supplied to the reactor by means of an electrically heated lead bath.

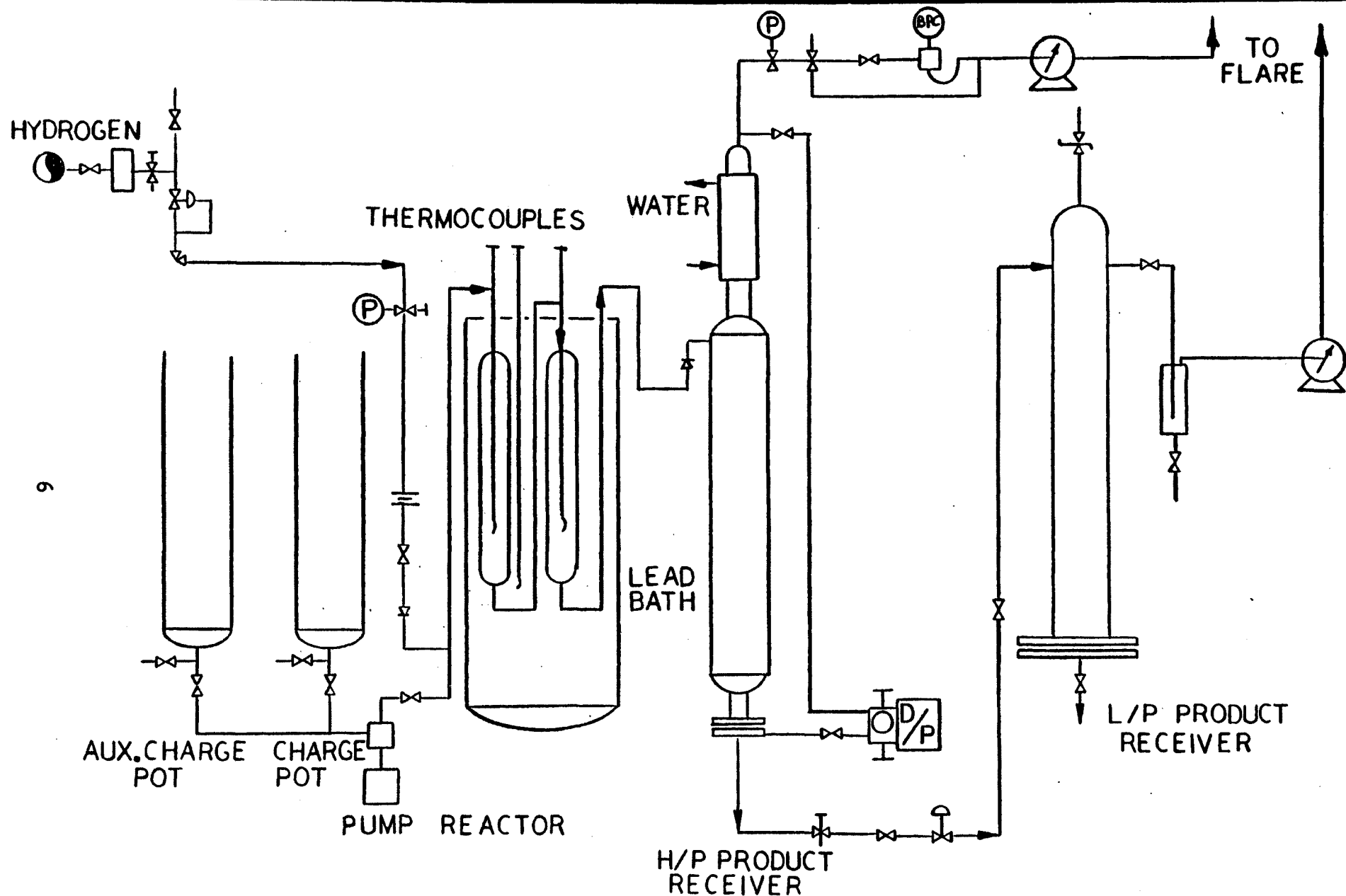
The reason two reactors were connected in series, was to increase production of demetallized product for subsequent desulfurization runs, while maintaining normal liquid space velocities for catalyst deactivation studies. A standard startup procedure was used to condition the catalyst at lower temperatures for a short period of time. The startup schedule was as follows:

Period	----- 1A -----			1B, 2, Etc.
Temperature	750	775	790	790
Pressure, psig	2000	2000	2000	2000
Hydrogen Rate, SCF/Bbl	4000	4000	4000	4000
Liquid Space Velocity, Vo/Hr/Vr	----- Constant -----			
Time on Temp., Hrs.	4	4	1	Continue at above conditions

All demetallization runs in this series were carried out at 790°F except one which was at 770°F. In that one case the final temperature was not exceeded in the startup procedure. Liquid space velocities varied from 0.25 to 2.0 Vo/Hr/Vr.

The melted charge stock was pumped to reactor pressure with a metering pump, mixed with hydrogen makeup gas, and fed to the top of the reactor. The hydrogen concentration of the makeup gas was 100% and no recycle of the exit gases was employed. The mixed vapor and liquid product from the reactors was cooled and passed to a high pressure receiver from which gas was

FIGURE 1



HYDROCARBON RESEARCH, INC.



a subsidiary of  
DYNALECTRON CORPORATION

REFER. AF-2552

FIXED BED  
DEMETALLIZATION UNIT

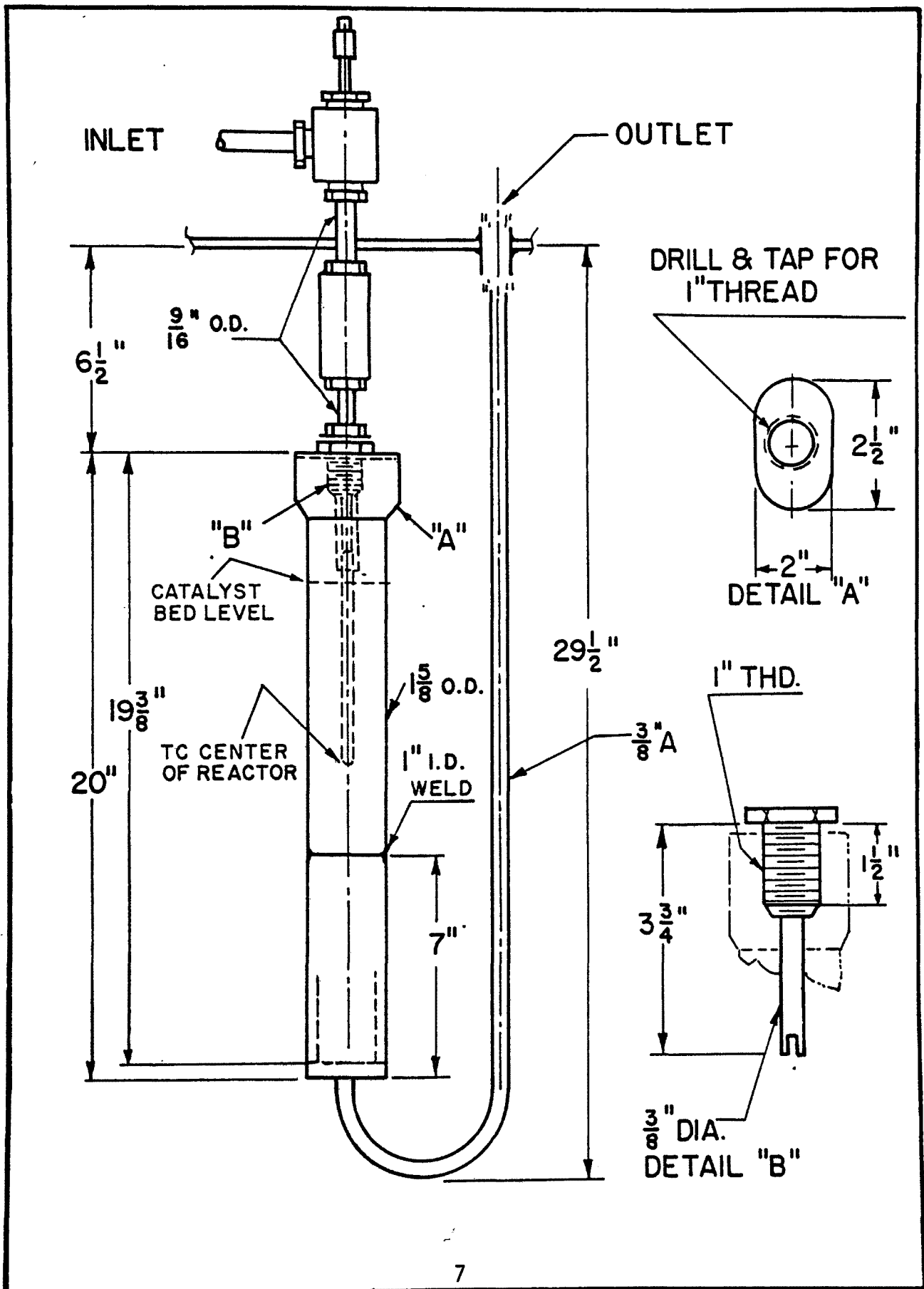
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Figure 2. FIXED BED DEMETALLIZATION REACTOR

Figure 2



sampled, metered, and vented. The net product was let down in pressure and passed to a low pressure receiver from which gas was sampled periodically, metered, and vented. The gases were analyzed twice weekly on a mass spectrometer, Du Pont Model 21-103C. The liquid product was collected and weighed periodically. Daily inspections of the liquid product included; gravity by hydrometer, atmospheric distillation to 550°F, sulfur analysis on the 550°F+ fraction by Leco induction furnace method ASTM-D-1552, and metals analysis for vanadium and nickel by atomic absorption Perkin Elmer Model 303. Besides the daily inspections, about twice weekly and after a change in operating condition, sulfurs were analyzed on the initial to 550°F fraction, and appropriate corrections made on total product sulfurs.

Detailed operating conditions and liquid product inspections for each run in this series is given in Appendix A.

Upon completion of a run, the catalyst was removed from each reactor and analyzed. First the oil was removed from the catalyst by means of a Soxhlet extractor using benzene, then analyzed for carbon, sulfur, vanadium and nickel.

Metals and sulfurs were analyzed using the same equipment as for liquid products while carbon was analyzed by high temperature combustion in oxygen using Perkin Elmer Model 240 C H N analyzer. Pore size distribution curves were obtained by mercury intrusion on Aminco's 60,000 PSI Porosimeter.

### 3.2 Catalyst Description and Inspections

The catalyst used in all demetallization runs was a representative portion from the 10,000 pound commercial production run made by Minerals and Chemical Division of Engelhard Corporation, and designated HRI 3634. This catalyst, activated bauxite impregnated with one weight per cent molybdenum, was developed by HRI under Phase I of the current contract and produced and evaluated under Phase II. Table 1 lists the physical and chemical characteristics and Figure 3 the pore size distribution of the catalyst.

### 3.3 Bachaquero Export Vacuum Residuum; Preparation and Inspections

The feed selected for this study was Bachaquero Export Vacuum Residuum. This feed originated in the Lake Maracaibo area of Venezuela. In 1974, the total production of this crude was about



Table 1. DEMETALLIZATION CATALYST INSPECTIONS

HRI Identification Number	3634
Size	20 x 50 U.S. Mesh
Molybdenum, W %	1.06
Volatile Matter, W %	2.0
Bulk Density, g/cc	1.01
Surface Area, M <sup>2</sup> /g	195.6
Pore Volume, cc/g	0.347
<u>Sieve Analysis, W %</u>	
20/30 Mesh	52.4
30/40 Mesh	30.7
40/50 Mesh	16.9

Figure 3. DEMETALLIZATION CATALYST HRI 3634

PORE SIZE DISTRIBUTION

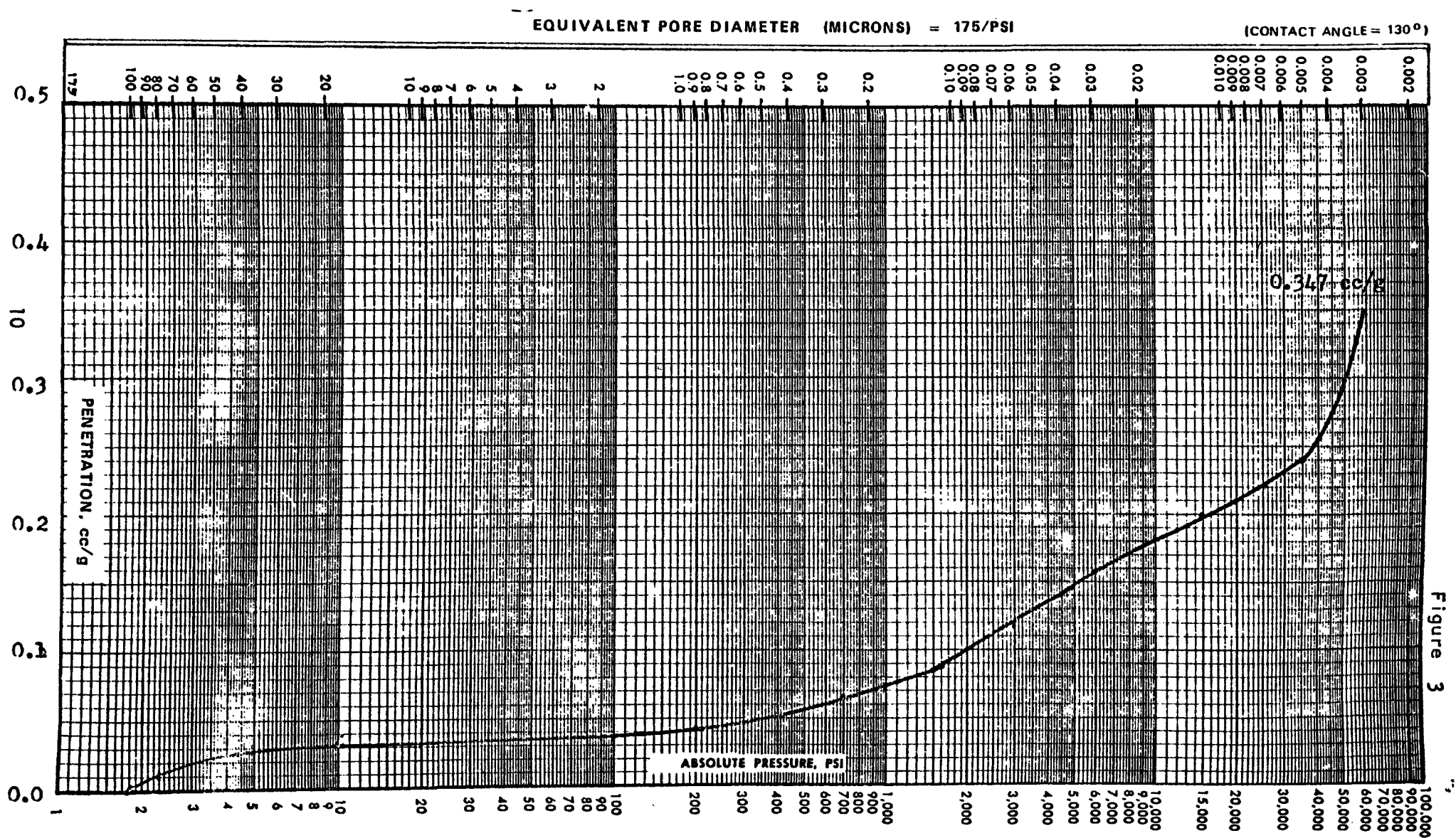


Figure 3

204 million barrels equivalent to about 98 million barrels of vacuum residuum (based on a typical 48 percent by volume of 950°F+ resid on crude), with an estimated crude reserve of about 1837 million barrels. The vacuum residuum used for the three levels of demetallization runs was prepared by vacuum distilling Bachaquero Export atmospheric residuum obtained from the Amuay Refinery of Creole Petroleum Corporation, a subsidiary of Exxon Corporation. Three drums of approximately 400 pounds each of vacuum residuum were recovered from 6.5 drums of atmospheric residuum. Inspections on this material designated as HRI L-397 are given in Table 2.

These inspections are somewhat different from published values for pure Bachaquero vacuum residua. Residua designated as "Export" in general contain small quantities of residua from different crudes from a refinery run. The refinery at Amuay obtains its crude from the Lake Maracaibo field in Venezuela through a pipeline. This field is a continuous field comprising Bachaquero, Lagunillas, and Tia Juana crudes, among others.

The Bachaquero Export atmospheric residuum shipped and used for this study contains unknown quantities of residua from these other crudes but is representative of residual oils from this major field available for world markets

### 3.3.1 Low Level Demetallization

The objective of this operation was to demetallize Bachaquero Export vacuum residuum to 45-50 percent vanadium removal level, produce sufficient feed for a subsequent 20 day desulfurization run, and obtain catalyst deactivation data.

The operation was carried out in Run 115-1233 at 790°F, hydrogen pressure of 2000 psig, liquid space velocity of 1.5 Vo/Hr/Vr and catalyst space velocity of 0.114 Bbl/D/Lb. The actual demetallization achieved was 44 percent vanadium removal and 35 percent desulfurization. Six days of operation produced sufficient feed for a 20 day desulfurization run.

Figure 4 shows the rate of vanadium removal,  $V_F/V_P$ , (vanadium in the feed/vanadium in the product) against catalyst age in Bbl/Lb. These results show that, at this level of vanadium removal, the catalyst deactivation is quite low. Desulfurization data obtained from this operation are summarized in Figure 5.

Table 2. FEEDSTOCK INSPECTIONS

Feedstock	Bachaquero Export Vacuum Residuum
HRI Identification No.	L-397
Gravity, °API	7.6
Sulfur, W %	3.08
RCR, W %	17.9
Carbon, W %	86.28
Hydrogen, W %	10.67
Nitrogen, ppm	5313
Vanadium, ppm	577
Nickel, ppm	81
Viscosity, SFS @ 210°F	1945
SUS @ 210°F	118
IBP-975°F, V %	10.0
Gravity, °API	20.3
Sulfur, W %	2.62
975°F+, V %	90.0
Gravity, °API	6.6
Sulfur, W %	3.10
RCR, W %	22.0

Figure 4. DEMETALLIZATION OF BACHAQUERO EXPORT VACUUM RESIDUUM  
OVER 1.0 W % MOLYBDENUM/20x50 MESH BAUXITE

Feed Composition		Demetallization	
		Low Level A	Medium Level B
Gravity, °API 7.5 to 7.6	Run No.	115-1233	115-1238
Sulfur, W % 2.95 - 3.08	Operating Conditions		
Vanadium, ppm 547	Hydrogen Pressure, psig	2000	2000
Nickel, ppm 74	Temperature, °F	790	790
Catalyst HRI No. 3634	Liquid Space Velocity, V/HR/V	1.5	0.5
	Catalyst Space Velocity, B/D/LB	0.114	0.037

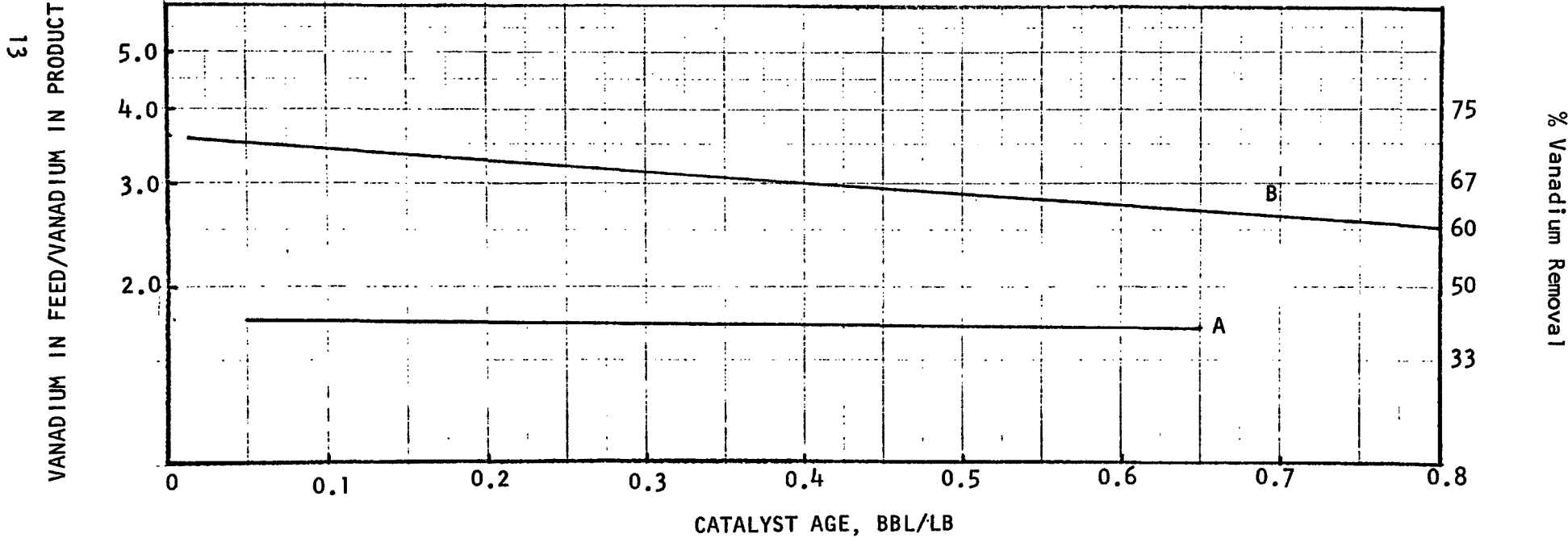


Figure 4

**Figure 5. DESULFURIZATION OBTAINED DURING DEMETALLIZATION OF BACHAQUERO EXPORT VACUUM RESIDUUM  
OVER 1.0 W % MOLYBDENUM/20x50 MESH BAUXITE**

Feed Composition		Demetallization	
		Low Level A	Medium Level B
Gravity, °API 7.5 to 7.6	Run No.	115-1233	115-1238
Sulfur, W % 2.95 - 3.08	Operating Conditions		
Vanadium, ppm 547	Hydrogen Pressure, psig	2000	2000
Nickel, ppm 74	Temperature, °F	790	790
Catalyst HRI No. 3634	Liquid Space Velocity, V/HR/V	1.5	0.5
	Catalyst, Space Velocity, B/D/LB	0.114	0.037

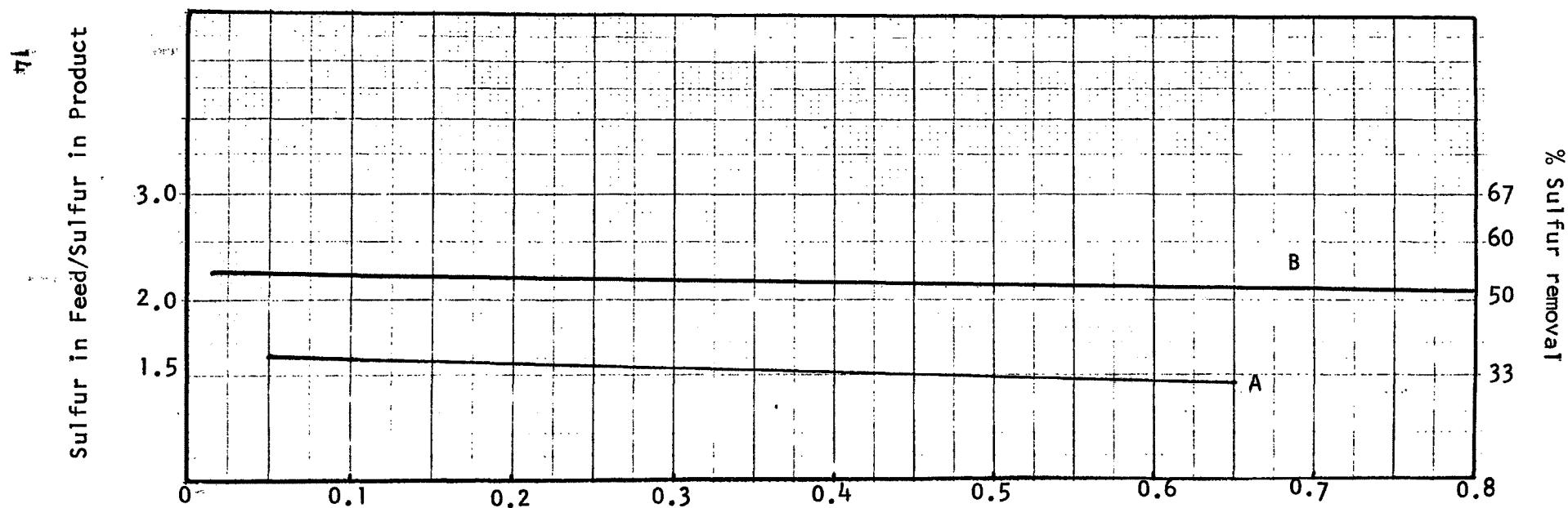


Figure 5

### 3.3.2 Medium Level Demetallization

The objective of this operation was to demetallize Bachaquero Export vacuum residuum to 65-70 percent vanadium removal level, produce sufficient feed for three desulfurization runs of 20 days each, and obtain catalyst deactivation data.

This operation was carried out in Run 115-1238 at 790°F, hydrogen pressure of 2000 psig, liquid space velocity of 0.5 Vo/Hr/Vr and catalyst space velocity of 0.037 Bbl/D/Lb. The initial vanadium removal rate was 70 percent which fell to 67 percent after 10 days, corresponding to a catalyst age of 0.36 Bbl/Lb. When the vanadium removal rate reached 60 percent after 20 days, corresponding to a catalyst age of 0.76 Bbl/Lb, the run was terminated. The average demetallization achieved during this run was 67 percent vanadium removal and 53 percent desulfurization.

The catalyst deactivation rate is shown in Figure 4 along with results from the low level demetallization operation. Desulfurization data obtained during this operation are given in Figure 5. Indications are that catalyst deactivation rates are strongly dependent on the level of vanadium removal. The catalyst deactivation slope from the low level demetallization operation (47 percent initial vanadium removal) was 0.11, but when the demetallization level was increased to 70 percent initial vanadium removal, the catalyst deactivation slope increased four-fold to 0.44. This rapid deactivation of the catalyst may limit the severity at which Bachaquero Export vacuum residuum can be demetallized over this catalyst.

This one medium level demetallization run produced insufficient feed to sustain three 20 day desulfurization runs. Consequently, a second run was started as Run 115-1239 under identical conditions. Demetallization and desulfurization from this operation are summarized in Figure 6. Initial demetallization and up to catalyst age of 0.1 Bbl/Lb was 74 percent vanadium removal. There was a sudden drop to 54 percent vanadium removal which gradually increased to 62 percent at catalyst age 0.5 Bbl/Lb. At this time, the feed rate was reduced from 0.5 to 0.35 Vo/Hr/Vr. This change resulted in improved demetallization to about 70 percent vanadium removal level. However, after catalyst age of 0.65 Bbl/Lb, the vanadium level again dropped unexpectedly to 50 percent. For this reason the run was terminated, the catalyst removed and analyzed. Visual inspection revealed no abnormalities in the reactors, catalyst, or product lines. Analysis of the used catalysts, (tabulated in Table 4 at the end of the demetallization section) showed the carbon level to be higher in the second reactor from this run than the corresponding reactor from the first run. This indicated that some coking may have

**Figure 6 DEMETALLIZATION AND DESULFURIZATION OBTAINED DURING DEMETALLIZATION OF**

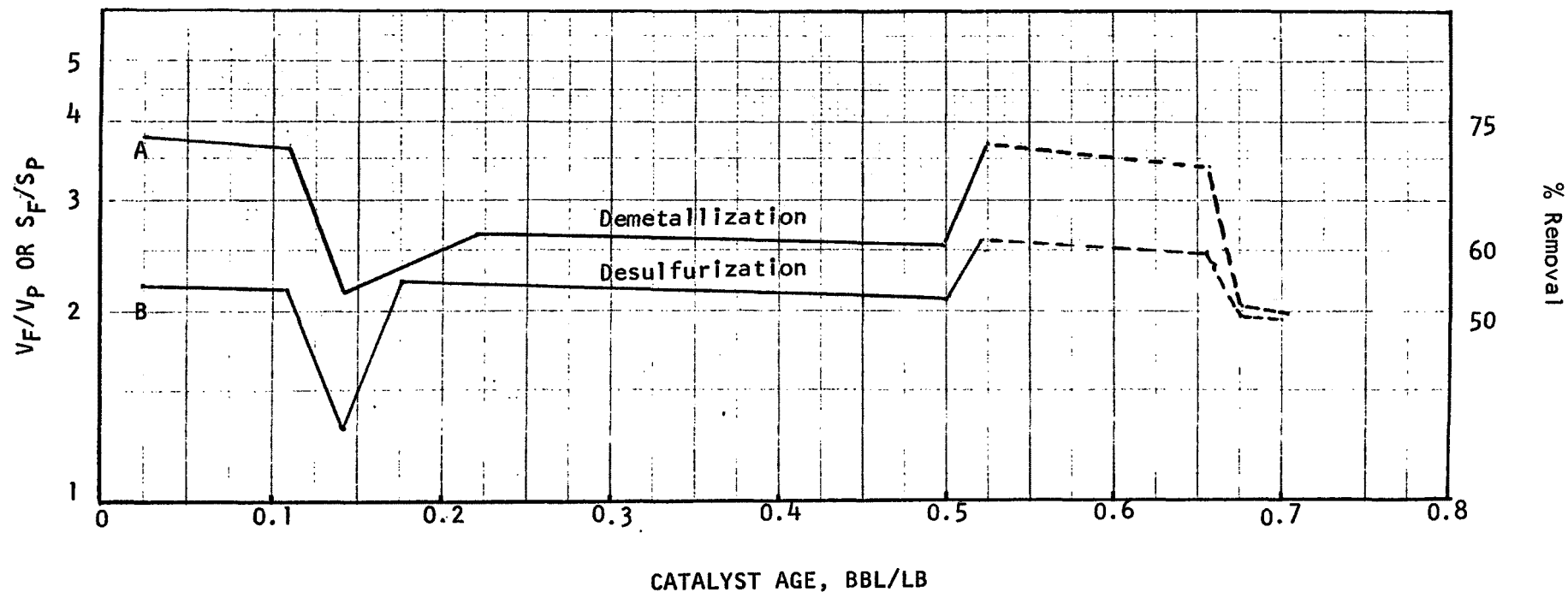
**BACHAQUERO EXPORT VACUUM RESIDUUM OVER 1.0 W % MOLYBDENUM/20x50 MESH BAUXITE**

**Feed Composition: 7.3 °API, 3.0 % S, 577 ppm V, 81 ppm Ni**

<u>Symbol</u>	<u>Run No.</u>	<u>Hydrogen Pressure psig</u>	<u>Temp °F</u>	<u>Liquid Space Velocity V/Hr/V</u>	<u>Catalyst Space Velocity B/D/LB</u>
—	115-1239	2000	790	0.5	0.038
----	115-1239	2000	790	0.35	0.027

A  $V_F/V_P$ , Vanadium in Feed/Vanadium in Product

B  $S_F/S_P$ , Sulfur in Feed/Sulfur in Product



**Figure 6**



occurred during the course of the second run. Since no difficulty was encountered in the first run under identical conditions, it was inferred that either the liquid feed and/or the hydrogen flow was interrupted during the course of the run. This condition may have existed for too short a period of time to be noted and logged on the daily log sheet.

### 3.3.3 High Level Demetallization

The objective of the high level demetallization operation was to demetallize Bachaquero Export vacuum residuum to 80-85 percent vanadium removal level, produce sufficient feed for a 20 day desulfurization run, and obtain catalyst deactivation data.

In all, five runs were required to produce sufficient feed for a 20 day desulfurization run. The first four runs were made at 790°F, hydrogen pressure of 2000 psig, liquid space velocity of 0.3 Vo/Hr/Vr and catalyst space velocity 0.023 Bbl/D/Lb.

The first run (115-1240) operated for nine days, at which time pressure buildup in the unit forced a premature shutdown. Average demetallization achieved was 84 percent vanadium removal and 69 percent desulfurization. Although catalyst dumped from the reactor was free-flowing, carbon level on catalyst from the second reactor was unusually high (17.62 W %), indicating coking had occurred during the course of the run.

The second run (115-1241) operated for five days before pressure buildup forced termination of the run. Average demetallization was 85 percent vanadium removal and 67 percent desulfurization. Carbon level on catalyst from second reactor was 15.62 weight percent.

The third run (115-1242) operated for five days before pressure buildup was encountered. An attempt was made to save the run by flushing the reactors with light oil, which restored normal pressure drop. However, on restarting the unit, vanadium removal was sharply reduced and the run had to be terminated. The average demetallization achieved during the first five days of operation was 85 percent vanadium removal and 69 percent desulfurization. Carbon levels on the catalyst were again unusually high indicating coking. It was believed at this time that coking was due to interruption of either feed or hydrogen flow at some time during the run because of difficulty in controlling the very low flow rates used, rather than the severity of the operating conditions.

After again changing the hydrogen metering orifice and clearing

product line and check valve, a fourth run (115-1243) was started. Pressure buildup was encountered after four days, forcing a shut-down. Demetallization was 84 percent vanadium removal and 67 percent desulfurization. Carbon levels were very high on catalysts from both reactors; 21.43 weight percent on catalyst from bottom of first reactor and 19.69 weight percent from the second reactor.

The fifth run (115-1244) was carried out at a lower temperature (770°F) and lower liquid space velocity (0.25 Vo/Hr/Vr). The initial vanadium removal was 79 percent dropping to 75 percent after six days on stream. At this time, the temperature was raised to 780°F which restored the vanadium removal level to 79 percent. After eight days on stream, this run was voluntarily terminated because sufficient demetallized product had been accumulated to make a 20 day desulfurization run. Since no evidence of coking was experienced during the course of the fifth run, the conclusion was that in this equipment and at the very low liquid space velocities used, 790°F reactor temperature is above the threshold of coking on this feedstock.

Figure 7 shows the catalyst deactivation plots of the five high level demetallization runs. The first four runs (115-1240, 1241, 1242, and 1243) are reproducible and show a rapid rate of deactivation. The fifth run (115-1244) operated at a lower temperature (770 and 780°F) and slightly lower liquid space velocity, showed a lower rate of deactivation.

Sulfur removal and nickel removal as function of vanadium removal are summarized in Figure 8.

It can be concluded from the results of the high level demetallization operation that:

1. High levels of demetallization, up to about 80 percent vanadium removal, can be achieved on Bachaquero Export vacuum residuum over the newly developed catalyst. However, deactivation slope of the catalyst was high.
2. In this equipment temperatures above about 780°F combined with very low liquid space velocities, below about 0.25 Vo/Hr/Vr may pose operability problems because of coking. At high reaction rates, hot spots in the reactor which were not recorded, may have been the cause of the coking in our test unit. However, run away temperatures in commercial equipment can be prevented where

Figure 7.. DEMETALLIZATION OF BACHAQUERO EXPORT VACUUM RESIDUUM

OVER 1.0 W % MOLYBDENUM/20x50 MESH BAUXITE

Feed Composition: 7.3 °API, 3.0 % S, 577 ppm V, 81 ppm Ni

Legend	Run No.	Hydrogen Pressure psig	Temp. °F	V/HR/V	B/D/LB
▲	115-1240	2000	790	0.30	0.023
●	115-1241	2000	790	0.30	0.023
◐	115-1242	2000	790	0.30	0.023
■	115-1243	2000	790	0.30	0.023
▲	115-1244	2000	780	0.25	0.019
△	115-1244	2000	770	0.25	0.019

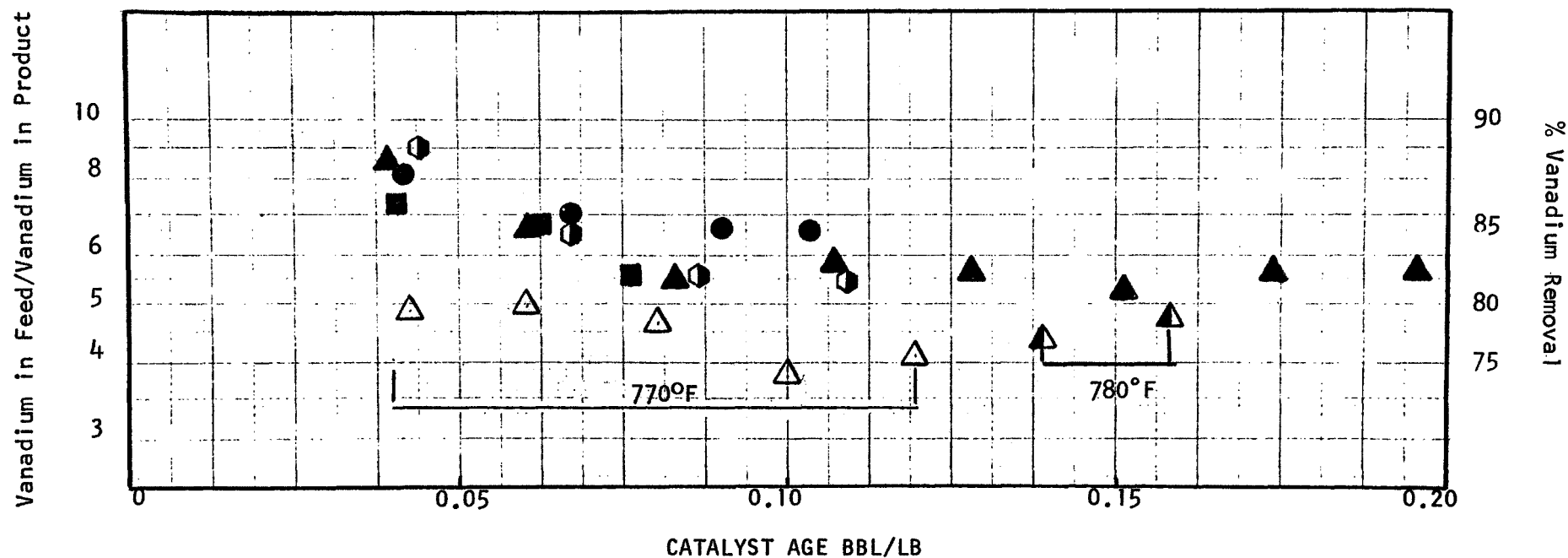
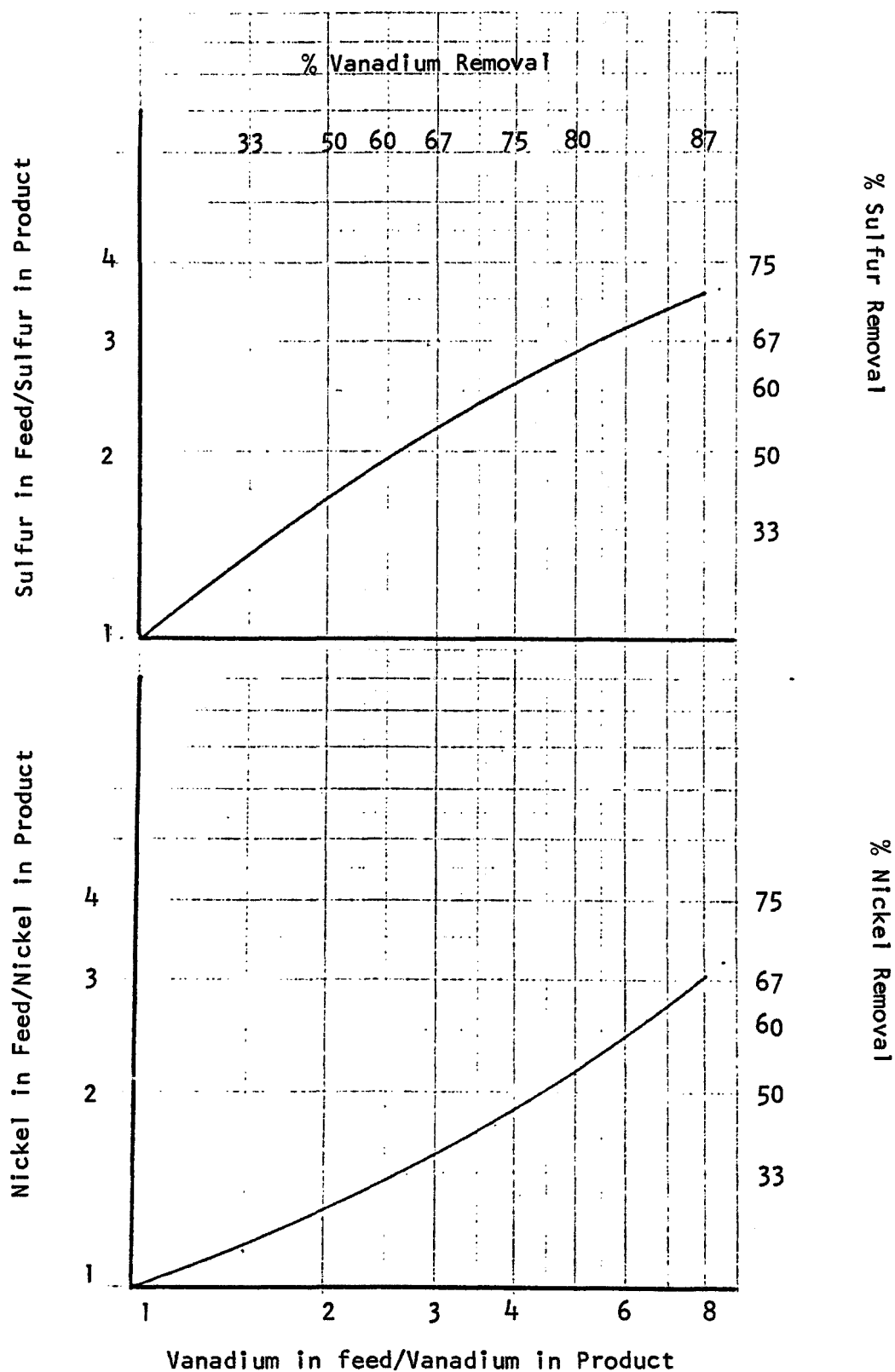


Figure 7

Figure 8. SULFUR AND NICKEL REMOVALS AS FUNCTION OF VANADIUM REMOVAL  
DURING DEMETALLIZATION OF BACHAQUERO EXPORT VACUUM RESIDUUM  
ON 1 % MOLYBDENUM/20x50 MESH BAUXITE



quenching is normally practiced.

3. Catalyst deactivation rates increase sharply with demetallization operations above 70 percent vanadium removal.

#### 3.4 Lloydminster Vacuum Residuum; Preparation and Inspections

Lloydminster crude originates in Western Canada in the provinces of Alberta and Saskatchewan. In 1975, the daily production rate of this crude was 33,000 barrels per day which corresponds to a yearly production of about 12 million barrels. The equivalent production of the vacuum residuum was about 6.6 million barrels.

The Lloydminster vacuum residuum used in this program was obtained from Husky Oil Ltd., Lloydminster, Alberta. This feed is high in sulfur content (5.4 % S) and contains moderate amounts of vanadium and nickel. Detailed inspections on this feed are give in Table 3.

##### 3.4.1 Demetallization to 45-60 Percent Vanadium Removal

The objective of this operation was to demetallize Lloydminster vacuum residuum to 45-60 percent vanadium removal, produce sufficient demetallized feed for a subsequent desulfurization run to last about 30 days and obtain catalyst deactivation data.

This operation was carried out in Run 115-1248 at 790°F, hydrogen pressure of 2000 psig, liquid space velocity of 2.0 Vo/Hr/Vr and catalyst space velocity of 0.15 Bbl/D/Lb. The run was started at a liquid space velocity of 1.5 Vo/Hr/Vr which resulted in 73 percent vanadium removal, higher than the intended demetallization level. The liquid space velocity was increased to 2.0 Vo/Hr/Vr after two days, lowering the demetallization level to 64 percent vanadium removal. The run was continued for nine days at the higher feed rate, at which time the run was voluntarily terminated because sufficient feed had been accumulated for the desulfurization run.

Figure 9 shows the catalyst deactivation with age and Figure 10 shows the desulfurization achieved during this operation. The average demetallization was 61 percent vanadium removal and average desulfurization was 50 percent.

Table 3. FEEDSTOCK INSPECTION

Feedstock	Lloydminster Vacuum Residue
HRI Identification No.	3744
Gravity, °API	6.4
Sulfur, W %	5.40
RCR, W %	15.8
Nitrogen, ppm	5900
Carbon, W %	83.18
Hydrogen, W %	10.37
Vanadium, ppm	164
Nickel, ppm	95
Viscosity, SFS @ 210°F	1489
IBP-975°F, V %	20.9
Gravity, °API	17.0
Sulfur, W %	3.49
975°F+, V %	79.1
Gravity, °API	3.1
Sulfur, W %	5.88
RCR, W %	20.8

# Figure 9 DEMETALLIZATION OF LLOYDMINSTER VACUUM RESIDUUM

OVER 1 W % MOLYBDENUM/20x50 MESH BAUXITE

HRI No. 3634

Feed Composition: 6.4 °API, 5.4 % Sulfur, 169 ppm V, 95 ppm NI  
HRI 3744

<u>Symbol</u>	<u>Run No.</u>	<u>Hydrogen Pressure psig</u>	<u>Temperature °F</u>	<u>V/Hr/V</u>	<u>B/D/Lb.</u>	<u>Data Corrected To</u>	
						<u>V/Hr/V</u>	<u>B/D/Lb</u>
A	115-1248	2000	790	1.5-2.0	0.112-0.15	2.0	0.15
B	115-1249	2000	790	0.62-0.77	0.048-0.059	0.65	0.05

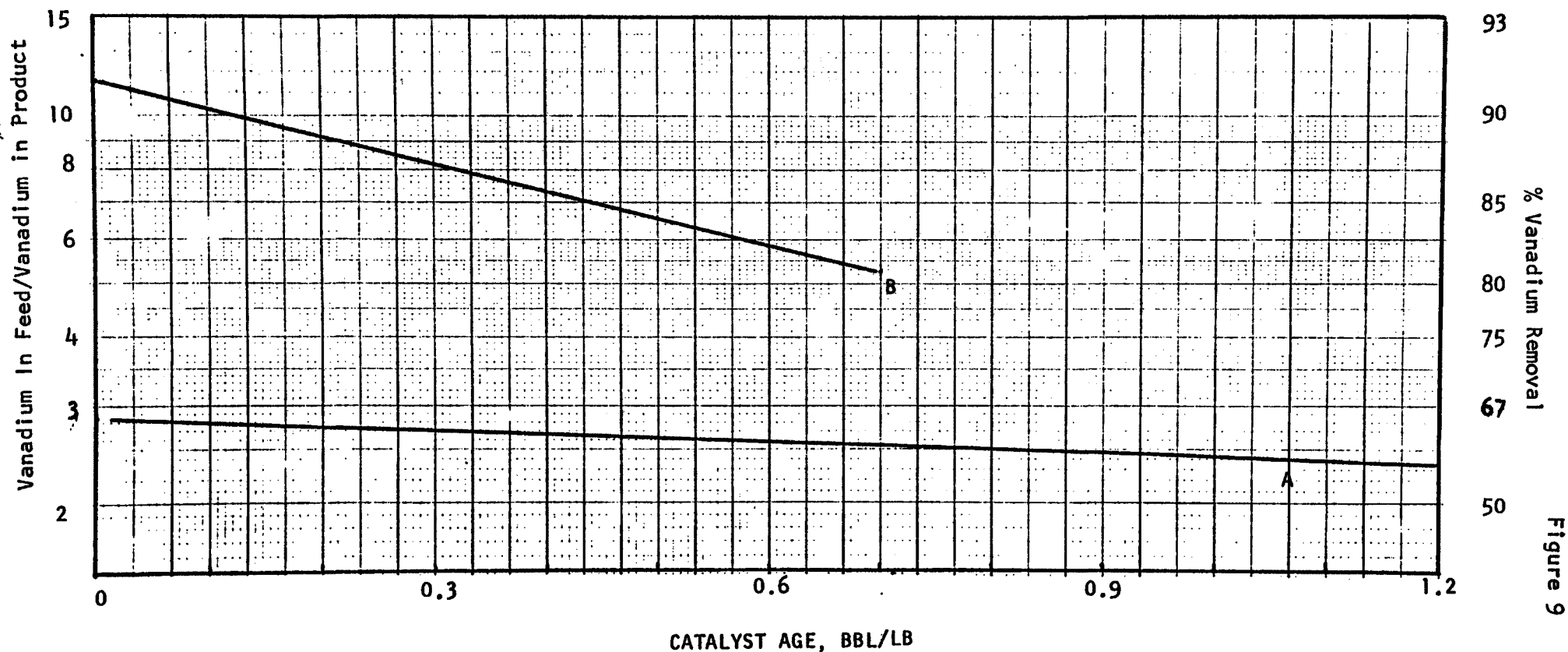


Figure 9

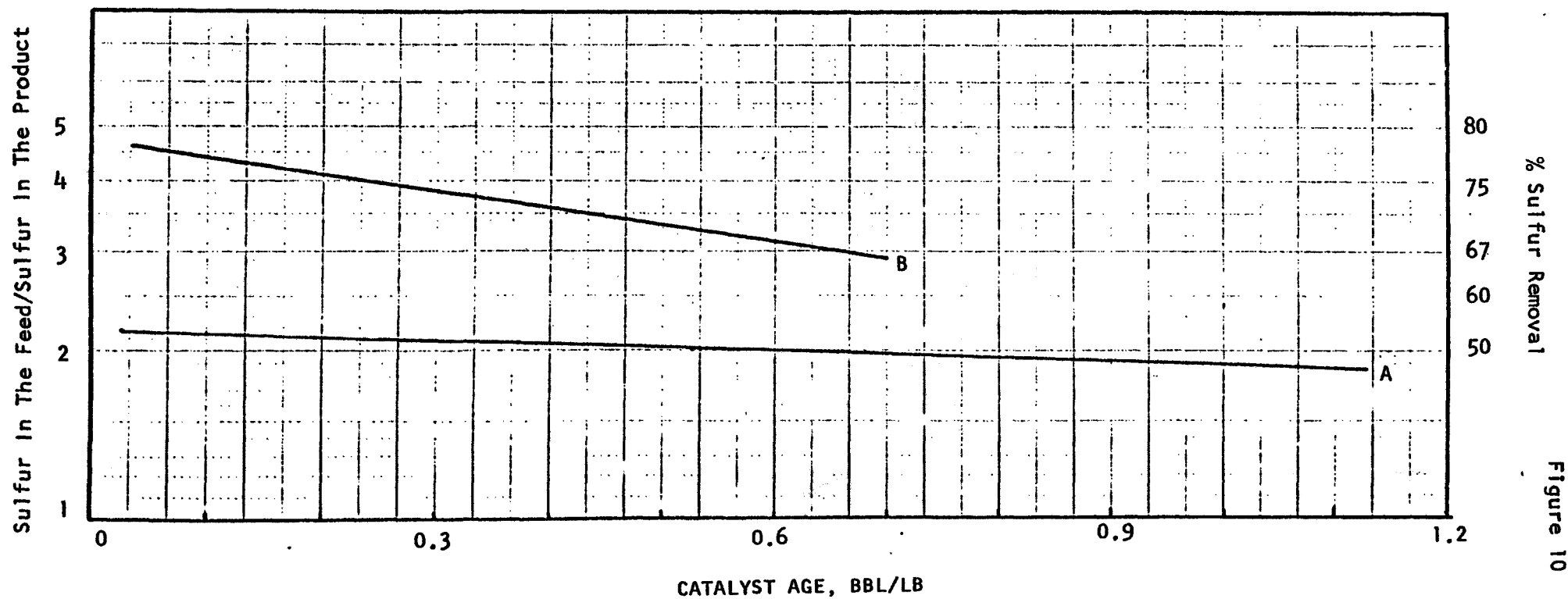
**Figure 10 DESULFURIZATION OBTAINED DURING DEMETALLIZATION OF LLOYDMINSTER VACUUM RESIDUUM**

**OVER 1 W % MOLYBDENUM/20x50 MESH BAUXITE**

**HRI 3634**

**Feed Composition: 6.4 °API, 5.4 % S, 169 ppm V, 95 ppm NI  
HRI 3744**

<u>Symbol</u>	<u>Run No.</u>	<u>Hydrogen Pressure psig</u>	<u>Temperature °F</u>	<u>V/Hr/V</u>	<u>B/D/Lb</u>	<u>Data Corrected to V/Hr/V</u>	<u>B/D/Lb</u>
A	115-1248	2000	790	1.5-2.0	0.15-0.112	2.0	0.15
B	115-1249	2000	790	0.62-0.77	0.048-0.059	0.65	0.05





### 3.4.2 Demetallization to 80-85 Percent Vanadium Removal

Lloydminster vacuum residuum was demetallized to 80-85 percent vanadium removal, sufficient demetallized feed was produced for a 25 day desulfurization run and catalyst deactivation data was obtained.

This operation was carried out in Run 115-1249 at 790°F, hydrogen pressure of 2000 psig, liquid space velocity ranged between 0.62 and 0.80 Vo/Hr/Vr and catalyst space velocity ranged between 0.048 and 0.059 Bbl/D/Lb.

Figure 9 shows the rate of catalyst deactivation with age and Figure 10 shows the desulfurization achieved during this demetallization run.

Initial demetallization was 87 percent vanadium removal which gradually fell to 79 percent after seven days on stream. At this time feed rate was lowered to 0.62 Vo/Hr/Vr restoring the demetallization level to 88 percent. After 13 days on stream the demetallization rate was still at about 82 percent but sufficient feed had been collected for a desulfurization run, so the unit was shut down.

Sulfur removal and nickel removal as function of vanadium removal are summarized in Figure 11.

### 3.5 Kinetics of Demetallization

Demetallization data obtained on Bachaquero Export vacuum residuum in the liquid space velocity range of 0.3 to 1.5 Vo/Hr/Vr corresponding to catalyst space velocities of 0.023 to 0.114 Bbl/D/Lb were used to develop a kinetic model for vanadium removal over a commercial demetallization catalyst containing 1 percent Molybdenum on 20 x 50 mesh activated bauxite. These data are summarized graphically in Figure 12, showing that the rates of vanadium removal over the given catalyst space velocities follow a pseudo first order kinetics. The kinetic model developed above also fits the data obtained on Lloydminster vacuum residuum over the same demetallization catalyst. These data are included in Figure 12 over the liquid space velocity range 0.65 to 2.0 Vo/Hr/Vr, corresponding to catalyst space velocity range 0.05 to 0.15 Bbl/D/Lb.

The kinetic equation used to correct for variations in space velocities to obtain rate constants for use later in this program

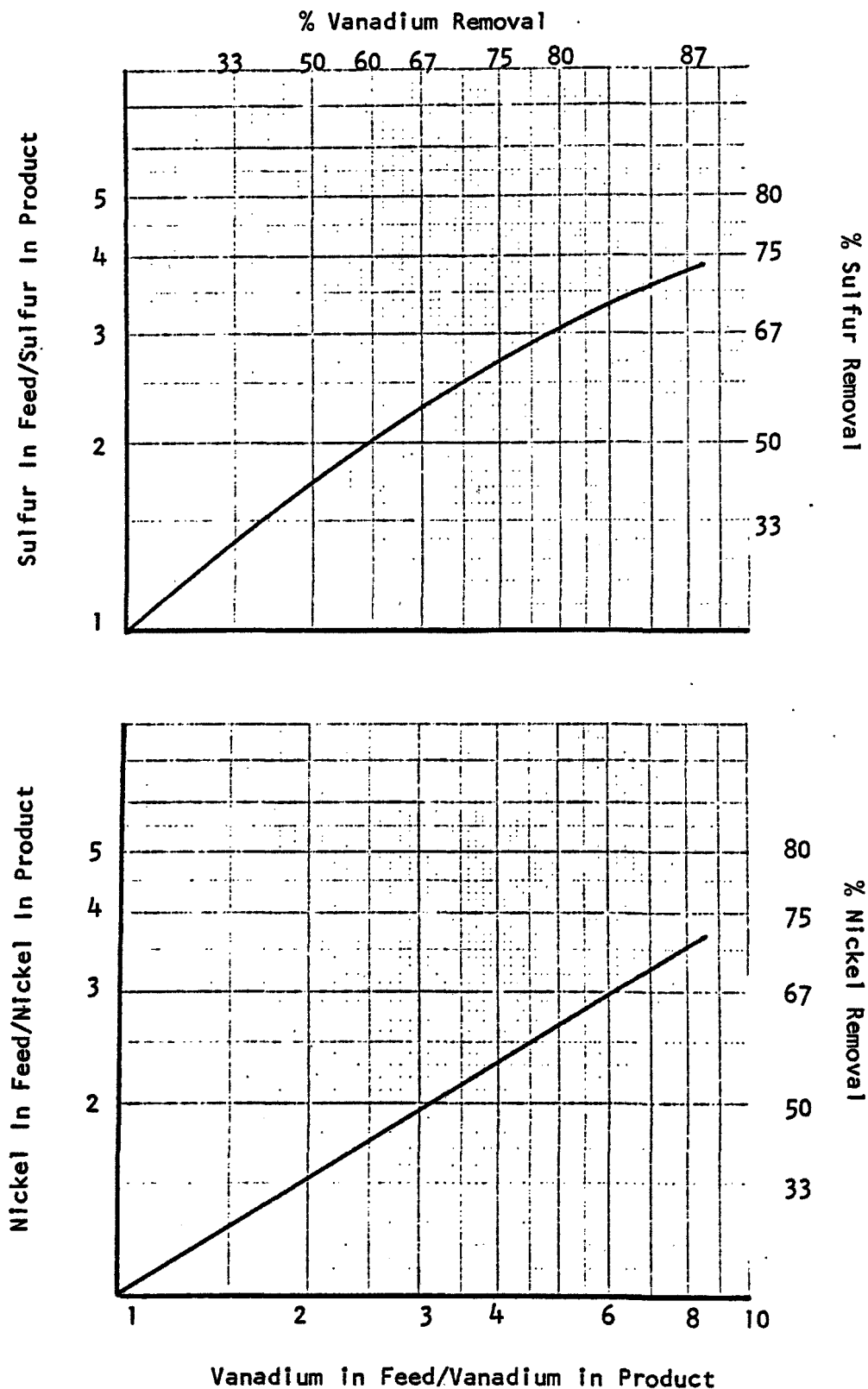
Figure 11. SULFUR AND NICKEL REMOVALS AS FUNCTION OF VANADIUM REMOVALDURING DEMETALLIZATION OF LLOYDMINSTER VACUUM RESIDUUMON 1 % MOLYBDENUM/20x50 MESH BAUXITE

Figure 12. KINETICS OF DEMETALLIZATION

PSEUDO FIRST ORDER

$$\ln \frac{V_F}{V_P} = K_m (C.S.V.)^{-n}$$

Where  $V_F/V_P$  = Vanadium in Feed/Vanadium in Product

$K_m$  = Pseudo rate constant

C.S.V. = Catalyst space velocity B/D/Lb

$$n = 0.8$$

C.S.V. Range 0.023 to 0.15 B/D/Lb

LHSV Range 0.3 to 2 V/Hr/V

27

Initial  $V_F/V_P$

Lloyminster Vacuum Resid

Bachaquero Export Vacuum Resid

$(C.S.V.)^{-0.8}$

Figure 12

is given in equation (1):

$$K_m = (C.S.V.)^n \ln \frac{V_F}{V_P} \text{ ----- (1)}$$

where  $K_m$  = Pseudo First order rate constant

C.S.V. = Catalyst space velocity, Bbl Oil/Day/Lb Catalyst

$V_F$  = Vanadium in feed, in ppm

$V_P$  = Vanadium in product, in ppm

$n = 0.8$

As seen from the slopes of initial rate constants for the two residua in Figure 12, the rate of vanadium removal for Lloydminster vacuum residuum is about twice that for Bachaquero Export. Actual slope for Lloydminster was 0.22, and for Bachaquero Export it was 0.10.

### 3.6 Spent Demetallization Catalyst Inspections

The results of analyses on spent demetallization catalysts are summarized in Table 4. Carbon levels ranged from about eight weight percent to over 20 weight percent. In all runs where operability problems were encountered with pressure buildup, the carbon level on catalyst was over 15 weight percent while no other operable runs exhibited this high level carbon content. No correlation could be found between carbon level and catalyst age. It appears carbon is deposited rapidly on the catalyst at the beginning of a run, the level being dependent on temperature and liquid space velocity, then remaining fairly constant for the duration of the run. The pore size distribution of the spent demetallization catalyst are summarized in Table 5. The pore volumes of the spent catalysts were corrected to fresh basis using the following relationship:

$$\text{cc/g Fresh Catalyst} = \frac{1}{1.000 - \sum F_i + \frac{1}{2} F_s} \times \text{cc/g Spent Catalyst}$$

where  $F_i$  = weight fraction impurities on spent catalyst

$F_s$  = weight fraction sulfur on spent catalyst

The loss in total pore volume of all demetallization catalysts fell

Table 4. ANALYSES OF SPENT DEMETALLIZATION CATALYSTS

<u>RUN NUMBER</u>	<u>FEED</u>	<u>REACTOR</u>	<u>LHSV Vo/Hr/Vr</u>	<u>CATALYST AGE BBL/LB</u>	<u>CARBON W %</u>	<u>SULFUR W %</u>	<u>VANADIUM W %</u>	<u>NICKEL W %</u>
115-1233	Bachaquero	No. 1	1.50	0.64	8.92	2.56	7.08	0.44
115-1233	Bachaquero	No. 2	1.50	0.64	10.46	2.16	3.44	0.30
115-1238	Bachaquero	No. 1	0.50	0.76	9.32	5.36	12.96	0.81
115-1238	Bachaquero	No. 2	0.50	0.76	12.83	3.51	3.90	0.39
115-1239	Bachaquero	No. 1	0.35-0.50	0.73	9.88	5.58	12.97	0.85
115-1239	Bachaquero	No. 2	0.35-0.50	0.73	15.22	2.86	2.81	0.36
115-1240	Bachaquero	No. 1	0.30	0.20	14.06	2.63	3.43	0.35
115-1240	Bachaquero	No. 2	0.30	0.20	17.62	2.37	1.05	0.16
115-1241	Bachaquero	No. 1	0.30	0.10	13.30	2.38	2.48	0.22
115-1241	Bachaquero	No. 2	0.30	0.10	15.62	2.24	0.69	0.14
115-1242	Bachaquero	No. 1 Top	0.30	0.22	8.45	2.21	8.27	0.41
115-1242	Bachaquero	No. 1 Bottom	0.30	0.22	17.84	2.20	1.20	0.18
115-1242	Bachaquero	No. 2	0.30	0.22	15.37	2.04	1.01	0.17
115-1243	Bachaquero	No. 1 Top	0.30	0.08	14.87	3.09	3.56	0.25
115-1243	Bachaquero	No. 1 Bottom	0.30	0.08	21.43	3.18	0.91	0.12
115-1243	Bachaquero	No. 2	0.30	0.08	19.69	2.56	0.47	0.09
115-1244	Bachaquero	No. 1	0.25	0.15	10.49	2.91	3.60	0.30
115-1244	Bachaquero	No. 2	0.25	0.15	13.77	2.53	0.95	0.15
115-1248	Lloydminster	No. 1	1.50-2.00	1.21	8.03	5.50	5.09	1.72
115-1248	Lloydminster	No. 2	1.50-2.00	1.21	8.01	3.78	2.51	1.10
115-1249	Lloydminster	No. 1	0.62-0.80	0.69	9.50	4.87	4.58	1.92
115-1249	Lloydminster	No. 2	0.62-0.80	0.69	11.40	2.78	1.18	0.64

TABLE 5 PORE SIZE DISTRIBUTION OF SPENT DEMETALLIZATION CATALYSTS

SPENT CATALYST From Run No.	CATALYST AGE Bbl/Lb	WT %		PORE DIAMETER RANGE ANGSTROMS				TOTAL PORE VOLUME cc/gm	LOSS IN TOTAL PORE VOLUME %
		C	V+Ni	30-100	100-500	500-1000	1000+		
				PORE VOLUME cc/gm					
Fresh 3634				0.142	0.078	0.034	0.057	0.311	
115-1233 R-1	0.64	8.92	7.52	0.039	0.047	0.017	0.034	0.137	55.9
115-1233 R-2	0.64	10.46	3.74	0.034	0.048	0.021	0.044	0.147	52.7
115-1238 R-1	0.76	9.32	13.77	0.021	0.046	0.014	0.035	0.116	62.7
115-1238 R-2	0.76	12.83	4.29	0.027	0.038	0.016	0.043	0.124	60.1
115-1239 R-1	0.73	9.88	13.82	0.031	0.039	0.012	0.042	0.124	60.1
115-1239 R-2	0.73	15.22	3.17	0.021	0.044	0.024	0.041	0.130	58.2
115-1241 R-1	0.10	13.30	2.70	0.030	0.033	0.019	0.042	0.124	60.1
115-1241 R-2	0.10	15.62	0.83	0.021	0.038	0.022	0.043	0.124	60.1
115-1242 R-1 Top	0.22	8.45	8.68	0.029	0.041	0.032	0.037	0.139	55.3
115-1242 R-1 Btm	0.22	17.84	1.38	0.033	0.054	0.014	0.043	0.144	53.7
115-1242 R-2	0.22	15.37	1.18	0.032	0.050	0.019	0.038	0.139	55.3
115-1244 R-1	0.15	10.49	3.90	0.025	0.042	0.021	0.046	0.134	56.9
115-1244 R-2	0.15	13.77	1.10	0.017	0.036	0.020	0.038	0.111	64.3
115-1248 R-1	1.21	8.03	6.81	0.026	0.058	0.024	0.039	0.147	52.7
115-1248 R-2	1.21	8.01	3.61	0.016	0.054	0.026	0.045	0.141	54.7
115-1249 R-1	0.69	9.50	6.50	0.026	0.046	0.015	0.054	0.141	54.7
115-1249 R-2	0.69	11.40	1.82	0.013	0.045	0.024	0.048	0.130	58.2

Note: Pore size distribution and total pore volumes on spent catalysts were corrected to fresh catalyst basis.

into a rather narrow range (53 to 63% loss) considering the large variation in catalyst age (0.1 to 1.21 Bbl/Lb), carbon level (8.0 to 17.8 W %) and metals deposited (0.83 to 13.8 % V & Ni). The greatest loss in pore volume occurred in micropores 30-100 Angstroms in diameter, however no significant correlation could be found between the loss in micropores and the variables catalyst age, carbon or metals level on catalysts.

### 3.7 Catalyst Deactivation Correlations

The correlation between demetallization level (vanadium removal level) and catalyst deactivation is shown in Figure 13. The data for curve A was obtained from runs made on Bachaquero Export vacuum residuum to produce demetallized feeds containing three levels of vanadium. Data from runs made on Tia Juana (point B) and Gach Saran (point D) vacuum residua, from Phase II work, as well as data from the operation on Lloydminster vacuum residuum (curve C) are included in this Figure.

Curve A indicated that for Bachaquero Export and Tia Juana vacuum residua, vanadium removal above 70 percent will result in rapid catalyst deactivation. The same phenomenon is observed in the case of the Lloydminster feed, but the level of vanadium removal where a sharp increase in deactivation started was about 80 percent. From a single data point on Gach Saran, the corresponding vanadium removal where a sharp increase in deactivation slope occurred is around 88 percent.

The above results also show that the deactivation slope of the catalyst does not depend on the amount of metals in the feed. Demetallization of the lower metals Lloydminster feed resulted in higher deactivation slope than from the corresponding operation on the higher metals Gach Saran feed.

Figure 14 shows the effect of catalyst vanadium loading on the rate constant for Bachaquero and Lloydminster vacuum residua. These results show that the demetallization rate constant depends on the vanadium loading on the catalyst as well as on the level of vanadium removal. For the same level of metals loading on the catalyst, the rate constant for the same feed is higher for the lower level vanadium removal operation. This observation is true for both Lloydminster (lines A and B) and Bachaquero (lines C and D) vacuum residua. However, the effect is lower with Bachaquero feed. For the Bachaquero feed, the variation of the rate constant at medium level (72% initial vanadium removal) and at high level (88% initial vanadium removal) versus vanadium loading on the catalyst (line D) was about the same.

Figure 13

# EFFECT OF LEVEL OF VANADIUM REMOVAL ON THE RATE OF CATALYST DEACTIVATION

Hydrogen pressure, Psig 2000  
Temperature °F 790

Legend:

- A Bachaquero Export vacuum residuum 7.5-7.6 °API, 2.95-3.08 % S  
547-577 ppm V, 74-81 ppm Ni
  - B Flu-Burner vacuum residuum 7.6 °API, 2.9 % S  
575 ppm V, 75 ppm Ni
  - C Lloydminster vacuum residuum 6.4 °API, 5.4 % S  
169 ppm V, 94 ppm Ni
  - D Gosh-Saran vacuum residuum 6.9 °API, 5.72 % S  
291 ppm V, 110 ppm Ni
- \* Slope of a plot of  $\ln (V/V_0)$  versus catalyst age.

CATALYST DEACTIVATION SLOPE\*

INITIAL LEVEL OF VANADIUM REMOVAL, %



Figure 14  
VARIATION OF DEMETALLIZATION RATE CONSTANT WITH VANADIUM  
LOADING ON THE CATALYST

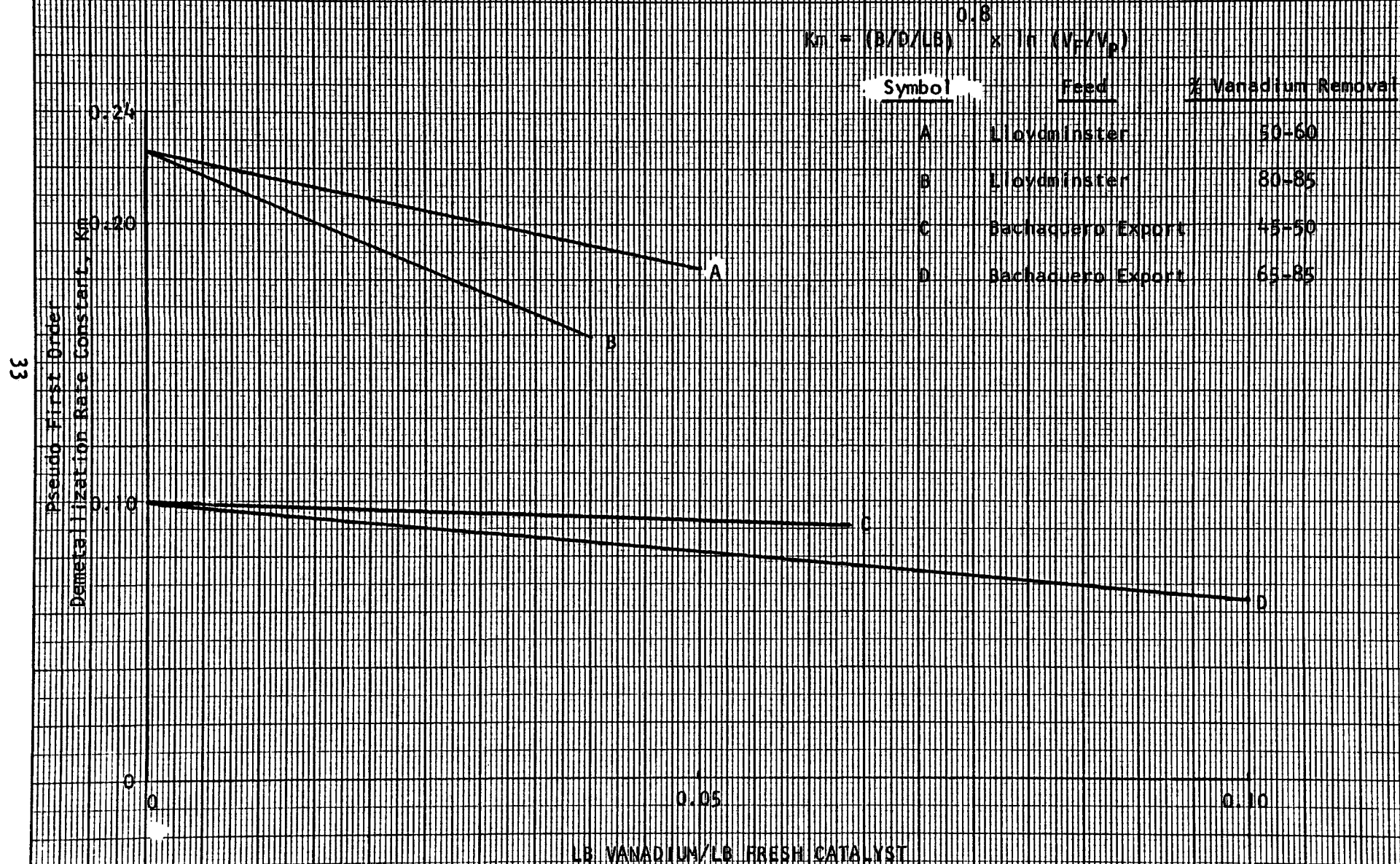


Figure 14

A drop in the value of the demetallization rate constant with increasing metals loading on the catalyst is expected. As the amount of metals deposition on the catalyst is increased the number of active sites is reduced with resulting drop in value of the rate constant.

The change in the value of the demetallization rate constant with level of vanadium removal is believed to be diffusion controlled. At low level vanadium removal operations, metals are removed from smaller molecules which readily diffuse through the pores of the catalyst to the active sites resulting in a high rate constant. At high level vanadium removal operations, metals from larger molecules must be removed which diffuse more slowly to the active sites resulting in lower rate constants.

Based on the above postulation, it appears that the metals containing molecules in Gach Saran feed are smaller than those in Lloydminster feed. Consequently the catalyst deactivation rate is lower for Gach Saran than for Lloydminster feeds at a given vanadium removal level even though Gach Saran has more metals.

The above results indicate that we cannot generalize the effect of metals content of the feed on the deactivation slope of the catalyst, and extrapolation to other feeds should be carried out with caution.

#### 4. EXPERIMENTAL; DESULFURIZATION

The objectives of the desulfurization operations were as follows:

1. Study the effect of metals level in the demetallized feed on the rate of deactivation of the desulfurization catalyst.
2. Study the effect of level of desulfurization on the deactivation rate of the desulfurization catalyst.
3. To determine operating conditions required to produce 0.3 weight percent fuel oil.

##### 4.1 Apparatus and Procedures

All desulfurization operations were carried out in continuous, downflow, fixed bed units 184 and 185. These units are identical to unit 115 shown in Figure 1 except for having a single reactor contained in the lead bath. The reactor shown in Figure 2 was used in all desulfurization runs. In all but three runs full reactor catalyst charge was used (approximately 200 cc loose). In runs 184-196, 197 and 185-248 the volume of catalyst charged to the reactor was approximately 100 cc (loose).

The reduced volume of catalyst charge enabled us to obtain longer catalyst ages, at normal liquid space velocities, using the limited quantities of feedstock available.

The startup and operating procedures used were similar to ones used with the demetallization runs described previously under the demetallization section.

Most of the aging runs were carried out to a catalyst age of 2 to 3 Bbl/Lb. Runs of this duration, together with results from aging desulfurization runs made during Phases I and II of this contract, provide an accurate measure of catalyst deactivation rates which can be translated to the catalyst utilization required to obtain a given product desulfurization level.

Detailed operating conditions and liquid product inspections for each run in this series are given in Appendix B.

##### 4.2 Catalyst Description and Inspections

The catalyst used in all desulfurization runs was high activity

HDS beads obtained from American Cyanamid, designated as HRI 3104. The small size, about 0.02 inch diameter spheres, makes this catalyst particularly resistant to deactivation due to metals deposition, thus making it a likely candidate for use in a commercial process. The properties of the catalyst are summarized in Table 6.

#### 4.3 Demetallized Bachaquero Export Vacuum Residuum

##### 4.3.1 Products from Low Level Demetallization

The demetallized products from Run 115-1233 were blended and designated as HRI L-400. Table 7 summarizes inspections on this blended feed. This operation was carried out in Run 184-194 at 760°F, hydrogen pressure of 2000 psig, liquid space velocity of 1.00 Vo/Hr/Vr corresponding to a catalyst space velocity of 0.107 Bbl/D/Lb. This run lasted 20 days to catalyst age of 2.2 Bbl/Lb at which time it was voluntarily shut down.

Figure 15 shows the desulfurization rate and catalyst deactivation. The initial sulfur removal rate was 65 percent producing 0.68 weight percent sulfur product oil and the final desulfurization rate was 55 percent producing 0.91 weight percent sulfur product. The vanadium removal rate at the beginning of this run was 21 percent and at the end it was 14 percent producing a product with 240 parts per million vanadium (ppm V) and 49 parts per million nickel (ppm Ni).

##### 4.3.2 Products from Medium Level Demetallization at Conditions A, B, and C

The demetallized products from the medium level, 65-75 percent vanadium removal operations, were blended and designated HRI L-401, 405, 406. Table 7 shows the inspections of these feeds.

Three conditions (A, B, and C) were run.

Condition A desulfurization was conducted in Run 184-195 at 760°F, hydrogen pressure of 2000 psig, liquid space velocity of 1.00 Vo/Hr/Vr corresponding to a catalyst space velocity of 0.107 Bbl/D/Lb. Feed designated L-401 was used in this run which lasted 20 days to a catalyst age of 2.3 Bbl/Lb.

Condition B was run using feed L-405 in unit 184-196 at 760°F, hydrogen pressure 2000 psig, liquid space velocity of 0.53 Vo/Hr/Vr corresponding to a catalyst space velocity of 0.056 Bbl/D/Lb. The run lasted 20 days to a catalyst age of 1.1 Bbl/Lb.

TABLE 6 SUMMARY OF INSPECTIONS ON AMERICAN  
CYANAMID 0.02" HIGH ACTIVITY BEADED CATALYST

HRI Identification Number	3104
---------------------------	------

Physical Properties

Surface Area, M <sup>2</sup> /g	250
H <sub>2</sub> O Pore Volume, cc/g	(0.67)
Hg Pore Volume, cc/g	0.62

Screen Analysis, U.S. Sieve No.

+20	1.3
20/30	16.9
30/40	76.2
40/50	5.0
50/70	0.5
70/100	0.1
-100	----

Chemical Analysis, W %

MoO <sub>3</sub>	(15.0)
CoO	(3.0)
Al <sub>2</sub> O <sub>3</sub>	Bal

( ) Manufacturers Specifications

TABLE 7 FEED STOCK INSPECTIONS

Feedstock: Demetallized Bachaquero Export Vacuum Residuum

Vanadium Removal, % <sup>(1)</sup>	45	65	65	65	83
HRI Identification No.	L-400	L-401	L-405	L-406	L-408
Gravity, °API	11.3	13.1	14.4	15.0	17.5
Sulfur, W %	1.98	1.39	1.40	1.25	1.00
RCR, W %		13.3	13.9	13.5	10.7
Nitrogen, ppm	4061	4637	4508	4501	3935
Carbon, W %					
Hydrogen, W %					
Vanadium, ppm	305	191	192	190	100
Nickel, ppm	65	48	50	50	34
Viscosity, SFS @ 210°F	216	58	50	32	
SUS @ 210°F			420	348	199
<u>IBP-650°F</u>					
Volume, %	4.0	7.0	9.0	11.0	13.0
Gravity, °API	33.0	33.8	35.2	35.9	36.1
Sulfur, W %	0.43	0.23	0.14	0.11	0.13
<u>650-975°F</u>					
Volume, %	18.7	20.0	23.3	24.7	23.3
Gravity, °API	18.9	20.3	20.7	21.3	21.8
Sulfur, W %	1.07	0.68	0.75	0.67	0.29
<u>975°F+</u>					
Volume, %	77.3	73.0	67.7	64.3	63.7
Gravity, °API	8.2	10.1	8.9	8.7	10.8
Sulfur, W %	2.19	1.71	1.68	1.75	1.29
RCR, W %	20.4	18.4	19.9	21.5	16.6

(1) Compared to feed into demetallization

FIGURE 15

DESULFURIZATION OF LOW LEVEL (40-45% VANADIUM REMOVAL) DEMETALLIZED BACHAQUERO EXPORT VACUUM RESIDUUM

OVER 0.02" HDS BEADS

RUN NO. 184-194

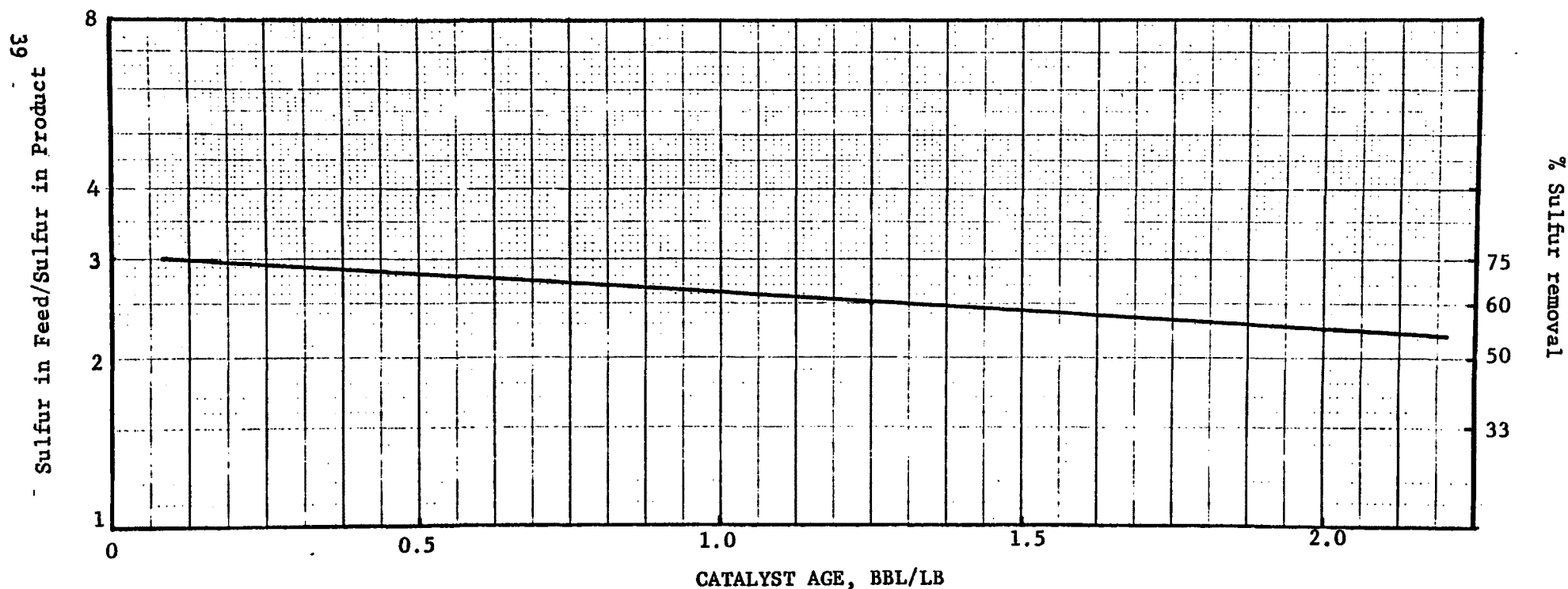
FEED COMPOSITION

HRI - L-400

Gravity, °API	11.3
Sulfur, W %	1.98
Vanadium, ppm	305
Nickel, ppm	65

OPERATING CONDITIONS

H <sub>2</sub> Pressure, psig	2000
Temperature, °F	760
Liquid Sp. Vel., V/Hr/V	1.00
Cat. Sp. Vel. B/D/Lb	0.107



Condition C desulfurization was carried out in Run 184-197 using L-405 and 406 feed. The conditions of this operation were 780°F, 2000 psig hydrogen pressure, liquid space velocity of 0.5 Vo/Hr/Vr and catalyst space velocity of 0.052 Bbl/D/Lb.

After six days of operation, hydrogen flow could not be maintained and the run had to be terminated. The hydrogen metering orifice was found to be partially restricted.

A new run was started in unit 185-248 under identical conditions. This run lasted 12 days to catalyst age 0.68 Bbl/Lb before the demetallized feed was exhausted.

The desulfurization results achieved using conditions A, B, and C are plotted in Figure 16. Under condition A, desulfurization achieved was 54 weight percent sulfur removal producing 0.64 weight percent sulfur product containing 159 ppm V and 41 ppm Ni. Under Condition B desulfurization was 72 percent producing 0.4 weight percent sulfur product containing 137 ppm V and 35 ppm Ni, and under condition C 78 percent desulfurization producing 0.3 weight percent sulfur product containing 88 ppm V and 26 ppm Ni.

The rate of catalyst deactivation increases with increasing level of desulfurization. At condition C, the highest level of desulfurization, the catalyst deactivation slope was 0.34 while condition B had a slope of 0.22 and condition A was 0.097.

Figure 17 shows the sulfur level in the products versus catalyst age for conditions A, B, and C.

#### 4.3.3 Products from High Level Demetallization

The demetallized products from the high level demetallization operations, 80-85 percent vanadium removal, were blended and designated as HRI L-408, inspections given in Table 7.

This blend was used as feed to Run 185-249 carried out at 760°F, hydrogen pressure of 2000 psig, liquid space velocity of 1.0 Vo/Hr/Vr corresponding to a catalyst space velocity of 0.107 Bbl/D/Lb. This run lasted 17 days to catalyst age of 1.9 Bbl/Lb using up all the available feedstock. Figure 18 shows the catalyst deactivation with age.

Average desulfurization level achieved during this run was 55 percent sulfur removal producing oil containing 0.45 weight percent sulfur and 66 ppm V and 24 ppm Ni. Figure 19 shows a plot of weight



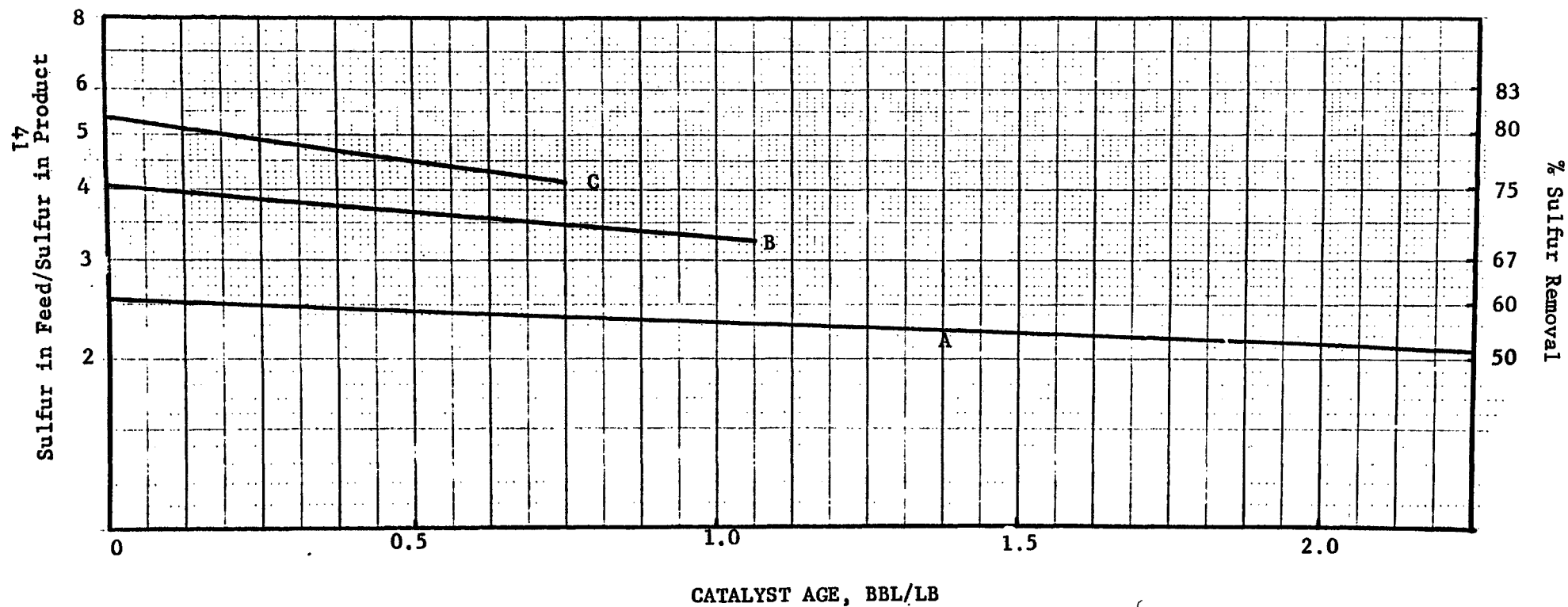
**FIGURE 16**

**DESULFURIZATION OF MEDIUM LEVEL (65-70% VANADIUM REMOVAL) DEMETALLIZED BACHAQUERO EXPORT VACUUM RESIDUUM**

**OVER 0.02 INCH BEADS**

**(VANADIUM REMOVED IN DEMETALLIZED STAGE ~ 65%)**

DESULFURIZATION FEED CHARACTERISTICS						OPERATING CONDITIONS				
Symbol	Run No.	$^{\circ}$ API	% S	ppm V	ppm Ni	Condition	Temp $^{\circ}$ F	PSIG	V/HR/V	B/D/Lb
A	184-195	13.1	1.39	191	48	A	760	2000	1.00	0.107
B	184-196	14.4	1.40	192	50	B	760	2000	0.53	0.056
C	185-248	15.0	1.25	190	47	C	780	2000	0.50	0.052



**Figure 16**

FIGURE 17

DESULFURIZATION OF MEDIUM LEVEL (65-70% VANADIUM REMOVAL) DEMETALLIZED BACHAQERO EXPORT VACUUM RESIDUUM  
OVER 0.02 INCH BEADS

## FEED COMPOSITION

## OPERATING CONDITIONS

Symbol	Run No.	$^{\circ}$ API	% S	ppm V	ppm Ni	Condition	Temp. $^{\circ}$ F	PSIG	V/HR/V	B/D/LB
A	184-195	13.1	1.39	191	48	A	760	2000	1.00	0.107
B	184-196	14.4	1.40	192	50	B	760	2000	0.53	0.056
C	185-248	15.0	1.25	190	47	B	780	2000	0.50	0.052

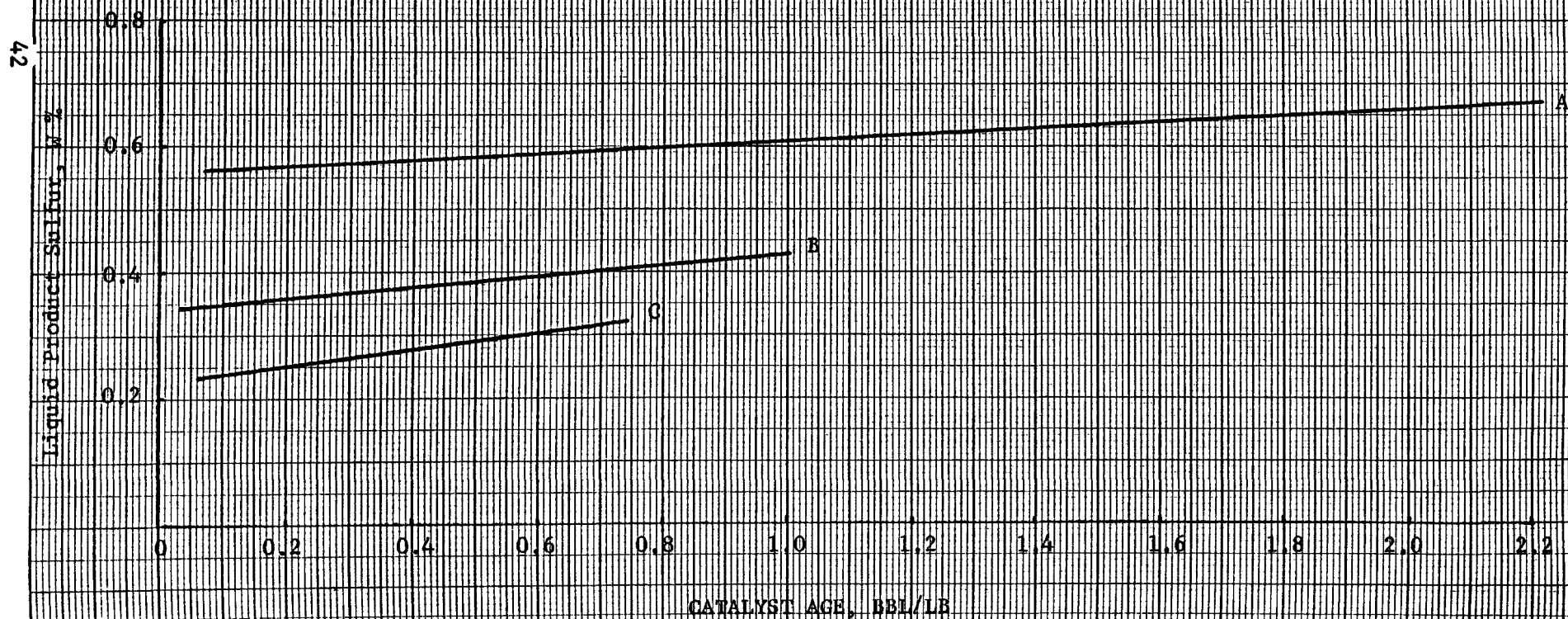


FIGURE 18

DESULFURIZATION OF HIGH LEVEL (80-85% VANADIUM REMOVAL) DEMETALLIZED BACHAQUERO EXPORT VACUUM RESIDUUM

OVER 0.02" BEADS

Run 185-249

FEED COMPOSITION

17.5 °API  
1.0 % Sulfur  
100 ppm V  
34 ppm Ni

OPERATING CONDITIONS

2000 Psig H<sub>2</sub> Pressure  
760°F, Reactor Temperature  
1.0 V/HR/V Liq. Sp. Vel.  
0.107 B/D/LB Cat. Sp. Vel.

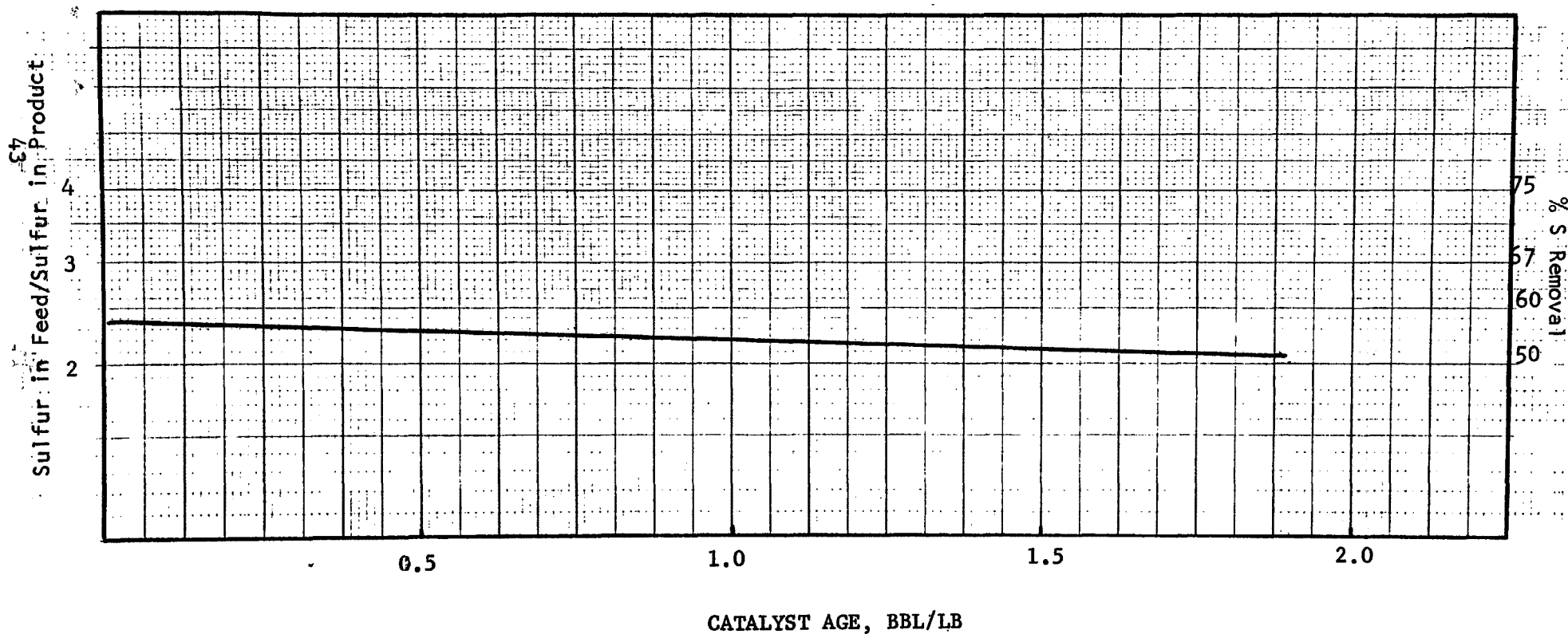
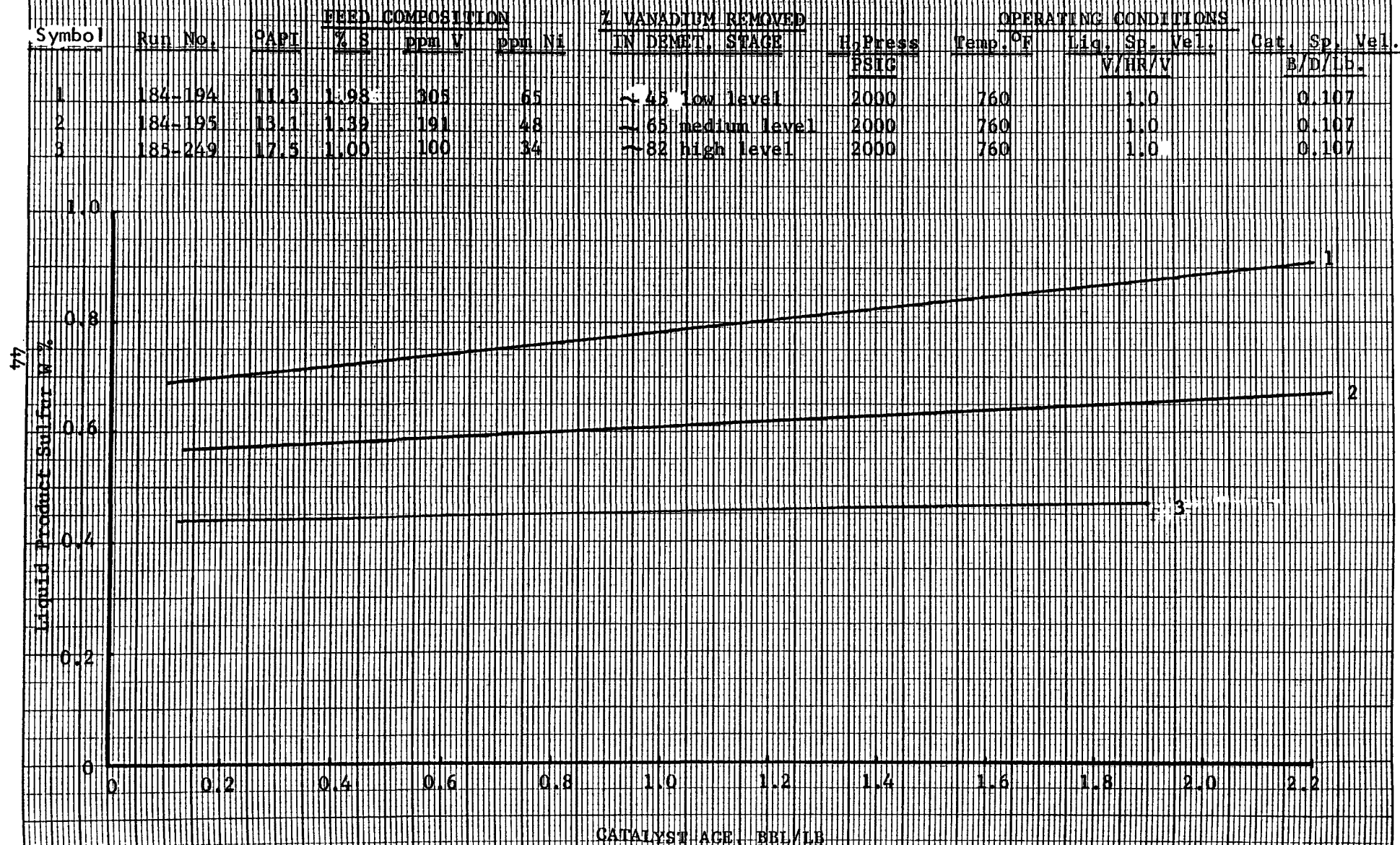


Figure 18

FIGURE 19

DESULFURIZATION OF DEMETALLIZED BACHAQUERO EXPORT VACUUM RESIDUUM  
OVER 0.02" BEADS

LIQUID PRODUCT SULFUR



percent sulfur in the product versus catalyst age and is compared with sulfur levels in the products from low level and medium level demetallization operations conducted at similar desulfurization conditions.

#### 4.4 Demetallized Lloydminster Vacuum Residuum

##### 4.4.1 Products from Medium Level Demetallization

Products from demetallization Run 115-1248 were blended and designated HRI L-422. The inspections on this blended feed are presented in Table 8.

This operation using L-422 as feed was carried out in Run 185-250 at 760°F, hydrogen pressure of 2000 psig, liquid space velocity of 1.0 Vo/Hr/Vr and catalyst space velocity of 0.107 Bbl/D/Lb. This run lasted for 26 days to a catalyst age of 3.0 Bbl/Lb. Aging results from this run are summarized in Figure 20.

##### 4.4.2 Products from High Level Demetallization

Products from demetallization Run 115-1249 were blended and designated HRI L-424, with inspections presented in Table 8.

This operation was carried out in Run 185-251 using L-424 as feed at 760°F, hydrogen pressure of 2000 psig, liquid space velocity of 1.0 Vo/Hr/Vr and catalyst space velocity of 0.107 Bbl/Hr/Lb. This run lasted for 24 days to a catalyst age of 2.9 Bbl/Lb.

Catalyst deactivation with age is plotted in Figure 20, along with results obtained on the lower demetallized feed (45-60% vanadium removal) carried out in Run 185-250. The catalyst slopes of these two runs are about the same, and correlate well with previously determined data on Tia Juana, Bachaquero and Gach Saran which showed that highly demetallized feeds generally give lower deactivation slopes.

Figure 21 shows the sulfur levels versus catalyst age which were achieved during desulfurization of the two levels of demetallized Lloydminster feeds. Sulfur levels ranged from 0.62 to 0.80 weight percent on the lower demetallized feed and from 0.46 to 0.65 weight percent sulfur on the higher demetallized feed. The overall desulfurization was lower on the higher demetallized feed because the last trace of sulfur is more difficult to remove.

TABLE 8 FEED STOCK INSPECTIONS

Feedstock:        Demetalized Lloydminster Vacuum Residuum

Vanadium Removed, % <sup>(1)</sup>	63	85
HRI Identification No.	L-422	L-424
Gravity, °API	13.2	16.4
Sulfur, W %	2.83	1.88
RCR, W %	13.5	9.5
Nitrogen, ppm	4375	3785
Carbon, W %	85.84	85.72
Hydrogen, W %	11.03	11.02
Vanadium, ppm	63	31
Nickel, ppm	59	31
Viscosity, SFS @ 210°F	111	24
SUS @ 210°F	1075	286
<u>IBP-650°F</u>		
Volume, %		12.0
Gravity, °API		34.5
Sulfur, W %		0.41
<u>650-975°F</u>		
Volume, %		27.7
Gravity, °API		20.2
Sulfur, W %		0.89
<u>975°F+</u>		
Volume, %	(65)	60.3
Gravity, °API		9.1
Sulfur, W %		2.21
RCR, W %		16.47

(1) Compared to feed into demetallization

**FIGURE 20**

**DESULFURIZATION OF DEMETALLIZED LLOYDMINSTER VACUUM RESIDUUM**  
**OVER 0.02" BEADS**

FEED CHARACTERISTICS							OPERATING CONDITIONS				
Symbol	Run No.	°API	% S	ppm V	ppm Ni	FEED HRI NO.	% VANADIUM REMOVED In Demet. Stage	psig	Temp. °F	V/Hr/V	B/D/Lb.
A	185-250	13.2	2.83	63	59	L-422	63	2000	760	1.0	0.107
B	185-251	16.4	1.88	31	31	L-424	82	2000	760	1.0	0.107

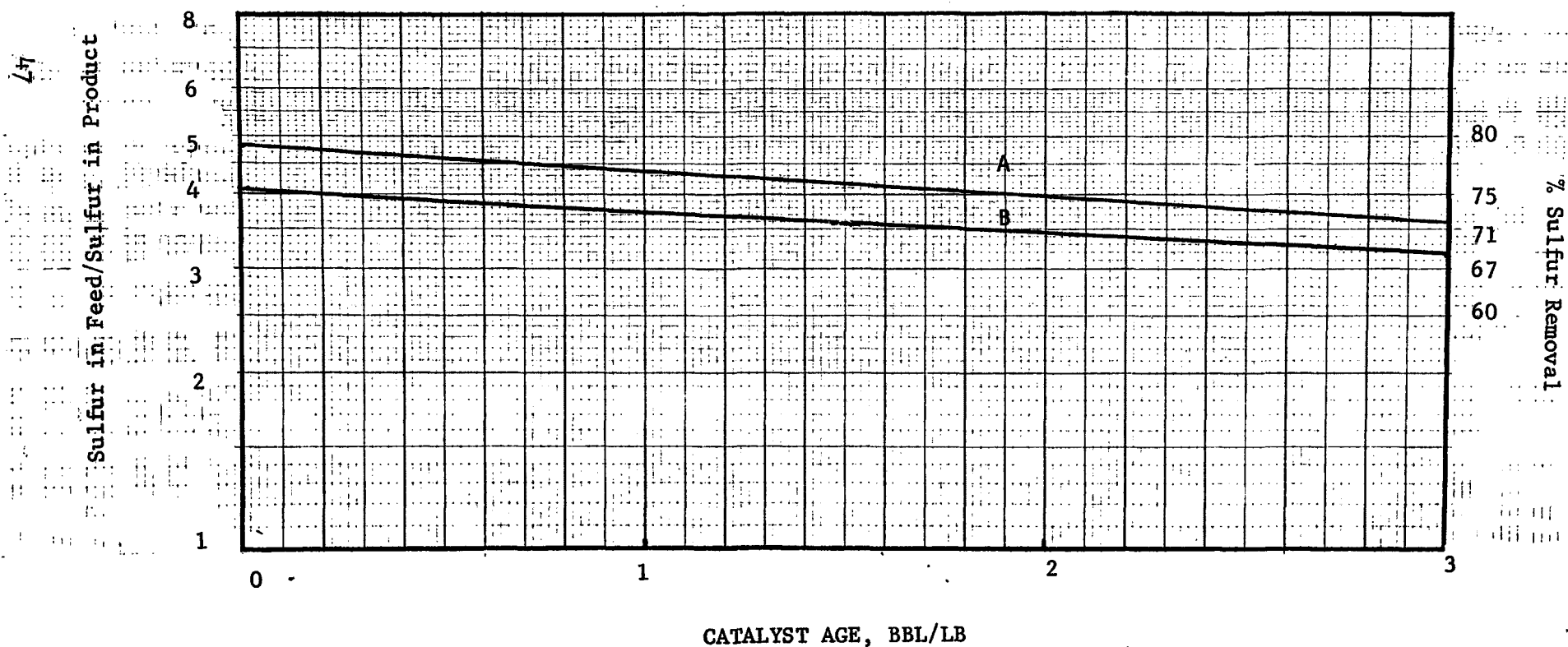


Figure 20



FIGURE 21

DESULFURIZATION OF DEMETALLIZED LLOYDMINSTER VACUUM RESIDUUM  
OVER 0.02" BEADS  
LIQUID PRODUCT SULFUR

FEED CHARACTERISTICS

Symbol	Run No.	°API	% S	ppm V	ppm Ni	FEED HRI No.	% VANADIUM REMOVED In Demet. Stage	psig	OPERATING CONDITIONS		
									Temp. °F	V/Hr/V	B/D/ Lb.
A	185-250	13.2	2.83	63	59	1-422	~63	2000	760	1.0	0.167
B	185-251	16.4	1.88	31	31	1-424	~82	2000	760	1.0	0.167

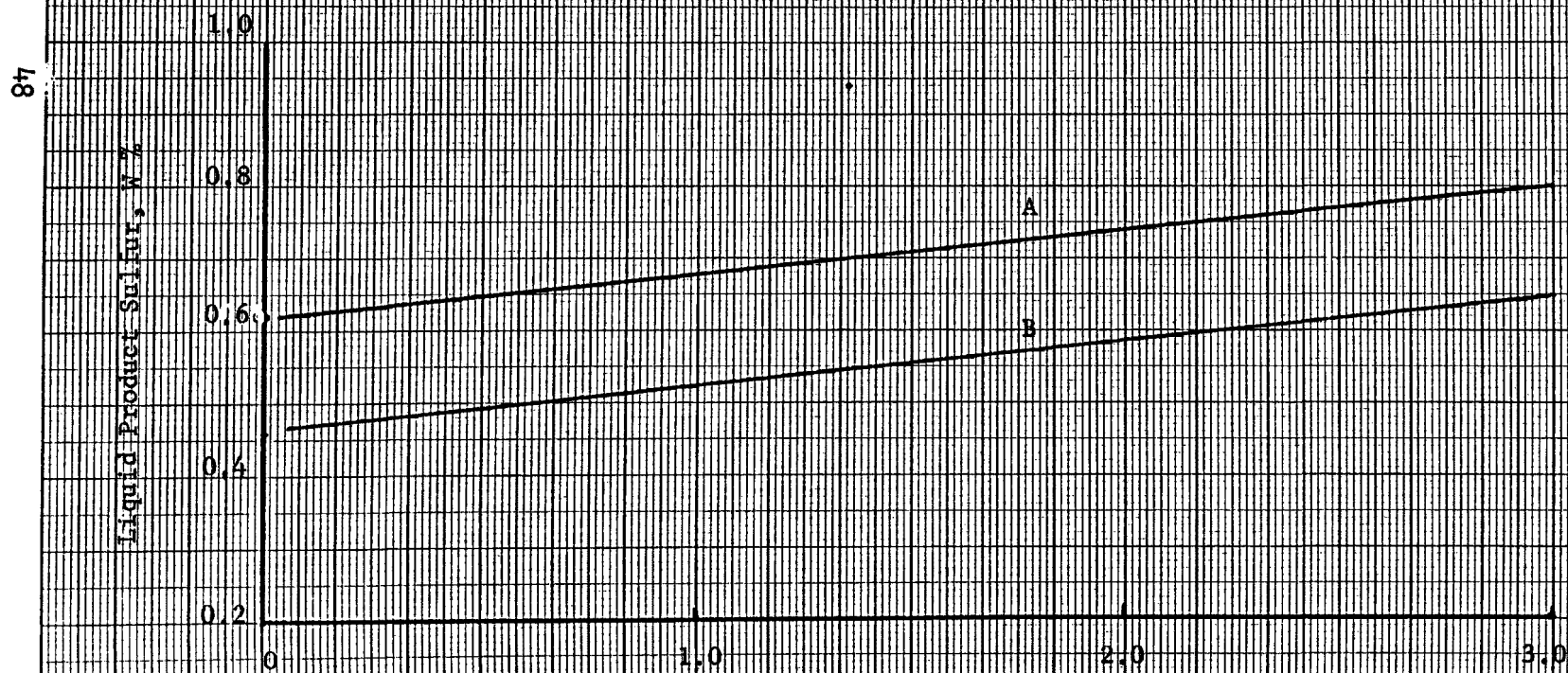


Figure 21



The amount of vanadium to be removed in the demetallization stage depends on the final sulfur level of the fuel oil. For a given sulfur level fuel oil the optimum combination of vanadium removal in the demetallization stage with optimum sulfur removal in the desulfurization stage is presented below.

Fuel Oil Sulfur Level	% Vanadium Removal in the Demetallization Stage	% Sulfur Removal in the Desulfurization Stage
1 W %	65	60
0.5 W %	75	76.5
0.3 W %	82.5	83.2

#### 4.5 Spent Desulfurization Catalyst Inspections

Analyses on the spent desulfurization catalysts are tabulated in Table 9. The carbon content ranged from about 12 to 20 weight percent but did not correlate with catalyst age, temperature or liquid space velocity.

However, the metals laydown (vanadium & nickel) was strongly influenced by the demetallization level achieved in the demetallization step. For example, feeding Bachaquero Export vacuum residuum which was demetallized to 44 percent metals removal level, deposited 3.65 weight percent metals on the commercial HDS catalyst while the same feed demetallized to 64 percent level deposited only 1.93 weight percent metals on the HDS catalyst at a comparable catalyst age and identical operating conditions.

Similar results were obtained on Lloydminster vacuum residuum. Feed which was demetallized to a 53 percent level, deposited 3.82 weight percent metals on the HDS catalyst while the feed demetallized to a 76 percent level deposited only 1.49 weight percent metals at a comparable catalyst age and operating conditions.

The results on Bachaquero and Lloydminster residua further prove the ability of the newly developed scavenger catalyst to substantially prolong the life of a commercial HDS catalyst as was the case previously demonstrated on Tia Juana and Gach Saran residua.

The pore size distribution of the spent desulfurization catalysts are shown in Table 10. The loss in total pore volumes was not as extensive as was the case with the demetallization catalysts.

TABLE 9 ANALYSES OF SPENT DESULFURIZATION CATALYSTS

RUN NO.		TEMP. °F	LHSV Vo/Hr/Vr	CATALYST AGE Bbl/Lb	WT %			
					C	S	V	Ni
184-194	Bachaquero 40-45% V-Removal	760	1.00	2.20	15.63	6.48	3.07	0.58
184-195	Bachaquero 65-70% V-Removal	760	1.00	2.30	18.44	4.58	1.47	0.46
184-196	Bachaquero 65-70% V-Removal	760	0.53	1.10	14.74	4.90	1.00	0.35
184-197	Bachaquero 65-70% V-Removal	780	0.50	0.45	15.80	2.52	0.52	0.21
184-248	Bachaquero 65-70% V-Removal	780	0.50	0.68	20.51	4.13	0.80	0.28
185-249	Bachaquero 80-85% V-Removal	760	1.00	1.90	20.28	3.68	0.80	0.30
185-250	Lloydminster 45-60% V-Removal	760	1.00	3.00	12.13	6.53	2.22	1.60
185-251	Lloydminster 80-85% V-Removal	760	1.00	2.90	17.73	4.80	0.69	0.80

**TABLE 10 PORE SIZE DISTRIBUTION OF SPENT DESULFURIZATION CATALYSTS**

SPENT CATALYST From Run No.	CATALYST AGE Bbl/Lb	WT %		PORE DIAMETER RANGE ANGSTROMS				TOTAL PORE VOLUME cc/g	LOSS IN TOTAL PORE VOLUME %
		C	V + Ni	30-50	50-70	70-100	100+		
				PORE VOLUME cc/g					
Fresh 3401	---	---	---	0.114	0.207	0.161	0.087	0.569	---
184-194	2.20	15.63	3.65	0.128	0.129	0.047	0.049	0.353	38.0
184-195	2.30	18.44	1.93	0.124	0.085	0.043	0.045	0.297	47.8
184-196	1.10	14.74	1.35	0.100	0.170	0.072	0.070	0.412	27.6
184-197	0.45	15.80	0.73	0.105	0.150	0.070	0.067	0.392	31.1
185-248	0.68	20.51	1.08	0.114	0.095	0.043	0.055	0.307	46.0
185-249	1.90	20.28	1.10	0.148	0.051	0.021	0.030	0.250	56.1
185-250	3.00	12.13	3.82	0.084	0.151	0.104	0.049	0.388	31.8
185-251	2.90	17.73	1.49	0.112	0.109	0.055	0.057	0.333	41.5

**Note:** Pore size distribution and total pore volumes on spent catalysts were corrected to fresh catalyst basis. (See section 4.6 for method used.)

#### 4.6 Desulfurization Correlations

The effect of residual metals (vanadium & nickel) in the demetallized feed on the deactivation slope of the commercial HDS catalyst is shown in Figure 22. Depicted are results obtained on Bachaquero Export and Lloydminster vacuum residua from the present Phase III work and data obtained on Tia Juana and Gach Saran vacuum residua under Phase II work.

Results from data accumulated on Bachaquero Export vacuum residuum indicated that the higher the level of metals removal in the demetallization stage, the lower would be the deactivation slope of the commercial HDS catalyst. However, above 65 percent vanadium removal, corresponding to about 240 ppm metals, the increase in the deactivation slope is only about one half of that between 45 and 65 percent vanadium removal.

For Lloydminster vacuum residuum the difference in the deactivation slopes between 63 and 82 percent vanadium removal was quite small, less than 0.1. Figure 23 summarizes the contaminant metals deposited on the desulfurization catalyst versus metals in the demetallized feed with each feed at approximately the same catalyst age. As expected, less metals are deposited on the catalyst feeding lower metals containing feed, with a corresponding increased life expectancy of the desulfurization catalyst.

The most important factor to influence deactivation of the desulfurization catalyst appears to be the level of the desulfurization operation being carried out. Figure 24 shows the variation in the deactivation slope versus desulfurization level on Bachaquero Export demetallized to 65 percent vanadium removal level. Variation in the desulfurization level was achieved by varying the liquid space velocity between 0.5 and 1.0  $\text{Vo}/\text{Hr}/\text{Vr}$  and varying the temperature between 760 and 780°F. The catalyst deactivation slope increases by a factor of three for an increase in the desulfurization level from 60 percent to 80 percent. This sharp increase in the rate of catalyst deactivation as indicated in Figure 24 seems to suggest that the rate of sulfur removal for Bachaquero Export feed is strongly diffusion controlled as was the case with vanadium removal in the demetallization step (See section 3.7 for explanation). A demetallization catalyst with the added ability to remove sulfur during demetallization would be an ideal catalyst to produce low sulfur fuel oil in a two stage demetallization process. This is so because the level of sulfur removal that is necessary in the second step to achieve a low sulfur fuel oil would be greatly decreased thus allowing HDS in the regime of slow catalyst deactivation. The newly developed demetallization catalyst appears to fit the above requirements.

FIGURE 22

EFFECT OF METALS CONTENT OF DEMETALLIZED FEEDS  
ON  
DEACTIVATION SLOPE OF THE DESULFURIZATION CATALYST

Symbol Feed Identification

- Lloydminster Vacuum Residuum
- Bachaquero Export Vacuum Residuum
- Gach Saran Vacuum Residuum
- △ Tia Juara Vacuum Residuum

$n$  Slope of a plot of  $\ln \frac{S_F}{S_P}$  vs catalyst age

$H_2$  Pressure 2000 ps g

Temperature, 760 °F

LHSV 1.0 V/M-Hr/V

Catalyst 0.02" HDS Beads

Slope of deactivation slope

VANADIUM + NICKEL  
IN  
DEMETALLIZED FEED, PPM

53

FIGURE 23

METALS LEVEL IN DEMETALLIZED FEED  
VERSUS  
METALS LOADING OF DESULFURIZATION CATALYSTS

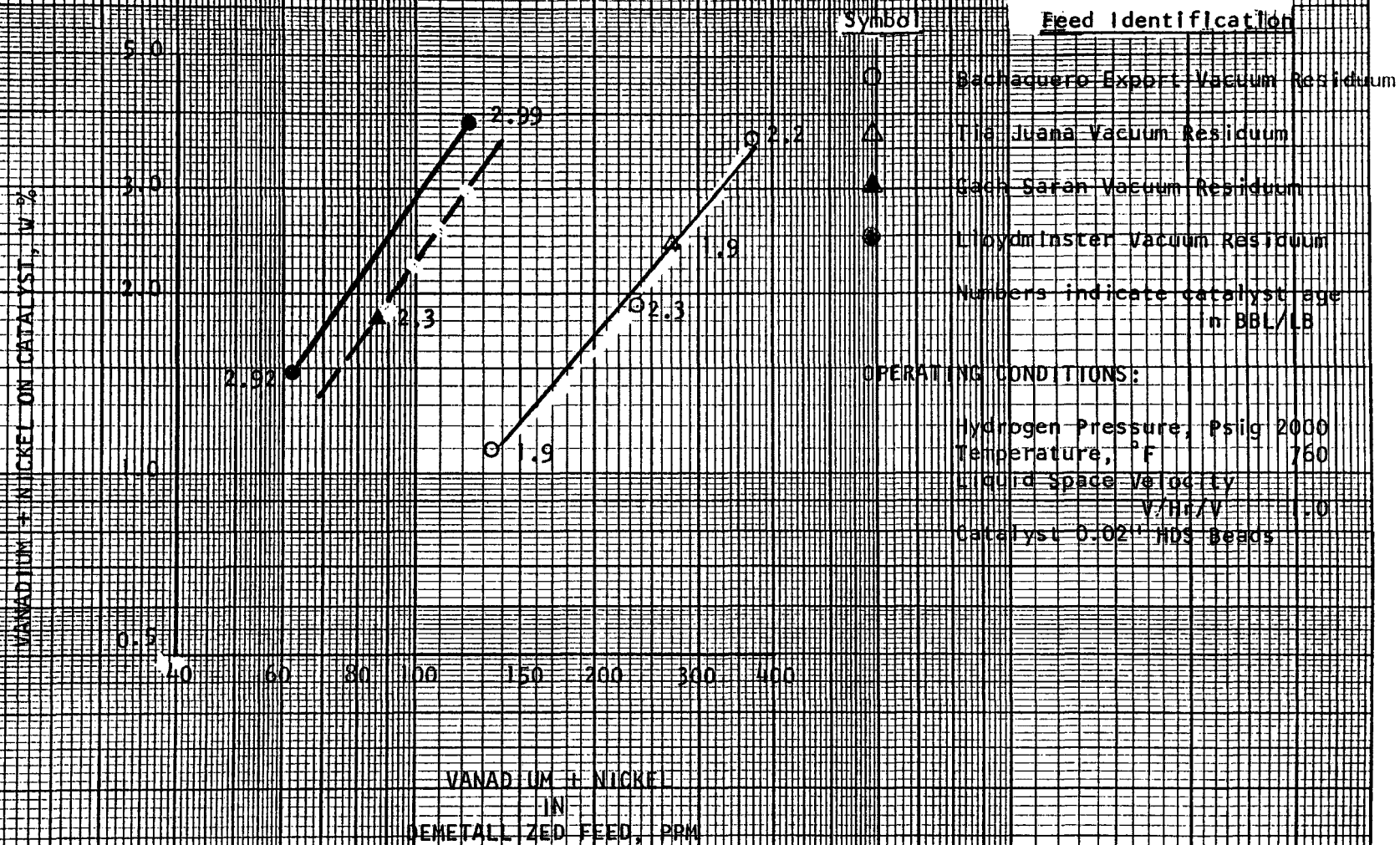


Figure 23

Figure 24

# EFFECT OF LEVEL OF DESULFURIZATION ON DEACTIVATION SLOPE OF DESULFURIZATION CATALYSTS

Feed: Demetallized Bachaquero Export Vacuum Residuum  
(191 PPM V, 48 PPM Ni)

## Operating Conditions:

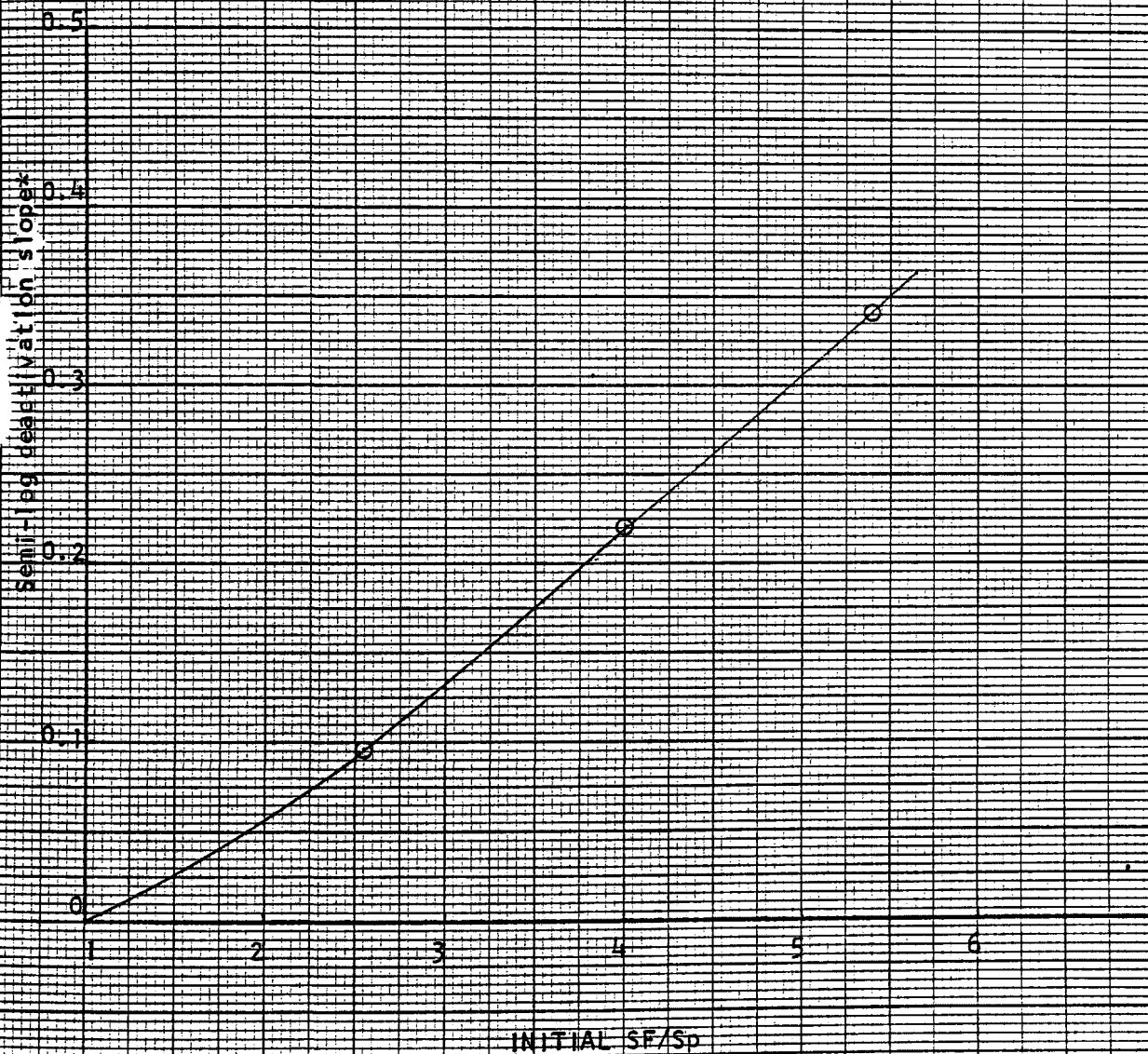
H<sub>2</sub> Pressure, Psig 2000

Temperature, °F 760-780

Liquid Space Velocity, V/HR/V 0.5 to 1.0

Catalyst 0.02" HDS Beads

\* Slope of a plot of  $\ln \frac{SF}{Sp}$  vs catalyst age



#### 4.7 Correlated Fuel Oil Properties

Detailed inspections were obtained on products from each desulfurization run. Two twenty-four hour periods were analyzed, one near the beginning of the run and the other near the end of the run. Summaries of product yields and inspections are given in Tables B-1 to B-13 of the Appendix B.

Viscosity variation as a function of API gravity for fuel oils obtained from Bachaquero Export and Lloydminster vacuum residua are presented in Figure 25. Variation of pour point with viscosity on the 400°F+ fuel oils is given in Figure 26, and for the 650°F+ fuel oils in Figure 27.

Viscosity determinations were performed using ASTM D-88 "Standard Method of Test for Saybolt Viscosity" at standard temperatures of 122 and 210°F.

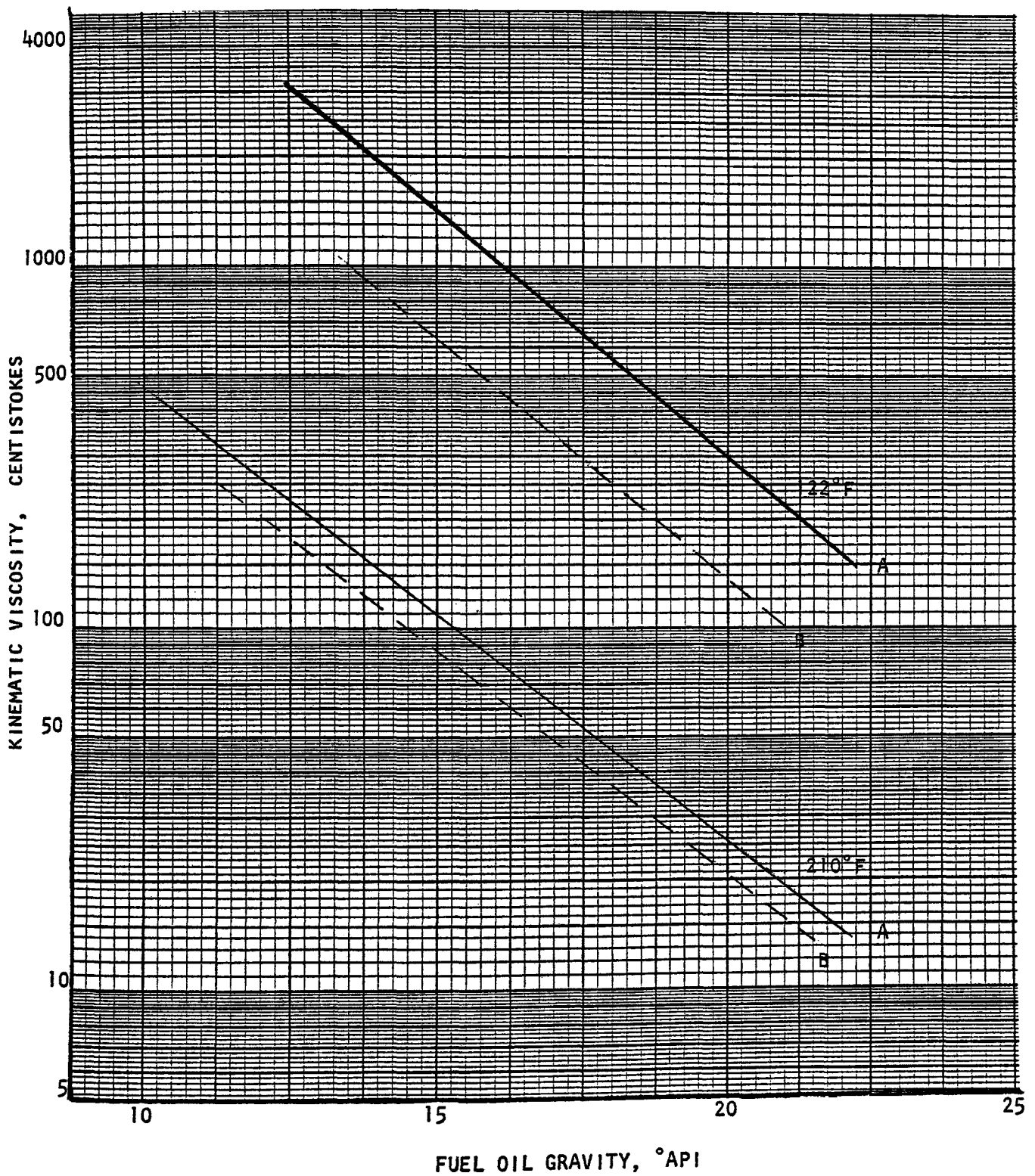
The pour point determinations were performed using ASTM D-97 "Standard Method of Test for Pour Point of Petroleum Oils."



FUEL OIL VISCOSITY VS. °API GRAVITY

A Bachaquero Export Vacuum Residuum

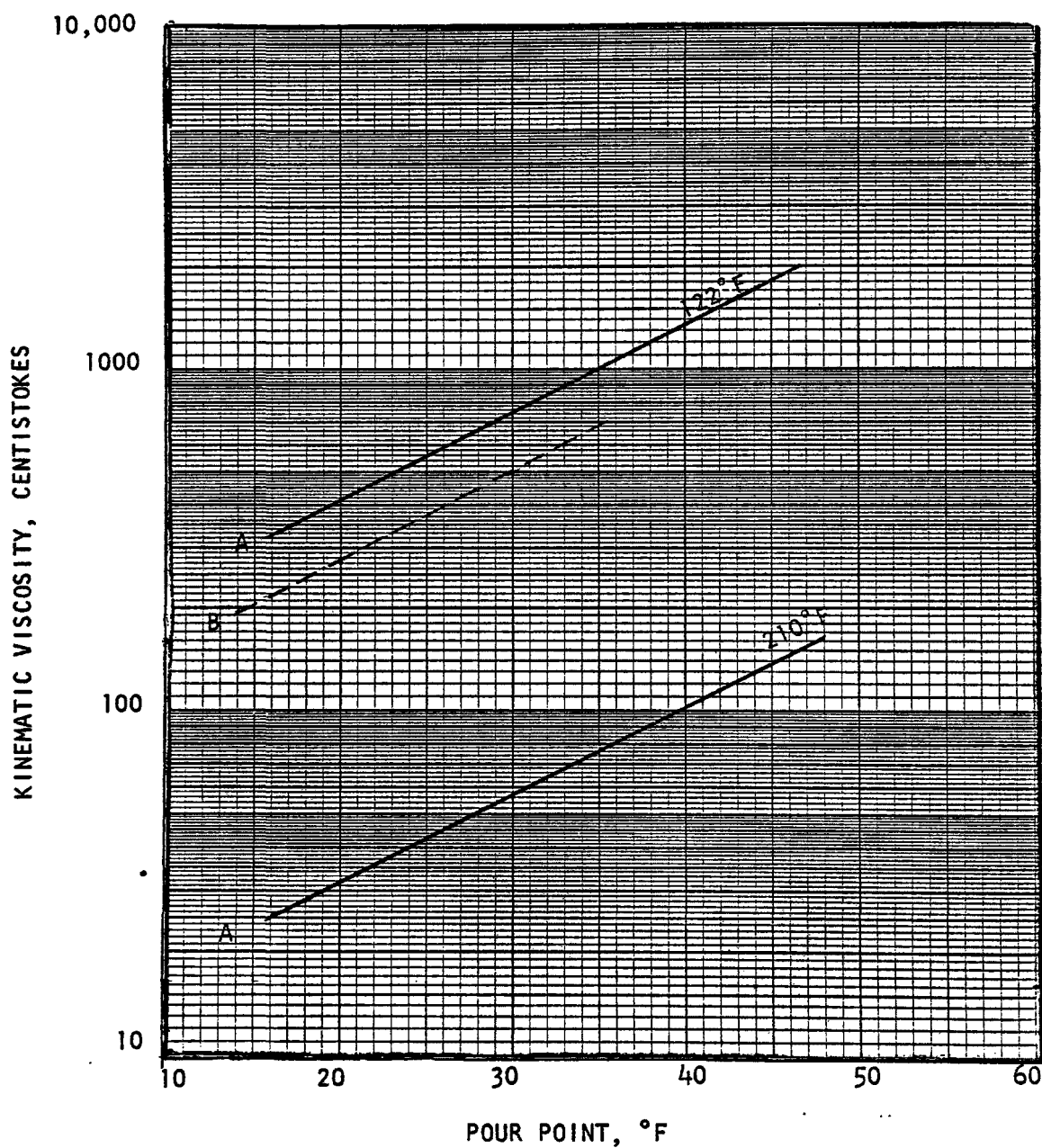
B Lloydminster Vacuum Residuum



400°F+ FUEL OIL VISCOSITY VS. POUR POINT

A Bachaquero Export Vacuum Residuum

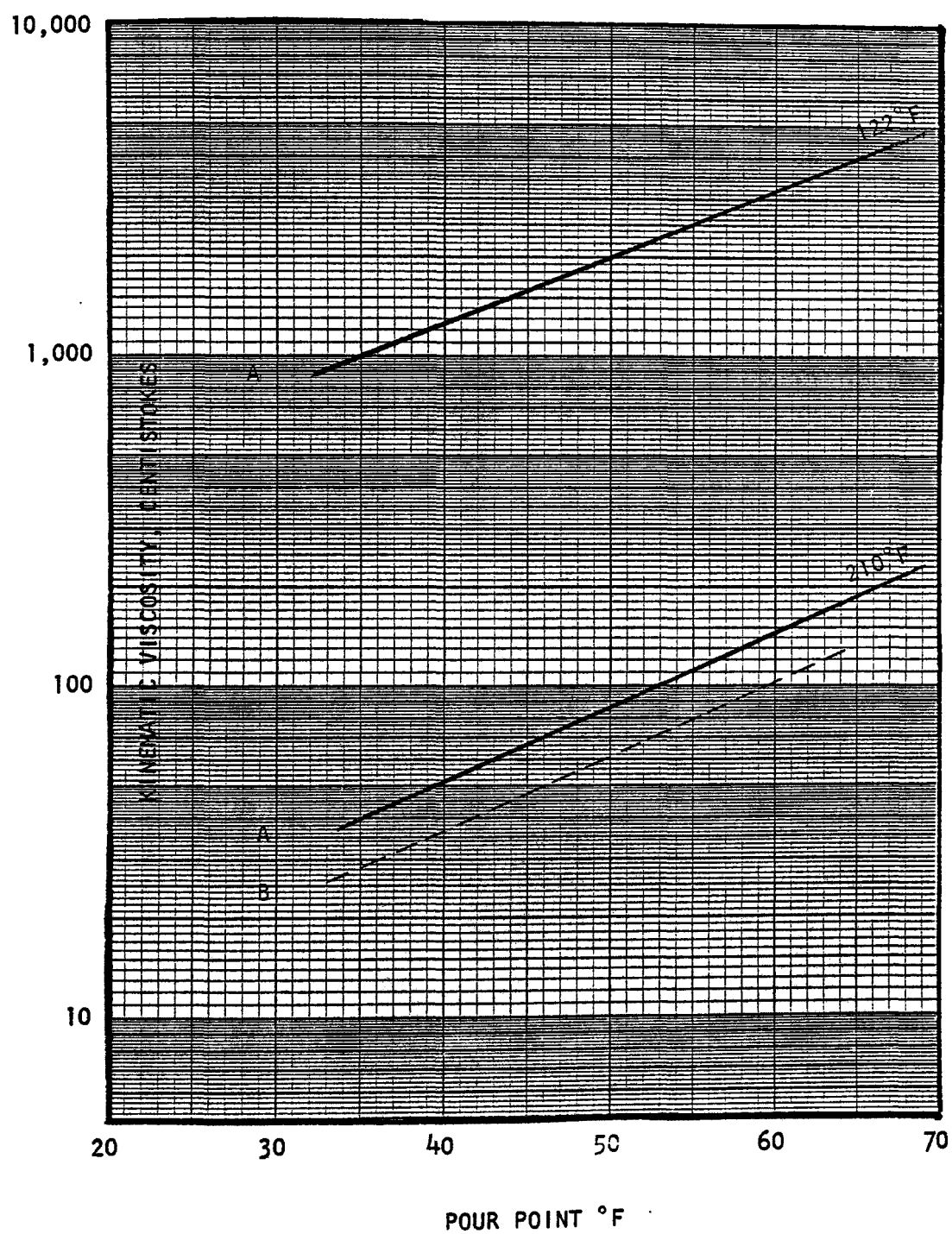
B Lloydminster Vacuum Residuum



650°F+ FUEL OIL VISCOSITY VS. POUR POINT

A Bachaquero Export Vacuum Residuum

B Lloydminster Vacuum Residuum





## 5. PROCESS ECONOMICS

The major costs in producing low sulfur fuel oil from vacuum residua depend on the cost of the facility necessary to carry out the demetallization and desulfurization operations, the amount of hydrogen consumed during the process, and the cost of the demetallization and desulfurization catalysts. Summaries have been prepared of the processing costs, including investment requirements for producing 1.0, 0.5 and 0.3 weight percent sulfur fuel oil from Bachaquero Export and Lloydminster vacuum residua utilizing the commercially prepared 1.0 weight percent molybdenum on 20 x 50 mesh activated bauxite in the demetallization step and commercial HDS beads in the desulfurization step. These results are given in Tables 11 and 12.

Data used in cost computations for the Bachaquero Export vacuum residuum cases and the 0.5 and 1.0 weight percent sulfur fuel oil cases for the Lloydminster residuum required only a small amount of extrapolation from the operating conditions used in the experimental program. For the 0.3 weight percent sulfur fuel oil case from the Lloydminster feed, a greater extrapolation of the data was necessary.

Curves showing the variation of the overall operating cost for producing 1.0, 0.5, and 0.3 weight percent sulfur fuel oil as a function of vanadium removal in the demetallization stage for the Bachaquero and Lloydminster feeds are given in the Exhibit A portion of Figures 28 and 29. These operating costs include capital charges of 25 percent on investment. The cost calculations are based on 1976 Gulf Coast construction costs and are for a 20,000 barrels per day plant, which is perhaps the minimum size plant that a refiner would build. These operating costs would be lowered as the plant capacity is increased.

Figure 28, Exhibit A shows that for Bachaquero Export vacuum residuum, there were optimum demetallization levels which minimize overall operating costs for the production of 1.0 and 0.5 percent sulfur fuel oil. The 0.5 weight percent sulfur fuel oil curve shows the optimum demetallization to be about 55 percent vanadium removal, corresponding to a total operating cost of \$2.72 per barrel. The optimum demetallization for producing 1.0 weight percent sulfur fuel oil appears to be about 45 percent vanadium removal, the condition utilized in the experimental program. At this optimum level, the total operating cost is \$2.01 per barrel. Costs for producing 0.3 weight percent sulfur fuel oil decreased with increasing levels of demetallization, but it was difficult to achieve sustained vanadium

TABLE 11  
INVESTMENT AND OPERATING COST FOR A TWO STAGE  
DEMETALLIZATION - DESULFURIZATION  
OPERATION OF BACHAQUERO EXPORT  
VACUUM RESIDUUM

BASES

- |   |  |
|---|--|
| 1. Plant Capacity - 20,000 BPSD   | 2. 1976 Gulf Coast Construction          |
| 3. Hydrogen Cost - \$1.0/MSCF   | 4. Power - \$0.025/KWH                   |
| 5. Fuel - \$2.0/MMBTU   | 6. Steam - \$2.5/1000 Lb.                |
| 7. Process Water - \$0.25/1000 Gal.                                     | 8. Cooling Water - \$0.04/1000 Gal.      |
| 9. Demetallization Catalyst - \$0.35/Lb.                                | 10. Desulfurization Catalyst - \$2.0/Lb. |
| 11. Capital Charges - 25% of investment included in the operating cost. |  |

% Vanadium removed  
in Demetallization Stage

45

65

80

1 W % Sulfur Fuel Oil

Investment, MM\$

15.93

18.89

25.51

Operating Cost, \$/BBL

2.017

2.155

2.575

0.5 W % Sulfur Fuel Oil

Investment, MM\$

20.58

23.80

30.98

Operating Cost, \$/BBL

2.763

2.740

3.029

0.3 W % Sulfur Fuel Oil

Investment, MM\$

24.12

28.13

35.22

Operating Cost, \$/BBL

4.323

3.737

3.528

TABLE 12  
INVESTMENT AND OPERATING COST FOR A TWO STAGE  
DEMETALLIZATION - DESULFURIZATION  
OPERATION OF LLOYDMINSTER  
VACUUM RESIDUUM

BASES

- |   |   |
|---|---|
| 1. Plant Capacity - 20,000 BPSD   | 2. 1976 Gulf Coast Construction         |
| 3. Hydrogen cost - \$1.0/MSCF   | 4. Power - \$0.025/KWH                  |
| 5. Fuel - \$2.0/MMBTU   | 6. Steam - \$2.5/1000 Lb.               |
| 7. Process Water - \$0.25/1000 Gal.                                     | 8. Cooling Water - \$0.04/1000 Gal.     |
| 9. Demetallization Catalyst - \$0.35/Lb                                 | 10. Desulfurization Catalyst - \$2.0/Lb |
| 11. Capital Charges - 25% of investment included in the operating cost. |   |

% Vanadium removed  
in Demetallization Stage

65

80

85

1 W % Sulfur Fuel Oil

Investment, MM\$

16.24

18.50

19.90

Operating Cost, \$/BBL

2.122

2.199

2.257

0.5 W % Sulfur Fuel Oil

Investment, MM\$

19.73

22.37

23.80

Operating Cost, \$/BBL

2.678

2.650

2.672

0.3 W % Sulfur Fuel Oil

Investment, MM\$

23.98

27.32

29.78

Operating Cost, \$/BBL

3.196

3.082

3.082

Figure 28  
TOTAL OPERATING COST FOR A

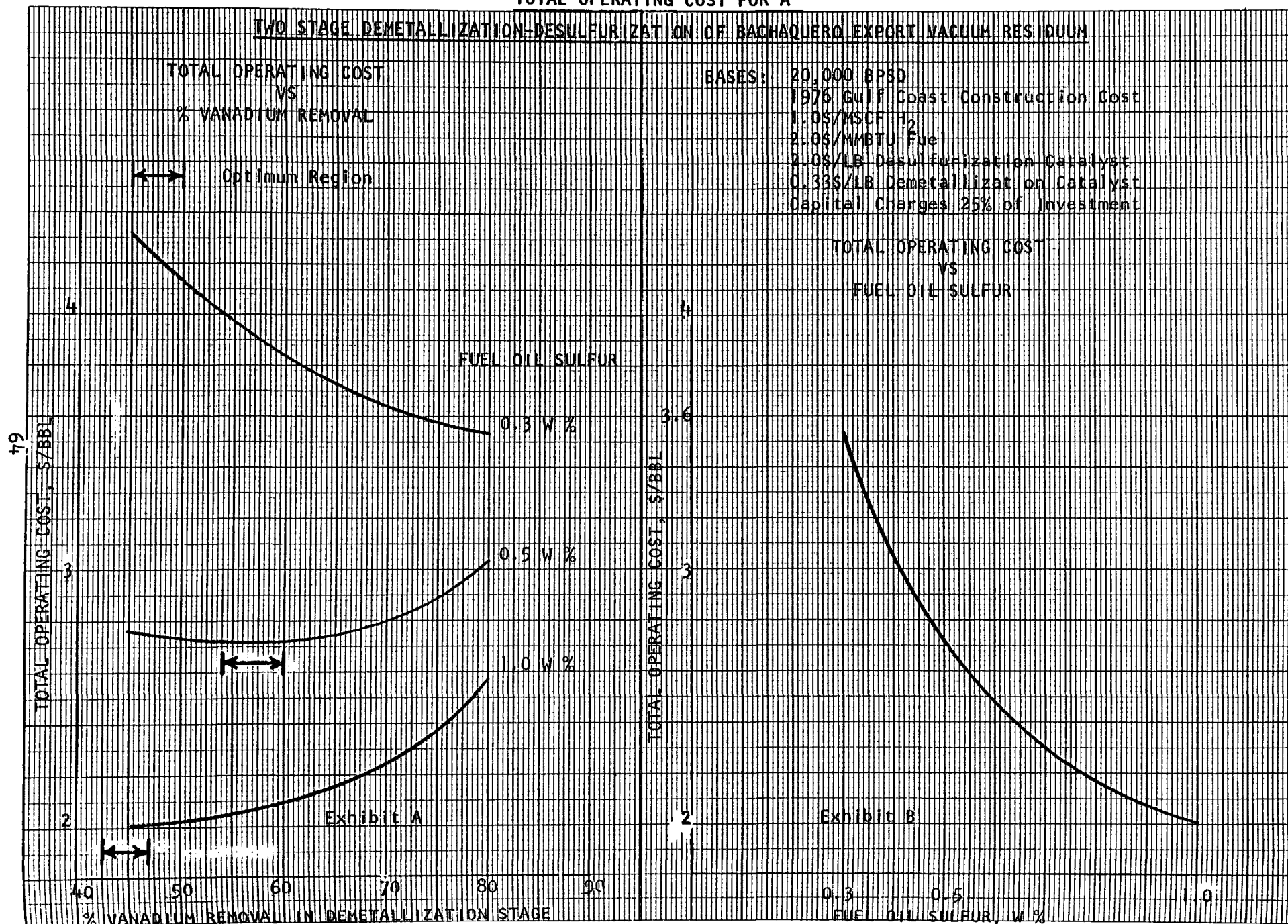


Figure 28



removal above 80 percent, due to the rapid rate of catalyst deactivation. However, the actual removal of metals beyond this level is believed to be of limited economic value since these metal compounds are hard to remove in the demetallization step and, therefore, are also not easily deposited on the desulfurization catalyst.

The variation in total operating cost as a function of fuel oil sulfur level for the Bachaquero feed is summarized in the form of a plot in Figure 28, Exhibit B. These results show that an additional cost of 71 cents per barrel was required to go from 1 to 0.5 weight percent sulfur and an additional 82¢/Bbl was required to go from 0.5 to 0.3 weight percent sulfur.

The saving in overall operating cost by the inclusion of the demetallization step in the process for the Bachaquero feed is summarized in Figure 30. The savings ranged from 44¢/Bbl for the one weight percent sulfur fuel oil to \$1.15/Bbl for the 0.3 weight percent sulfur fuel oil.

Figure 29, Exhibit A shows that for Lloydminster vacuum residuum feed (lower metals, high sulfur feed), there were also optimum demetallization levels which minimize overall costs for the production of fuel oils. The one weight percent fuel oil curve shows the optimum demetallization to be about 65 percent vanadium removal which corresponds to a total operating cost of \$2.12 per barrel. The optimum demetallization for producing 0.5 weight percent sulfur fuel oil is about 75 percent vanadium removal and corresponds to a total operating cost of \$2.64 per barrel. The optimum demetallization for producing 0.3 weight percent sulfur fuel oil is about 83 percent vanadium removal. The overall operating cost for this operation is \$3.08 per barrel.

Figure 29, Exhibit B summarized the variation in overall operating cost as a function of fuel oil sulfur levels for the Lloydminster feed. These results indicate that the incremental cost to produce 0.5 weight percent sulfur fuel oil is 52¢/Bbl over the cost to produce one weight percent sulfur fuel oil. Another incremental cost of 44¢/Bbl, over the cost of producing 0.5 weight percent sulfur fuel oil, is necessary for the production of 0.3 weight percent fuel oil.

No direct desulfurization data on Lloydminster vacuum residuum was available to make a cost comparison against a two stage demetallization/desulfurization operation.

Estimated yield structure and product properties for the

Figure 29

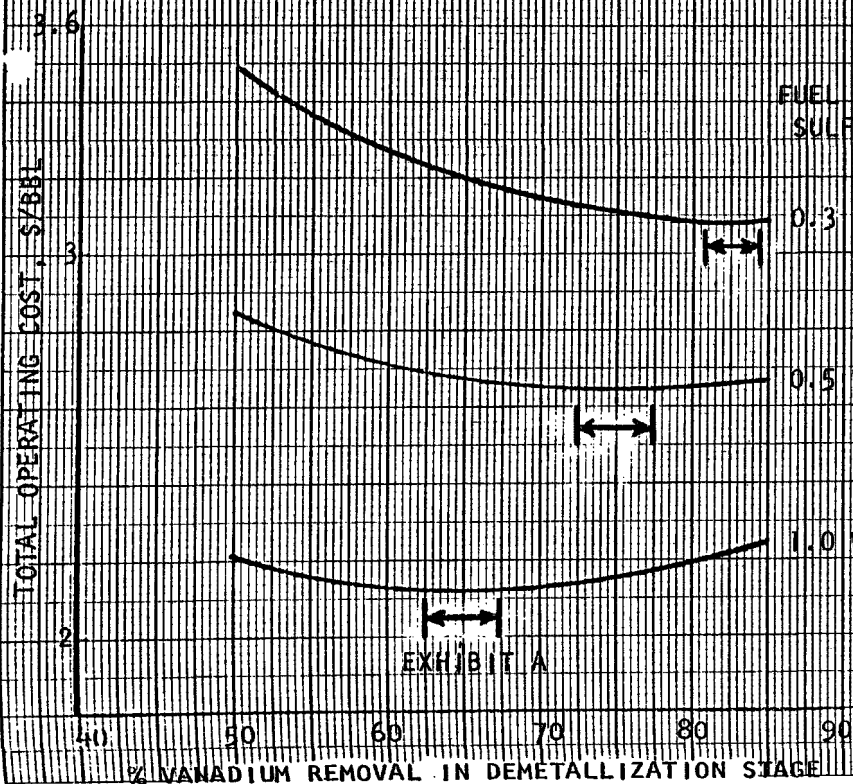
TOTAL OPERATING COST FOR A

TWO STAGE DEMETALLIZATION-DESULFURIZATION OF LLOYDMINSTER VACUUM RESIDUUM

BASES: 20,000 BPSD  
1976 Gulf Coast Construction Cost  
1.0\$/MSCF H<sub>2</sub>  
2.0\$/MMBTU Fuel  
2.0\$/LB Desulfurization Catalyst  
0.33\$/LB Demetallization Catalyst  
Capital Charges 25% of Investment

TOTAL OPERATING COST  
VS  
% VANADIUM REMOVAL

Optimum Region



TOTAL OPERATING COST  
VS  
FUEL OIL SULFUR

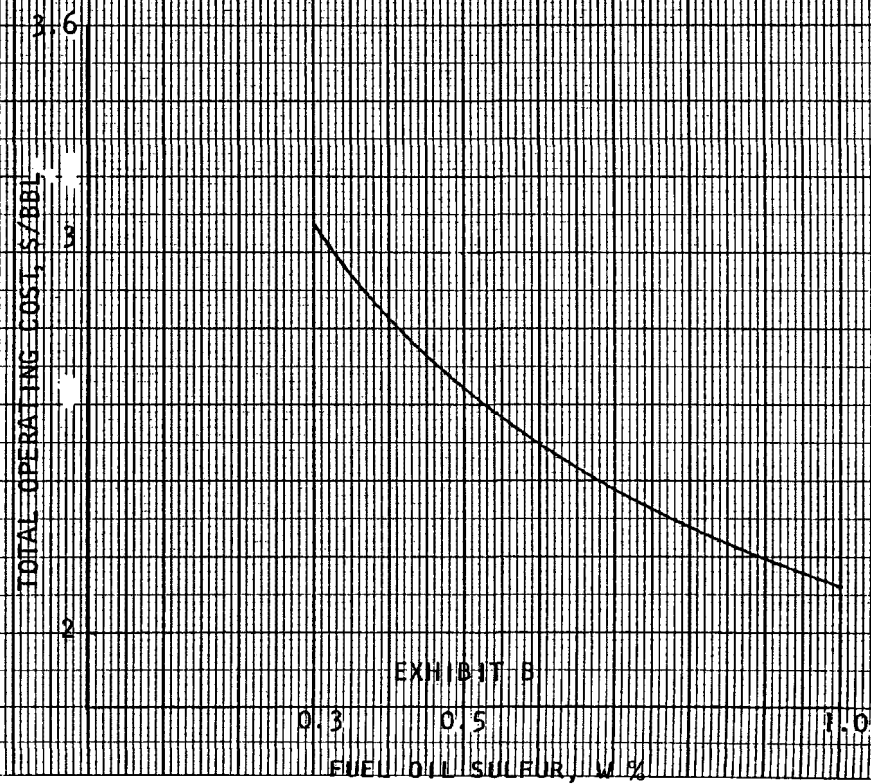
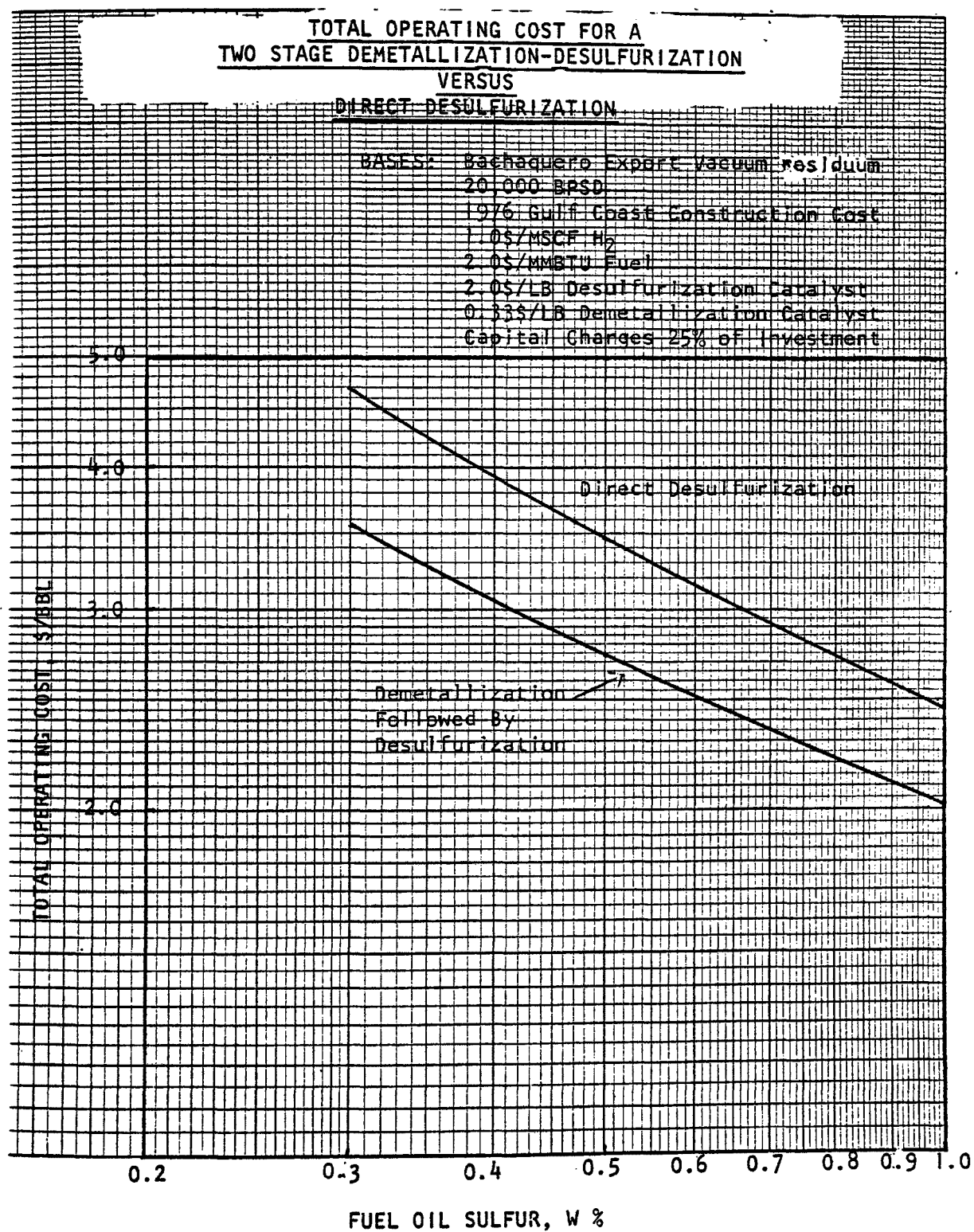


Figure 29



production of 400°F+ fuel oil containing 1.0, 0.5 and 0.3 weight percent sulfur from Bachaquero Export and Lloydminster vacuum residua are given in Table 13 and 14 respectively.

Table 13 ESTIMATED OVERALL YIELDS AND PRODUCT PROPERTIES FROM  
CONSECUTIVE DEMETALLIZATION AND DESULFURIZATION OF BACHAQUERO EXPORT VACUUM RESIDUUM

400°F+ Fuel Oil Sulfur, W %	1.0 -----				0.5 -----				0.3 -----			
<u>Yields</u>												
	<u>W%</u>	<u>V%</u>	<u>°API</u>	<u>%S</u>	<u>W%</u>	<u>V%</u>	<u>°API</u>	<u>%S</u>	<u>W%</u>	<u>V%</u>	<u>°API</u>	<u>%S</u>
H <sub>2</sub> S & NH <sub>3</sub>	2.4				3.0				3.3			
C <sub>1</sub> -C <sub>3</sub>	0.8				1.5				1.7			
<sup>69</sup> C <sub>4</sub> -400°F	1.5	2.0	60	<0.03	3.6	5.0	60	<0.03	5.1	7.0	60	<0.03
400-650°F	6.8	8.0	33	0.07	10.6	12.6	33	<0.05	12.4	14.7	33	<0.03
650-975°F	23.9	26.4	22	0.29	30.0	33.4	23	0.12	32.0	35.5	23	0.07
975°F+	65.6	67.4	11.5	1.35	52.8	54.5	12	0.81	47.1	48.8	12.5	0.53
400°F+	96.3	101.8	15.6	1.0	93.4	100.5	18.3	0.5	91.5	99	19	0.30
TOTAL	101.0	103.8	16.2	0.97	101.5	105.5	19.7	0.47	101.6	106.0	21.2	0.28

Table 14 ESTIMATED OVERALL YIELDS AND PRODUCT PROPERTIES FROM  
CONSECUTIVE DEMETALLIZATION AND DESULFURIZATION OF LLOYDMINSTER VACUUM RESIDUUM

400°F+ Fuel Oil Sulfur, W %	1.0 -----				0.5 -----				0.3 -----			
<u>Yields</u>												
	<u>W%</u>	<u>V%</u>	<u>°API</u>	<u>%S</u>	<u>W%</u>	<u>V%</u>	<u>°API</u>	<u>%S</u>	<u>W%</u>	<u>V%</u>	<u>°API</u>	<u>%S</u>
H <sub>2</sub> S & NH <sub>3</sub>	5.1				5.7				5.9			
C <sub>1</sub> -C <sub>3</sub>	1.1				1.6				2.0			
C <sub>4</sub> -400	1.7	2.2	55	<0.03	2.2	3.0	55	<0.03	2.7	3.6	55	<0.03
400-650°F	8.0	9.4	30	<0.03	11.3	13.3	30	<0.03	13.2	15.6	31	<0.03
650-975°F	34.4	38.0	21	0.28	39.3	43.5	21	0.19	43.0	47.9	22	0.14
975°F+	51.0	52.7	11	1.64	41.5	43.2	12	0.92	34.9	36.6	13	0.59
400°F+	93.4	100.1	16.3	1.0	92.1	100.0	18.2	0.5	91.1	100.1	20	0.3
TOTAL	101.3	102.3	16.9	0.98	101.6	103.0	19.2	0.49	101.7	103.7	21.0	0.29

## APPENDICES





APPENDIX A

SUMMARY OF DEMETALLIZATION RUNS



Table A SUMMARY OF DEMETALLIZATION RUNS

Run No.-Period	Catalyst HRI No.	Catalyst Base	Catalyst Promoter	Preparation	Feed	Temp. °F	H <sub>2</sub> Pres. psig	Space Velocity		H <sub>2</sub> Rate SCF/Bbl	Cat. Age. Bbl/Lb	Product Inspections				
								V/Hr/Vr	B/D/Lb			Gravity °API	% S	V ppm	NI ppm	IBP- 550°F V %
115-1233-1C	3634	Porocel	1% Mo	Engelhard	Bachaquero	789	2030	1.47	.111	4300	.136	12.8	2.09	310	65	3
2A		20 x 50 Mesh		Commercial	Export	791	2020	1.44	.109	4580	.190					
2B					Vacuum	791	2020	1.52	.115	4580	.248	12.7	2.01	311	67	1
3A					Residuum	789	1990	1.54	.117	3920	.307					
3B					L-397	789	1990	1.51	.114	3920	.364	12.5	2.01	315	65	1
4A						790	2000	1.50	.114	4370	.421					
4B						790	2000	1.48	.112	4370	.477	12.1	2.00	310	63	6
5A						790	2000	1.49	.113	3950	.534					
5B						790	2000	1.46	.110	3950	.589	11.6	2.02	308	63	7
6A						792	1950	1.32	.100	3650	.639	12.0	1.97	307	67	6
75 115-1237-18	3634	Porocel	1% Mo	Engelhard	Bachaquero	775	1990	.52	.040	6280	.024	12.7	1.87	216	49	6
2		20 x 50 Mesh		Commercial	Export	774	2000	.48	.036	6440	.072	15.5	1.50	206	48	6
3					Vacuum	778	2015	.51	.039	5100	.111	16.1	1.52	199	49	4
4					Residuum	778	2000	.49	.037	5570	.148	16.4	1.41	172	46	7
115-1238-18	3634	Porocel	1% Mo	Engelhard	Bachaquero	792	2010	.50	.037	4320	.031	16.0	1.50	149	40	3
2		20 x 50 Mesh		Commercial	Export	790	2005	.51	.038	4240	.069	16.1	1.38	161	45	7
3					Vacuum	791	2000	.51	.038	4780	.107	15.5	1.35	175	49	8
4					Residuum	790	2000	.51	.038	4500	.145	14.9	1.41	186	55	2
5						789	2000	.53	.040	3750	.185	15.6	1.40	180	50	5
6						789	1990	.53	.040	4250	.225	15.0	1.37	189	52	6
7						792	2005	.52	.039	4150	.264	12.5	1.37	188	52	6
8						790	2015	.51	.038	4190	.302	13.6	1.39	177	51	4
9						790	2000	.52	.039	4430	.341	15.1	1.37	175	51	4
10						790	2000	.51	.038	4240	.379	15.0	1.43	183	51	5
11						791	2000	.53	.040	4220	.419	15.1	1.46	181	51	5
12						790	2000	.51	.038	4390	.457	15.0	1.36	187	50	6
13						790	2010	.51	.038	4090	.495	14.0	1.44	186	55	6
14						790	2000	.50	.037	3600	.532	15.9	1.33	184	55	10
15						788	2010	.51	.039	4290	.571	15.7	1.38	199	49	9
16						790	2000	.51	.038	3960	.609	13.7	1.34	203	49	9
17						790	2015	.49	.037	3920	.646	15.4	1.35	209	50	8
18						790	2020	.48	.036	4580	.682	16.0	1.38	207	49	10
19						790	2000	.51	.038	4190	.720	15.8	1.33	214	51	8
20						791	2010	.51	.038	4200	.758	15.6	1.52	219	52	7

Table A SUMMARY OF DEMETALLIZATION RUNS

Run No.-Period	Catalyst HRI No.	Catalyst Base	Catalyst Promoter	Preparation	Feed	Temp. °F	H <sub>2</sub> Pres. psig	Space Velocity		H <sub>2</sub> Rate SCF/Bbl	Cat. Age. Bbl/Lb	Product Inspections				
								V/Hr/Vr	B/D/Lb			Gravity °API	% S	V ppm	NI ppm	IBP- 550°F V %
115-1239-18	3634	Porocel	1% Mo	Engelhard	Bachaquero	790	2010	.52	.039	4450	.030	16.0	1.40	137	37	8
2		20 x 50 Mesh		Commercial	Export	790	2000	.51	.039	4620	.069	16.5	1.51	158	44	8
3					Vacuum	793	2005	.50	.038	4560	.107	17.2	1.24	136	41	10
4					Residuum	790	2030	.48	.037	4680	.144	16.4	1.51	250	46	12
5					L-397	790	2000	.50	.038	4190	.182	16.8	1.24	214	45	11
6						790	2010	.50	.038	3970	.220	17.5	1.29	203	44	9
7						790	2015	.50	.038	3880	.258	16.8	1.39	202	46	9
8						789	1995	.51	.039	3500	.297	16.5	1.33	205	46	9
9						789	1985	.52	.039	4050	.336	16.0	1.53	201	49	8
10						790	2000	.49	.038	3920	.374	16.7	1.21	209	49	9
11						790	2000	.50	.038	4590	.424	16.2	1.23	218	51	6
12						790	2000	.49	.038	4130	.462	16.8	1.32	213	49	7
13						790	1990	.43	.033	4050	.495	17.1	1.28	206	52	9
14						790	1990	.35	.026	4720	.521	17.6	1.18	163	46	9
15						792	1990	.36	.028	4300	.549	18.1	1.19	157	44	8
16						790	1990	.34	.026	4450	.575	17.5	1.14	157	45	12
17						790	1990	.34	.026	5030	.601	16.5	1.13	161	45	13
18						790	1990	.35	.027	4130	.628	17.4	1.13	162	45	13
19						790	2000	.33	.026	5660	.654	17.2	1.21	173	45	18
20						791	2000	.35	.027	4740	.681	17.4	1.52	283	53	12
21						790	2010	.34	.026	4640	.707	16.6	1.51	284	52	16
22						792	2000	.36	.027	5340	.734					
115-1240-18	3634	Porocel	1% Mo	Engelhard	Bachaquero	789	1990	.30	.023	6170	.016	17.5	.99	84	27	11
2		20 x 50 Mesh		Commercial	Export	790	1975	.29	.022	4840	.039	18.6	.87	62	25	12
3					Vacuum	790	2000	.30	.022	5220	.061	17.9	.89	81	31	12
4					Residuum	790	1995	.29	.022	5040	.083	18.4	.90	99	35	11
5						790	1990	.30	.023	4310	.106	18.1	1.00	98	34	11
6						790	2000	.29	.022	5070	.128	18.4	.93	96	34	12
7						790	2000	.30	.023	5670	.151	18.3	.94	109	36	12
8						791	2005	.30	.023	4570	.174	16.8	.98	102	38	14
9						790	2010	.29	.022	5080	.196	16.9	.98	95	38	13

Table A SUMMARY OF DEMETALLIZATION RUNS

Run No.-Period	Catalyst HRI No.	Catalyst Base	Catalyst Promoter	Preparation	Feed	Temp. °F	H <sub>2</sub> Pres. psig	Space Velocity		H <sub>2</sub> Rate SCF/Bbl	Cat. Age Bbl/Lb	Product Inspections				
								V/Hr/Vr	B/D/Lb			Gravity °API	% S	V ppm	NI ppm	IBP- 550°F V %
115-1241-1B	3634	Porocel	1% Mo	Engelhard	Bachaquero	789	2000	.35	.026	5590	.018	17.9	1.12	76	26	8
2		20 x 50 Mesh		Commercial	Export	790	2015	.31	.024	4580	.042	19.0	.89	75	26	15
3					Vacuum	789	2015	.32	.024	4310	.066	17.9	.94	87	30	10
4					Residuum	790	1995	.32	.024	4090	.090	18.5	.97	91	30	11
5						789	2000	.33	.025	3260	.103	17.6	1.04	99	35	12
115-1242-1B	3634	Porocel	1% Mo	Engelhard	Bachaquero	791	2000	.53	.040	3730	.021	18.0	1.11	84	28	8
2		20 x 50 Mesh		Commercial	Export	791	1980	.30	.023	5880	.044	19.8	.83	64	27	12
3					Vacuum	788	2000	.30	.022	5310	.066	17.5	.87	89	31	13
4					Residuum	790	2005	.28	.021	4470	.087	18.2	.78	92	32	12
5*						789	2010	.29	.022	5300	.109	17.0	1.02	100	32	13
6A								.34	.026		.207					
6B						790	2010	.29	.022	5040	.271	17.6	1.52			10
7						790	2005	.31	.023	4690	.294	17.7	1.13			15
8						790	2000	.31	.023	5590	.317					
115-1243-1B	3634	Porocel	1% Mo	Engelhard	Bachaquero	791	2005	.31	.023	4270	.018	18.4	1.07	103	28	11
2		20 x 50 Mesh		Commercial	Export	791	2005	.31	.023	5240	.041	18.7	.88	79	29	12
3					Vacuum	790	2010	.31	.024	5060	.065	18.2	.97	88	30	13
4					Residuum	790	2000	.30	.023	6210	.077	16.9	1.00	104	32	11
115-1244-1B	3634	Porocel	1% Mo	Engelhard	Bachaquero	769	1990	.25	.019	6890	.024	17.6	1.09			9
2		20 x 50 Mesh		Commercial	Export	770	2000	.25	.019	6150	.043	16.8	.99	120	33	9
3					Vacuum	770	1995	.25	.019	5450	.062	17.2	1.09	118	35	11
4					Residuum	770	2000	.25	.019	5260	.081	16.7	1.07	124	35	9
5						770	1985	.25	.019	7500	.100	16.5	1.15	152	43	10
6						770	1975	.25	.019	6450	.119	17.2	1.11	143	42	8
7						780	1990	.25	.019	5910	.138	17.1	1.00	131	41	10
8						780	2000	.25	.019	5570	.157	17.1	.88	118	44	10

\* After Period 5, the Unit was on Wash for 8 hours.

Table A SUMMARY OF DEMETALLIZATION RUNS

Run No.-Period	Catalyst HRI No.	Catalyst Base	Catalyst Promoter	Preparation	Feed	Temp. °F	H <sub>2</sub> Pres. psig	Space Velocity		H <sub>2</sub> Rate SCF/Bbl	Cat. Age Bbl/Lb	Product Inspections				
								V/Hr/Vr	B/D/Lb			Gravity °API	% S	V ppm	NI ppm	IBP- 550°F V %
115-1248-1B	3634	Porocel 20 x 50 Mesh	1 %	Engelhard Commercial	Lloydminster	792	2020	1.54	.115	3970	.069	13.3	2.12	46	51	4
2A					Vacuum	791	2020	1.50	.112		.125					
2B					Residuum	791	2020	1.49	.111	3770	.181	13.6	2.15	42	47	8
3A					HRI 3744	788	2010	1.65	.123		.243					
3B						788	2010	1.87	.140	4300	.313	15.2	2.61	57	48	4
4A						791	2000	1.93	.144		.385					
4B						791	2000	1.86	.139	3870	.455	15.5	2.42	58	49	8
5A						790	2000	1.93	.144		.527					
5B						790	2000	1.98	.148	4640	.601	16.5	2.63	62	48	4
6A						792	1950	2.09	.156		.679					
6B						792	1950	2.06	.154	4200	.756	13.8	2.71	61	61	8
7A						790	2010	2.06	.154		.833					
7B						790	2010	2.03	.152	4320	.909	12.4	2.75	68	48	10
8A						791	2000	2.02	.151		.985					
8B						791	2000	2.00	.150	4240	1.060	12.7	2.76	67	47	8
9A						789	2000	1.97	.147		1.134					
9B						789	2000	2.00	.149	4240	1.209	12.8	2.92	67	55	6
115-1249-1B	3634	Porocel 20 x 50 Mesh	1 %	Engelhard Commercial	Lloydminster	790	2015	.80	.061	3700	.043	16.7	1.50	22	25	6
2					Vacuum	789	2000	.77	.059	4110	.102	17.5	1.45	24	30	6
3					Residuum	791	2010	.77	.059	4660	.161	16.8	1.40	20	29	9
4						774	2010	.77	.059	4110	.220	16.1	1.73	36	33	6
5						792	2000	.77	.059	4170	.279	15.9	1.68	35	33	8
6						786	2000	.78	.060	4550	.339	17.4	1.27	34	33	6
7						786	1995	.76	.058	4150	.397	16.5	1.73	31	32	5
8						788	1990	.63	.048	3650	.445	17.6	1.64	27	31	7
9						791	1985	.62	.048	4260	.493	17.7	1.59	21	31	7
10						791	1980	.62	.048	4190	.541	17.0		20	29	7
11						790	2000	.63	.048	5160	.589	15.7	1.82	30	37	5
12						791	2000	.67	.051	4320	.640	16.1	1.79	27	39	7
13						792	2025	.67	.051	5630	.691	15.8	1.88	39	43	8

APPENDIX A-1

DEMETALLIZATION OPERATING CONDITIONS, YIELDS AND PRODUCT PROPERTIES





DEMETALLIZATION

Table A-1. OPERATING CONDITIONS, YIELDS, AND PRODUCT PROPERTIES

Run Number	115-1233-5B
Catalyst Age, BBL/LB	0.59
Feed	Bachaquero Export Vacuum Residuum

HRI Identification No.	L-397
Catalyst	(7.6 °API, 3.08 W% S) Engelhard Commercial (20 x 50 Mesh Porocel - 1% Mo)
HRI No.	

OPERATING CONDITIONS

Hydrogen Pressure, psig	2000
Temperature, °F	790
Liquid Space Velocity, $V_F/Hr/V_R$	1.46
Catalyst Space Velocity, B/D/LB	0.11
Reactor Type	Two-Stage Downflow
Hydrogen Rate, SCF/BBL	3950
Hydrogen Consumption, SCF/BBL	320
975°F+ Conversion, V %	14.3

<u>YIELDS</u>	<u>W %</u>	<u>V %</u>
H <sub>2</sub> S & NH <sub>3</sub>	1.07	
C <sub>1</sub> -C <sub>3</sub>	0.23	
C <sub>4</sub> -650°F	4.35	5.24
650-975°F	18.17	19.67
975°F+	76.66	77.17
Total	100.48	
C <sub>4</sub> +	99.17	102.08
Gravity, °API	11.7	
Sulfur, W %	2.07	

<u>FRACTION, °F</u>	<u>Coll. Liq.</u>	<u>IBP- 650°F</u>	<u>650°F+ 650°F</u>	<u>650- 975°F</u>	<u>975°F+ 975°F</u>	<u>975- 1050°F</u>	<u>1050°F+ 1050°F</u>
V % on Collected Liquid	100	5.0	95	19.3	75.7	9.52	66.18
Gravity, °API	11.6	34.5	10.4	19.2	8.0	18.8	7.3
Sulfur, W %	2.02	0.37	2.13	1.18	2.37	1.30	2.37
Carbon, W %	86.23						
Hydrogen, W %	11.05						
H/C Atomic Ratio	1.53						
Nitrogen, ppm	5394						
Aniline Point, °F				179			
Flash Point, °F			550				
Pour Point, °F			65				
RCR, W %	16.8				20.2		22.1
Vanadium, ppm	292						453
Nickel, ppm	46						90
Viscosity, SFS @210°F			438				
SFS @250°F			103				
Asphaltenes, W %							
Sulfur, W %	3.93						
Vanadium, ppm	269						
Nickel, ppm	70						
Asphaltene - free oil							
Vanadium, ppm	30						
Nickel, ppm	12						

# DEMETALLIZATION

Table A-2. OPERATING CONDITIONS, YIELDS, AND PRODUCT PROPERTIES

Run Number	115-1238-4
Catalyst Age, BBL/LB	0.14
Feed	Bachaquero Export Vacuum Residuum
HRI Identification No.	L-397
	(7.6 °API, 3.07 W % S)
Catalyst	Engelhard Commercial
	(20 x 50 Mesh Porocel - 1% Mo)
HRI No.	3634

## OPERATING CONDITIONS

Hydrogen Pressure, psig	2000
Temperature, °F	790
Liquid Space Velocity, V/Hr/V	0.51
Catalyst Space Velocity, B/D/LB	0.04
Reactor Type	Two-stage-Downflow
Hydrogen Rate, SCF/BBL	4500
Hydrogen Consumption, SCF/BBL	400
975 °F + Conversion, V %	18.7

<u>YIELDS</u>	<u>W %</u>	<u>V %</u>
H <sub>2</sub> S & NH <sub>3</sub>	2.00	
C <sub>1</sub> -C <sub>3</sub>	1.58	
C <sub>4</sub> -650°F	7.20	8.88
650-975°F	18.50	20.33
975°F+	71.31	73.17
Total	100.59	102.38
C <sub>4</sub> +	97.01	
Gravity, °API		15.3
Sulfur, W %	1.30	

<u>FRACTION, °F</u>	<u>Coll.</u> <u>Liq.</u>	<u>IBP-</u> <u>650°F</u>	<u>650°F+</u>	<u>650-</u> <u>975°F</u>	<u>975°F+</u>
V % on Collected Liquid	100	8.0	92.0	20.0	72.0
Gravity, °API	14.9	35.1	11.6	20.2	10.2
Sulfur, W %	1.41	0.13	1.81	0.67	1.57
Carbon, W %	87.75				
Hydrogen, W %	11.21				
H/C Atomic Ratio	1.52				
Nitrogen, ppm	4878				
Aniline Point, °F		140		172	
Flash Point, °F					
Pour Point, °F			535		
RCR, W %			70		
Vanadium, ppm					18.6
Nickel, ppm	186				
	55				
Bromine No., cgs/gm		10.5			
Viscosity, SFS @210°F				130	
SFS @250°F				49	

# DEMETALLIZATION

Table A-3. OPERATING CONDITIONS, YIELDS, AND PRODUCT PROPERTIES

Run Number	115-1238-14
Catalyst Age, BBL/LB	0.53
Feed	Bachaquero Export Vacuum Residium

HRI identification No.	L-397
Catalyst	(7.6 °API, 3.08 W % S) Engelhard Commercial (20 x 50 Mesh Porocel - 1% Mo)
HRI No.	3634

OPERATING CONDITIONS

Hydrogen Pressure, psig	2000
Temperature, °F	790
Liquid Space Velocity, $V_F/Hr/V_R$	0.50
Catalyst Space Velocity, B/D/LB	0.04
Reactor Type	Two-Stage Downflow
Hydrogen Rate, SCF/BBL	3600
Hydrogen Consumption, SCF/BBL	620
975°F+ Conversion, V %	16.6

<u>YIELDS</u>	<u>W %</u>	<u>V %</u>
H <sub>2</sub> S & NH <sub>3</sub>	2.00	
C <sub>1</sub> -C <sub>3</sub>	1.45	
C <sub>4</sub> -650°F	8.03	9.97
650-975°F	16.50	18.51
975°F+	72.95	75.07
Total	100.93	
C <sub>4</sub> +	97.48	103.55
Gravity, °API		16.3
Sulfur, W %	1.32	

<u>FRACTION, °F</u>	<u>Coll. Liq.</u>	<u>IBP- 650°F</u>	<u>650°F+</u>	<u>650- 975°F</u>	<u>975°F+</u>
V % on Collected Liquid	100	9.0	91.0	18.0	73.0
Gravity, °API	15.9	36	14.2	23.4	10.2
Sulfur, W %	1.33	0.16	1.45	0.64	1.61
Carbon, W %	86.15				
Hydrogen, W %	11.28				
H/C Atomic Ratio	1.56				
Nitrogen, ppm	4364				
Bromine No., cgs/gm		8.5			
Aniline Point, °F		140		173	
Flash Point, °F			515		
Pour Point, °F			60		
RCR, W %					18.4
Vanadium, ppm	184				
Nickel, ppm	55				
Viscosity, SFS @250°F			44		

# DEMETALLIZATION

Table A-4. OPERATING CONDITIONS, YIELDS AND PRODUCT PROPERTIES

Run Number	115-1240-3
Catalyst Age, BBL/LB	0.06
Feed	Bachaquero Export Vacuum Residuum
HRI Identification No.	L-397
Catalyst	(7.6 °API, 3.08 W %) Engelhard Commercial (20 x 50 Mesh Porocel - 1% Mo)
HRI No.	3634

## OPERATING CONDITIONS

Hydrogen Pressure, psig	2000
Temperature, °F	790
Liquid Space Velocity, $V_F/Hr/V_R$	0.3
Catalyst Space Velocity, B/D/LB	0.02
Reactor Type	Two-Stage Downflow
Hydrogen Rate, SCF/BBL	5220
Hydrogen Consumption, SCF/BB1	720
975°F+ Conversion V %	29.3

## YIELDS

	<u>W %</u>	<u>V %</u>
H <sub>2</sub> S & NH <sub>3</sub>	2.46	
C <sub>1</sub> -C <sub>3</sub>	0.53	
C <sub>4</sub> -650°F	13.50	15.54
650-975°F	22.99	25.47
975°F+	61.58	63.61
Total	101.06	
C <sub>4</sub> +	98.08	105.62
Gravity, °API		18.3
Sulfur, W %	0.97	

<u>FRACTION, °F</u>	<u>Coll.</u> <u>Liq.</u>	<u>IBP-</u> <u>650°F</u>	<u>650°F+</u>	<u>650-</u> <u>975°F</u>	<u>975°F+</u>
V % on Collected Liquid	100	15.0	85.0	24.3	60.7
Gravity, °API	17.9	35.5	15.2	21.5	11.2
Sulfur, W %	0.89	0.07	1.12	0.59	1.30
Carbon, W %	86.50				
Hydrogen, W %	11.54				
H/C Atomic Ratio	1.59				
Nitrogen, ppm	3467				
Bromine No., cgs/gm		9.4			
Aniline Point, °F		140		170	
Flash Point, °F			485		
Pour Point, °F			40		
RCR, W %					17.8
Vanadium, ppm	81				122
Nickel, ppm	31				46
Viscosity, SFS @ 122°F			1420		
—SFS @ 210°F			57		230

# DEMETALLIZATION

Table A-5. OPERATING CONDITIONS, YIELDS, AND PRODUCT PROPERTIES

Run Number	115-1240-8
Catalyst Age, BBL/LB	0.17
Feed	Bachaquero Export Vacuum Residuum
HRI identification No.	L-397
Catalyst	(7.6 °API, 3.08 W % S) Engelhard Commercial (20 x 50 Mesh Porocel - 1% Mo)
HRI No.	3634

## OPERATING CONDITIONS

Hydrogen Pressure, psig	2000
Temperature, °F	791
Liquid Space Velocity, $V_F/Hr/V_R$	0.30
Catalyst Space Velocity, B/D/LB	0.02
Reactor Type	Two-Stage Downflow
Hydrogen Rate, SCF/BBL	4570
Hydrogen Consumption, SCF/BBL	634
975°F+ Conversion, V %	32.11

<u>YIELDS</u>	<u>W %</u>	<u>V %</u>
H <sub>2</sub> S & NH <sub>3</sub>	2.28	
C <sub>1</sub> -C <sub>3</sub>	0.52	
C <sub>4</sub> -650°F	11.93	14.66
650-975°F	26.25	29.15
975°F+	59.96	61.10
Total	100.94	
C <sub>4</sub> +	98.13	104.91
Gravity, °API		17.2
Sulfur, W %	0.98	

<u>FRACTION, °F</u>	<u>Coll. Liq.</u>	<u>IBP- 650°F</u>	<u>650°F+</u>	<u>650- 975°F</u>	<u>975°F+</u>
V % on Collected Liquid	100	13.3	86.7	28.0	58.7
Gravity, °API	16.8	35.5	13.7	21.6	9.0
Sulfur, W %	0.98	0.13	1.25	0.57	1.36
Carbon, W %	86.24				
Hydrogen, W %	11.41				
H/C Atomic Ratio	1.58				
Nitrogen, ppm	4585				
Bromine No., cgs/gm		13.2			
Aniline Point, °F		142		168	
Flash Point, °F			510		
Pour Point, °F			55		
RCR, W %					19.1
Vanadium, ppm	102				
Nickel, ppm	38				
Viscosity, SFS @122°F			1587		
SFS @210°F			60		425

# DEMETALLIZATION

Table A-6. OPERATING CONDITIONS, YIELDS, AND PRODUCT PROPERTIES

Run Number	115-1248-9B
Catalyst Age, BBL/LB	1.21
Feed	Lloyminster Vacuum Residuum
HRI Identification No.	3744
	(6.4 °API, 5.4 W % S)
Catalyst	Engelhard Commercial
	(20 x 50 Mesh Porocel - 1% Mo)
HRI No.	3634

## OPERATING CONDITIONS

Hydrogen Pressure, psig	2000
Temperature, °F	789
Liquid Space Velocity, V <sub>F</sub> /Hr/V <sub>R</sub>	2.00
Catalyst Space Velocity, B/D/LB	0.15
Reactor Type	Two-stage Downflow
Hydrogen Rate, SCF/BBL	4240
Hydrogen Consumption, SCF/BBL	420
975°F+, Conversion, V %	16.6

<u>YIELDS</u>	<u>W %</u>	<u>V %</u>
H <sub>2</sub> S & NH <sub>3</sub>	2.99	
C <sub>1</sub> -C <sub>3</sub>	0.49	
C <sub>4</sub> -650°F	5.74	6.95
650-975°F	26.23	28.74
975°F+	65.17	66.01
Total	100.62	
C <sub>4</sub> +	97.14	101.70
Gravity, °API		12.9
Sulfur, W %	2.92	

<u>FRACTION, °F</u>	<u>Coll. Liq.</u>	<u>IBP- 650°F</u>	<u>650°F+</u>	<u>650- 975°F</u>	<u>975°F+</u>
V % on Collected Liquid	100	6.7	93.3	28.3	65.0
Gravity, °API	12.8	32.8	10.2	18.0	6.7
Sulfur, W %	2.92	0.72	3.05	1.45	3.67
Carbon, W %	85.57				
Hydrogen, W %	11.05				
H/C Atomic Ratio	1.54				
Nitrogen, ppm	4080				
Aniline Point, °F		131		163	
Flash Point, °F			510		
Pour Point, °F			65		
RCR, W %					16.9
Vanadium, ppm	67				
Nickel, ppm	55				
Viscosity, SFS @210°F			144		

# DEMETALLIZATION

Table A-7. OPERATING CONDITIONS, YIELDS, AND PRODUCT PROPERTIES

Run Number	115-1249-9
Catalyst Age, BBL/LB	0.49
Feed	Lloydminster Vacuum Residuum
HRI Identification No.	3744
Catalyst	(6.4 °API, 5.4 W % S) Engelhard Commercial 20 x 50 Mesh Porocel - 1% Mo)
HRI No.	3634

## OPERATING CONDITIONS

Hydrogen Pressure, psig	1980
Temperature, °F	791
Liquid Space Velocity, $V_F/Hr/V_R$	0.62
Catalyst Space Velocity, B/D/LB	0.05
Reactor Type	Downflow
Hydrogen Rate, SCF/BBL	3960
Hydrogen Consumption, SCF/BBL	640
975°F+ Conversion, V %	30.9

<u>YIELDS</u>	<u>W %</u>	<u>V %</u>
H <sub>2</sub> S & NH <sub>3</sub>	4.46	
C <sub>1</sub> -C <sub>3</sub>	0.54	
C <sub>4</sub> -650°F	10.97	13.63
650-975°F	33.17	35.57
975°F+	51.80	34.65
Total	100.94	
C <sub>4</sub> +	95.94	103.86
Gravity, °API		17.8
Sulfur, W %	1.59	

<u>FRACTION, °F</u>	<u>Coll. Liq.</u>	<u>IBP- 650°F</u>	<u>650°F+</u>	<u>650- 975°F</u>	<u>975°F+</u>
V % on Collected Liquid	100	13	87	34.3	52.7
Gravity, °API	17.7	32.9	10.8	19.7	8.5
Sulfur, W %	1.59	0.14	1.63	0.74	2.27
Carbon, W %	86.13				
Hydrogen, W %	11.35				
H/C Atomic Ratio	1.57				
Nitrogen, ppm	3360				
Aniline Point, °F		137		167	
Flash Point, °F			475		
Pour Point, °F			60		
RCR, W %					17.2
Vanadium, ppm	21				
Nickel, ppm	31				
Viscosity, SFS @210°F			42		





APPENDIX B

SUMMARY OF DESULFURIZATION RUNS



Table B SUMMARY OF DESULFURIZATION RUNS

Run No.-Period	Catalyst HRI No.	Catalyst Base	Demetallized Feed	Demetallized Over	Temp. °F	Hydrogen Pressure psig	Space Velocity		Hydrogen Rate SCF/Bbl	Catalyst Age Bbl/Lb	Product Inspections				
							V/Hr/Vr	B/D/Lb			Gravity °API	% S	V ppm	Ni ppm	IBP-550°F V %
184-194-1B	3104	Amer. Cy. 0.02" Beads	Bachaquero Export Vacuum Residuum L-400	Comm. Demet. Catalyst HRI 3634	756 760 761 761 762 760 761 762 760 759 760 760 763 762 762 751 760 759 757 756	1960 2025 2005 2000 2010 2000 2000 1990 1975 1990 1950 1985 2000 2000 2000 2000 2000 1995 2010 2025	1.13 1.06 1.03 1.00 .95 .99 1.02 1.05 .94 1.04 1.05 1.03 1.15 1.11 1.05 1.02 1.05 1.10 1.04 1.07	.121 .113 .110 .107 .101 .105 .109 .112 .100 .111 .112 .110 .123 .119 .112 .109 .112 .118 .111 .114	4500 4460 4040 4210 4400 4820 4690 4150 4260 4270 4770 5080 4190 4270 4780 4820 3950 3900 3900 4270	.083 .196 .306 .413 .514 .619 .728 .840 .940 1.051 1.163 1.273 1.396 1.515 1.627 1.736 1.848 1.966 2.077 2.191	14.2 15.5 15.5 15.3 15.1 14.9 14.7 15.7 15.5 16.4 16.4 15.9 16.2 16.2 16.6 16.5 16.3 16.0 15.5 14.0	1.31 .69 .68 .80 .69 .75 .75 .82 .82 .82 .83 .84 .83 .91 .93 .97 .90 .86 .91 .91	230 240 236 231 229 248 248 245 215 216 217 220 221 260 253 254 254 254 260 263	43 44 42 42 47 48 49 49 47 47 47 46 50 54 54 54 59 59 54	1 6 4 4 6 2 1 1 1 1 1 1 1 1 4 1 1 1 2 5
184-195-1B	3104	Amer. Cy. 0.02" Beads	Bachaquero Export Vacuum Residuum L-401	Comm. Demet. Catalyst HRI 3634	761 759 761 761 760 761 759 762 761 761 760 762 762 760 758 760 761 759 762 760	2020 2010 2000 2005 2000 1990 2010 2020 2025 2015 2005 2010 2000 2005 2010 2025 2000 2005 2010 1985	1.19 1.22 1.11 1.07 1.01 1.11 0.99 1.12 1.05 1.03 1.06 1.03 1.09 1.05 1.06 .97 1.05 1.12 1.16	.127 .131 .119 .114 .108 .119 .106 .120 .112 .110 .113 .110 .117 .112 .113 .103 .112 .120 .099 .124	3860 3660 4340 4310 3710 4050 4430 3580 4980 4910 4050 4660 3980 4030 4280 4360 4300 3880 5110 2.272	.110 .241 .360 .474 .582 .701 .807 .927 1.039 1.149 1.262 1.372 1.489 1.601 1.714 1.817 1.929 2.049 2.148 2.272	16.9 17.5 17.0 16.7 16.3 15.8 15.9 16.8 16.6 16.7 17.2 16.7 15.8 17.6 17.4 17.8 17.2 17.4 17.1 16.4	.59 .64 .63 .69 .67 .59 .57 .64 .66 .65 .65 .68 .59 .69 .68 .71 .60 .63 .64 .68	148 155 154 153 153 158 152 169 168 168 168 161 168 159 159 164 164 164	39 40 41 45 45 40 41 40 41 41 38 37 37 39	4 6 6 8 7 5 9 6 5 5 4 6 6 5 5 5 5 5 5 4

Table B SUMMARY OF DESULFURIZATION RUNS

Run No.-Period	Catalyst HRI No.	Catalyst Base	Demetallized Feed	Demetallized Over	Temp. °F	Hydrogen Pressure psig	Space Velocity		Hydrogen Rate SCF/Bbl	Catalyst Age Bbl/Lb	Product Inspections				
							V/Hr/Vr	B/D/Lb			Gravity °API	% S	V ppm	NI ppm	IBP-550°F V %
184-196-18	3104	Amer. Cy.	Bachaquero	Comm. Demet.	760	1950	.32	.034	4970	.029	20.6	.45	95	25	9
2		0.02" Beads	Export	Catalyst	760	2010	.57	.061	3980	.089	19.2		118	27	8
3			Vacuum	HRI 3634	760	2000	.54	.057	4390	.146	18.5	.38	118	30	12
4			Residuum		762	2000	.53	.057	3860	.203	19.4	.37	124	29	9
5			L-405		760	2010	.53	.056	3810	.258	20.2	.45	129	35	9
6					759	2000	.52	.055	4150	.313	19.6	.43	133	35	7
7					760	1995	.55	.058	3730	.371	23.7	.51	130	39	10
8					760	2000	.53	.056	4220	.424	19.2	.44	131	39	12
9					759	2000	.54	.055	4200	.478	19.8	.39	142	40	11
10					760	1990	.54	.055	4400	.532	19.8	.37	144	39	9
11					762	2010	.52	.054	3780	.584	21.1	.39	135	37	10
12					760	2000	.53	.055	4560	.637	19.4	.38	143	35	13
13					760	2010	.52	.055	4050	.692	19.3	.37	146	34	10
14					761	2000	.49	.052	4710	.744	19.9	.35	142	36	9
15					760	1995	.54	.057	4620	.801	20.0	.41	145	35	9
16					761	2020	.50	.053	4440	.854	19.7	.36	145	37	10
17					760	1995	.55	.058	4280	.909	18.6	.40	148	37	12
18					760	2000	.57	.060	4220	.969	19.0	.45	150	38	9
19					759	2000	.56	.059	4310	1.028	18.0	.44	158	37	9
20					760	1995	.57	.061	4530	1.088	19.3	.48	160	38	11
184-197-18	3104	Amer. Cy.	Bachaquero	Comm. Demet.	780	2000	.58	.061	3650	.041	20.9	.27			12
2		0.02" Beads	Export	Catalyst	779	2000	.56	.059	4140	.100	21.0	.29	96	26	11
3			Vacuum	HRI 3634	782	2010	.57	.060	3530	.160	19.7	.33	111	30	10
4			Residuum		781	2010	.54	.057	4280	.217	19.6	.31	118	30	13
5			L-405		779	2010	.55	.058	4310	.275	20.5	.33	120	32	13
6					781	2010	.52	.055	4140	.330	20.7	.34	126	32	14
7					749	2000	.58	.062	4080	.384	20.0	.51	148	36	14
8					782	1990	.62	.065	3310	.449	20.9	.42/.46	137	32	13
9							.57	.061		.454					
184-198-18	3104	Amer. Cy.	Bachaquero	Comm. Demet.	770	1990	.46	.048	5400	.038	21.7	.40			12
2		0.02" Beads	Export	Catalyst	772	2000	.46	.048	4050	.086	21.7	.31	99	29	13
3			Vacuum	HRI 3634	771	2000	.49	.051	3590	.137	21.5	.33	106	29	15
4			Residuum		767	2000	.47	.049	1850	.172	20.4	.65	106	30	13
			L-406												

Table B      SUMMARY OF DESULFURIZATION RUNS

Run No.-Period	Catalyst HRI No.	Catalyst Base	Demetallized Feed	Demetallized Over	Temp. °F	Hydrogen Pressure psig	Space Velocity		Hydrogen Rate SCF/Bbl	Catalyst Age Bbl/Lb	Product Inspections				
							V/Hr/Vr	B/D/Lb			Gravity °API	% S	V ppm	NI ppm	IBP-550°F V %
185-248-18	3104	Amer. Cy. 0.02" Beads	Bachaquero	Comm. Demet. Catalyst HRI 3634	780	1970	.56	.059	4710	.039	22.0				13
2			Export		782	2010	.55	.059	3540	.098	22.1	.24	63	19	15
3			Vacuum		780	2000	.56	.059	4060	.157	22.5	.28	77	23	14
4			Residuum		778	2000	.57	.061	3870	.218	20.3	.31	90	27	15
5			L-406		779	2000	.60	.063	4540	.281	20.4	.33	90	28	14
6					781	2000	.56	.060	3090	.341	21.3	.26	87	27	16
7					783	2010	.56	.060	3770	.401	21.4	.31	92	27	17
8					781	2000	.56	.059	4340	.460	21.6	.32	99	28	16
9					785	2000	.50	.052	4530	.512	21.5	.27	95	27	17
10					781	1990	.53	.056	4440	.568	21.6	.26	98	25	16
11					780	2015	.55	.058	4310	.626	21.2	.30			16
12					781	2000	.53	.056	3970	.682	21.2	.31			16
															IBP-600°F
185-249-18	3104	Amer. Cy. 0.02" Beads	Bachaquero	Comm. Demet. Catalyst HRI 3634	763	2020	1.21	.129	3690	.084	19.7	.56			12
2			Export		762	2005	1.11	.119	4290	.203	19.6	.43	63	29	14
3			Vacuum		762	1990	1.15	.123	4430	.326	19.0	.47	62	30	17
4			Residuum		760	2000	1.11	.119	4360	.445	17.9	.51	63	20	10
5			L-408		761	2010	1.08	.115	4250	.560	17.7	.41	66	20	10
6					760	2015	1.06	.113	4350	.673	17.5	.52	67	20	10
7					759	2010	1.11	.119	3950	.792	17.4	.50	66	22	12
8					760	2010	1.13	.121	3840	.913	18.4	.45	70	24	11
9					761	2010	1.11	.119	3960	1.032	18.5	.45	70	24	13
10					759	2010	1.11	.119	3950	1.151	19.1	.56			10
11					760	2015	1.10	.118	4770	1.269	18.7	.48	68	26	13
12					760	2005	1.18	.125	3580	1.394	18.2	.45			13
13					759	2000	1.18	.125	3690	1.519	18.0	.50			11
14					759	2000	1.19	.127	3750	1.640	18.0	.41	63	26	13
15					761	2000	1.07	.114	4160	1.760	18.6	.47			11
16					761	2005	.84	.090	5430	1.850	18.8	.49			12
17					761	2010	1.03	.110	4510	1.905	18.2	.60			13
															IBP-550°F
185-250-18	3104	Amer. Cy. 0.02" Beads	Lloydminster	Comm. Demet. Catalyst HRI 3634	760	2015	1.00	.107	9510	.100	15.0	.79	40	27	6
2			Vacuum		763	2015	1.07	.114	8680	.214	18.6	.66	40	27	5
3			Residuum		759	1985	1.08	.115	8890	.329	18.3	.66	38	28	5
4			L-422		761	1980	1.11	.119	8280	.448	18.5	.65	38	28	5
5					758	1995	1.09	.117	8450	.565	17.8	.72	39	28	5
6					758	2005	1.11	.119	7960	.684	18.3	.72	40	29	4

Table B SUMMARY OF DESULFURIZATION RUNS

Run No.-Period	Catalyst HRI No.	Catalyst Base	Demetallized Feed	Demetallized Over	Temp. °F	Hydrogen Pressure psig	Space Velocity		Hydrogen Rate SCF/Bbl	Catalyst Age Bbl/Lb	Product Inspections				
							V/Hr/Vr	B/D/Lb			Gravity °API	% S	V ppm	NI ppm	IBP-550°F V %
185-250-7	3104	Amer. Cy.	Lloydminster	Comm. Demet.	759	1960	1.25	.134	7040	.818	18.4	.73	40	31	4
8		0.02" Beads	Vacuum	Catalyst	760	1985	1.08	.115	5650	.933	18.2	.68	39	30	4
9			Residuum	HRI 3634	755	2010	.94	.100	4350	1.033	19.0	.68	38	30	4
10			L-422		755	2020	.87	.093	5410	1.126	17.1	.73			3
11					760	2015	1.16	.124	4460	1.250	17.1	.79			5
12					752	2000	1.27	.136	3220	1.386	16.8	.92	49	33	4
13					760	1995	.88	.094	5000	1.480	17.9	.70			4
14					764	2005	1.21	.130	3610	1.610	17.6	.69	43	34	4
15					759	2005	1.10	.118	3930	1.728	18.2	.75			4
16					760	1995	1.15	.123	3770	1.851	17.6	.78	40	34	3
17					759	2000	1.00	.107	4340	1.958	16.7	.72	50	31	4
18					761	2010	.99	.106	4420	2.064	17.6	.65	49	30	4
19					760	1995	1.00	.107	4500	2.171	17.9	.71	50	30	2
20					766	2010	1.23	.132	3830	2.303	15.9	.80			3
21					766	2015	1.23	.132	3720	2.435	17.6	.81	46	33	4
22					770	2010	1.19	.127	3920	2.562	17.1	.82			1
23					760	2000	1.01	.108	4270	2.670	18.4	.72	38	29	4
24					758	1985	1.06	.113	4560	2.783	17.9	.79	44	32	4
25					758	1980	1.04	.111	5150	2.894	17.2	.85	45	33	4
26					759	1995	.93	.100	5110	2.994	17.9	.79	45	32	4
185-251-18	3104	Amer. Cy.	Lloydminster	Comm. Demet.	758	2000	1.18	.124	4230	.130	18.3	.58			4
2		0.02" Beads	Vacuum	Catalyst	757	2000	1.15	.122	4150	.252	19.4	.59	12	21	3
3			Residuum	HRI 3634	761	2015	1.14	.121	4450	.373	19.3	.40	12	22	4
4			L-424		760	2005	1.11	.118	4730	.491	18.9	.49	18	16	4
5					761	2000	1.18	.124	5290	.620	19.2	.55	18	16	4
6					761	2010	1.06	.112	4300	.732	19.4	.47	17	19	5
7					759	1995	1.11	.118	4110	.850	18.9	.50	16	20	5
8					761	1995	1.24	.131	3900	.981	18.4	.53	16	20	6
9					760	2000	1.20	.127	3710	1.108	18.7	.65	18	20	5
10					761	2000	1.21	.128	3660	1.236	18.0	.61	20	20	5
11					760	2005	1.12	.119	3990	1.355	18.6	.66	20	22	5
12					761	1990	1.01	.107	5090	1.462	18.9	.45	20	20	3
13					759	2000	1.05	.111	3760	1.573	18.5	.57	21	21	6
14					760	1990	1.15	.122	3980	1.695	19.1	.54			4
15					760	1980	1.30	.138	3620	1.833	18.2	.61	18	21	5

**Table B SUMMARY OF DESULFURIZATION RUNS**

Run No.-Period	Catalyst HRI No.	Catalyst Base	Demetallized Feed	Demetallized Over	Temp. °F	Hydrogen Pressure psig	Space Velocity		Hydrogen Rate SCF/Bbl	Catalyst Age Bbl/Lb	Product Inspections				
							V/Hr/Vr	B/D/Lb			Gravity °API	% S	V ppm	NI ppm	IBP-550°F V %
185-251-16	3104	Amer. Cy.	Lloydminster	Comm. Demet.	760	1980	1.21	.128	3340	1.961	18.3	.69			4
17		0.02" Beads	Vacuum	Catalyst	761	1990	1.16	.122	3780	2.083	18.7	.58	18	23	4
18			Residuum	HRI 3634	761	2000	1.09	.115	4540	2.198	18.7	.64			6
19			L-424		758	1990	1.15	.122	5100	2.320	18.6	.64			6
20					761	1990	1.13	.120	3670	2.440	18.5	.59	20	24	5
21					760	1995	1.20	.127	3550	2.567	18.5	.64			6
22					759	1980	1.08	.114	3740	2.681	18.0	.73	20	24	5
23					760	1995	1.08	.114	4150	2.795	19.6	.70			6
24					760	2000	1.13	.120	3250	2.915	18.8	.65	20	25	5





APPENDIX B-1

DESULFURIZATION OPERATING CONDITIONS, YIELDS AND PRODUCT PROPERTIES



## DESULFURIZATION

Table B-1. OPERATING CONDITIONS, YIELDS, AND PRODUCT PROPERTIES

Run Number	184-194-17
Catalyst Age, BBL/LB	1.85
Feed	Demetallized Bachaquero Export Vacuum Residuum
HRI Identification No.	L-400
Catalyst	(11.3 °API, 1.98 W % S) American Cyanamid Co-Mo 0.02" diameter beads
HRI No.	3104

### OPERATING CONDITIONS

Hydrogen Pressure, psig	2000
Temperature, °F	760
Liquid Space Velocity, $V_F/Hr/V_R$	1.05
Catalyst Space Velocity, B/D/LB	0.112
Reactor Type	Downflow
Hydrogen Rate, SCF/BBL	3950
Hydrogen Consumption, SCF/BBL	365
975°F+ Conversion, V %	9.2

<u>YIELDS</u>	<u>W %</u>	<u>V %</u>
H <sub>2</sub> S & NH <sub>3</sub>	1.23	
C <sub>1</sub> -C <sub>3</sub>	1.07	
C <sub>4</sub> -650°F	6.98	8.38
650°F-975°F	21.60	23.55
975°F	69.67	70.15
Total	100.55	
C <sub>4</sub> +	98.25	102.08
Gravity, °API		16.9
Sulfur, W %	0.89	

<u>FRACTION, °F</u>	<u>Coll. Liq.</u>	<u>IBP- 650°F</u>	<u>650°F+</u>	<u>650- 975°F</u>	<u>975°F+</u>
V % on Collected Liquid	100	7.3	92.7	23.3	69.4
Gravity, °API	16.3	32.1	14.4	22.9	11.1
Sulfur, W %	0.90		1.03	0.13	1.22
Carbon, W %	86.92				
Hydrogen, W %	11.54				
Nitrogen, ppm	3735				
Aniline Point, °F		137		155	
Flash Point, °F			535		
Pour Point, °F			50		
RCR, W %					16.7
Viscosity, SFS @210°F			124		

# DESULFURIZATION

Table B-2. OPERATING CONDITIONS, YIELDS, AND PRODUCT PROPERTIES

Run Number	184-195-4
Catalyst Age, BBL/LB	0.47
Feed	65-70% Demetallized Bachaquero Export
	Vacuum Residium
HRI Identification No.	L-401
	(13.1 °API, 1.39 W % S)
Catalyst	American Cyanamid Co-Mo
	0.02" diameter beads
HRI No.	3104

## OPERATING CONDITIONS

Hydrogen Pressure, psig	2000
Temperature, °F	761
Liquid Space Velocity, V/Hr/V	1.07
Catalyst Space Velocity, B/D/LB	0.11
Reactor Type	Downflow
Hydrogen Rate, SCF/BBL	4300
Hydrogen Consumption, SCF/BBL	310
975°F+ Conversion, V %	5.6

YIELDS	W %	V %
H <sub>2</sub> S & NH <sub>3</sub>	0.92	
C <sub>1</sub> -C <sub>3</sub>	0.40	
C <sub>4</sub> -400°F	1.24	1.65
400-650°F	7.57	8.78
650-975°F	22.29	24.26
975°F+	68.06	68.92
Total	100.48	
C <sub>4</sub> +	99.16	103.61
Gravity, °API		19.6
Sulfur, W %	0.67	

FRACTION, °F	Coll. Liq.	IBP- 400°F	400°F+ 400°F+	400- 650°F	650°F+ 650°F+	650- 975°F	975°F+ 975°F+
V % on Collected Liquid	100	1.25	98.75	8.50	90.25	23.5	66.75
Gravity, ° API	16.7	47.2	15.7	32.5	14.2	22.4	11.7
Sulfur, W %	0.69	<0.03	0.68	<0.03	0.72/0.69	0.15	0.92
Carbon, W %	86.34						
Hydrogen, W %	11.59						
H/C Atomic Ratio	1.60						
Nitrogen, ppm	3527						
Bromine No. cgs/gm		4.4		6.1			
Aniline Point, °F				141		177	
Flash Point, °F			360		510		
Pour Point, °F			25		60		
Smoke Point, °F							
ASTM Color				L-4.5			
RCR, W %							16.8
Vanadium, ppm	153						
Nickel, ppm	45						
Viscosity, SUS @210°F			364		693		
SFS @122°F			521		960		
SFS @210°F							330
SFS @250°F							114

# DESULFURIZATION

Table B-3. OPERATING CONDITIONS, YIELDS, AND PRODUCT PROPERTIES

Run Number	184-195-19
Catalyst Age, BBL/LB	2.15
Feed	65-70% Demetallized Bachaquero Export Vacuum Residium
HRI Identification No.	L-401
Catalyst	(13.1 °API, 1.39 W % S) American Cyanamid Co-Mo 0.02" diameter beads
HRI No.	3104

## OPERATING CONDITIONS

Hydrogen Pressure, psig	2010
Temperature, °F	762
Liquid Space Velocity, V/Hr/V	0.93
Catalyst Space Velocity, B/D/LB	0.10
Reactor Type	Downflow
Hydrogen Rate, SCF/BBL	5110
Hydrogen Consumption, SCF/BBL	275
975°F+ Conversion, V %	9.7

YIELDS	W %	V %
H <sub>2</sub> S & NH <sub>3</sub>	1.12	
C <sub>1</sub> -C <sub>3</sub>	0.40	
C <sub>4</sub> -400°F	1.03	1.37
400-650°F	7.54	8.62
650-975°F	24.24	25.87
975°F+	66.09	65.91
Total	100.42	
C <sub>4</sub> +	98.90	101.77
Gravity, °API		17.3
Sulfur, W %	0.48	

FRACTION, °F	Coll. Liq.	IBP- 400°F	400°F+	400- 650°F	650°F+	650- 975°F	975°F+
V % on Collected Liquid	100	1.0	99.0	8.5	90.5	25.5	65.0
Gravity, ° API	17.1	49.4	15.6	32.9	14.2	22.0	12.0
Sulfur, W %	0.64	<0.03	0.49	<0.03	0.63	0.13	0.76
Carbon, W %	86.50						
Hydrogen, W %	11.59						
H/C Atomic Ratio							
Nitrogen, ppm	3540						
Bromine No. cgs/gm		3.7		5.9		176	
Aniline Point, °F				139			
Flash Point, °F			430		500		
Pour Point, °F			35		55		
Smoke Point, °F							
ASTM Color				6.0			
RCR, W %							15.9
Vanadium, ppm	164						
Nickel, ppm	39						
Viscosity, SUS @210°F			335		630		
SFS @122°F			644		956		
SFS @210°F							356
SFS @250°F							105

# DESULFURIZATION

Table B-4. OPERATING CONDITIONS, YIELDS, AND PRODUCT PROPERTIES

Run Number	184-196-4
Catalyst Age, BBL/LB	0.20
Feed	65-70% Demetallized Bachaquero Export
	Vacuum Residium
HRI Identification No.	L-405
	(14.4 °API, 1.40 W % S)
Catalyst	American Cyanamid Co-Mo
	0.02" diameter beads
HRI No.	3104

## OPERATING CONDITIONS

Hydrogen Pressure, psig	2000
Temperature, °F	762
Liquid Space Velocity, $V_F/Hr/V_R$	0.53
Catalyst Space Velocity, B/D/LB	0.06
Reactor Type	Downflow
Hydrogen Rate, SCF/BBL	3860
Hydrogen Consumption, SCF/BBL	410
975°F+ Conversion, V %	8.0

YIELDS	W %	V %
H <sub>2</sub> S & NH <sub>3</sub>	1.35	
C <sub>1</sub> -C <sub>3</sub>	0.40	
C <sub>4</sub> -400°F	2.6	3.42
400-650°F	9.43	10.72
650-975°F	24.48	26.02
975°F+	62.32	62.25
Total	100.64	
C <sub>4</sub> +	98.89	102.41
Gravity, °API		19.6
Sulfur, W %	0.34	

FRACTION, °F	Coll. Liq.	IBP-400°F	400°F+	400-650°F	650°F+	650-975°F	975°F+
V % on Collected Liquid	100	3.0	97.0	10.5	86.5	25.5	61.0
Gravity, °API	19.4	50.4	18.5	33.2	15.7	22.5	13.2
Sulfur, W %	0.37	<0.03	0.33	<0.03	0.50	0.05	0.52
Carbon, W %	86.68						
Hydrogen, W %	11.77						
H/C Atomic Ratio	1.62						
Nitrogen, ppm	3316						
Bromine No. cgs/gm		4.1		6.7			
Aniline Point, °F		129		141		176	
Flash Point, °F			390		500		
Pour Point, °F			30		60		
Smoke Point, °F				11			
ASTM Color		L-2.5		5.0			
RCR, W %							14.9
Vanadium, ppm	124						
Nickel, ppm	29						
Viscosity, SUS @210°F			202		526		
SFS @122°F			180		582		
SFS @210°F					37		226
							90

# DESULFURIZATION

Table B-5. OPERATING CONDITIONS, YIELDS, AND PRODUCT PROPERTIES

Run Number	184-196-20
Catalyst Age, BBL/LB	1.09
Feed	65-70% Demetallized Bachaquero Export Vacuum Residuum
HRI Identification No.	L-405
Catalyst	(14.4 °API, 1.40 W % S) American Cyanamid Co-Mo 0.02" diameter beads
HRI No.	3104

## OPERATING CONDITIONS

Hydrogen Pressure, psig	1990
Temperature, °F	760
Liquid Space Velocity, $V_F/Hr/V_R$	0.57
Catalyst Space Velocity, B/D/LB	0.06
Reactor Type	Downflow
Hydrogen Rate, SCF/BBL	4530
Hydrogen Consumption, SCF/BBL	345
975°F+ Conversion, V %	16.6

YIELDS	W %	V %
H <sub>2</sub> S & NH <sub>3</sub>	1.20	
C <sub>1</sub> -C <sub>3</sub>	0.40	
C <sub>4</sub> -400°F	3.54	4.38
400-650°F	9.44	10.59
650-975°F	28.35	29.76
975°F+	57.60	56.49
Total	100.53	
C <sub>4</sub> +	98.93	101.22
Gravity, °API		17.8
Sulfur, W %	0.48	

FRACTION, °F	Coll. Liq.	IBP- 400°F	400°F+	400- 650°F	650°F+	650- 975°F	975°F+
V % on Collected Liquid	100	4.0	96.0	10.5	85.5	29.5	56.0
Gravity, °API	19.3	47.3	17.2	33.2	15.3	22.5	12.4
Sulfur, W %	0.48		0.45		0.56	< 0.03	0.80
Carbon, W %	86.57						
Hydrogen, W %	11.67						
H/C Atomic Ratio	1.60						
Nitrogen, ppm	3322						
Bromine No. cgs/gm		2.6		5.8			
Aniline Point, °F		131		137		181	
Flash Point, °F			410		500		
Pour Point, °F			20		45		
Smoke Point, °F				12.0			
ASTM Color				L-5.0			
RCR, W %							16.5
Vanadium, ppm	160						
Nickel, ppm	38						
Viscosity, SUS @210°F			236		540		
SFS @122°F			195		650		
SFS @210°F							393
SFS @250°F							120

# DESULFURIZATION

Table B-6. OPERATING CONDITIONS, YIELDS, AND PRODUCT PROPERTIES

Run Number	185-248-3
Catalyst Age, BBL/LB	0.15
Feed	65-70% Demetallized Bachaquero Export Vacuum Residuum
HRI Identification No.	L-406
Catalyst	(15.0 °API, 1.25 W % S) American Cyanamid Co-Mo 0.02" diameter beads
HRI No.	3104

## OPERATING CONDITIONS

Hydrogen Pressure, psig	2000
Temperature, °F	780
Liquid Space Velocity, V/Hr/V	0.56
Catalyst Space Velocity, B/D/LB	0.06
Reactor Type	Downflow
Hydrogen Rate, SCF/BBL	4060
Hydrogen Consumption, SCF/BBL	480
975°F+ Conversion, V %	16.0

YIELDS	W %	V %
H <sub>2</sub> S & NH <sub>3</sub>	1.25	
C <sub>1</sub> -C <sub>3</sub>	0.81	
C <sub>4</sub> -400°F	5.33	6.82
400-650°F	12.21	13.84
650-975°F	27.40	29.24
975°F+	53.74	54.03
Total	100.74	
C <sub>4</sub> +	98.69	103.93
Gravity, °API		22.8
Sulfur, W %	0.37	

FRACTION, °F	Coll. Liq.	IBP- 400	400°F+	400- 650°F	650°F+	650- 975°F	975°F+
V % on Collected Liquid	100	6.0	94.0	13.4	80.6	28.3	52.3
Gravity, °API	22.5	50.6	19.9	32.4	17.8	22.8	13.9
Sulfur, W %	0.28		0.31	0.04	0.40	0.12	0.61
Carbon, W %	86.41						
Hydrogen, W %	11.93						
H/C Atomic Ratio	1.64						
Nitrogen, ppm	2635						
Bromine No., cgs/gm		3.7		4.8			
Aniline Point, °F		128		141		180	
Flash Point, °F			365		480		
Pour Point, °F			35		45		
Smoke Point, °F				12.5			
ASTM Color		L-2.0		4.5			
RCR, W %							14.6
Vanadium, ppm	77						
Nickel, ppm	23						
Viscosity, SUS @210°F			117		272		
SFS @210°F							155



# DESULFURIZATION

Table B-7. OPERATING CONDITIONS, YIELDS, AND PRODUCT PROPERTIES

Run Number	185-248-11
Catalyst Age, BBL/LB	0.63
Feed	65-70% Demetalized Bachaquero Export
	Vacuum Residium
HRI Identification No.	L-406
	(15 °API, 1.25 W % S)
Catalyst	American Cyanamid Co-Mo
	0.02" diameter beads
HRI No.	3104

## OPERATING CONDITIONS

Hydrogen Pressure, psig	2010
Temperature, °F	780
Liquid Space Velocity, V/Hr/V	0.55
Catalyst Space Velocity, B/D/LB	0.06
Reactor Type	Downflow
Hydrogen Rate, SCF/BBL	4300
Hydrogen Consumption, SCF/BBL	480
975°F+ Conversion, V %	26.7

YIELDS	W %	V %
H <sub>2</sub> S & NH <sub>3</sub>	1.33	
C <sub>1</sub> -C <sub>3</sub>	0.71	
C <sub>4</sub> -400°F	6.60	8.44
400-650°F	12.72	13.33
650-975°F	32.06	34.14
975°F+	47.27	47.16
Total	100.75	
C <sub>4</sub> +	98.71	103.06
Gravity, °API		21.5
Sulfur, W %	0.30	

FRACTION, °F	Coll. Liq.	IBP- 400°F	400°F+	400- 650°F	650°F+	650- 975°F	975°F+
V % on Collected Liquid	100	7.7	92.3	13.0	79.3	33.3	46.0
Gravity, ° API	21.2	49.9	20.1	32.4	17.6	22.6	12.9
Sulfur, W %	0.31		0.36	0.04	0.37		0.67
Carbon, W %	86.66						
Hydrogen, W %	11.98						
H/C Atomic Ratio	1.64						
Nitrogen, ppm	2487						
Bromine No., cgs/gm		3.1		4.6			
Aniline Point, °F		130		140		184	
Flash Point, °F			335		475		
Pour Point, °F			35		50		
Smoke Point, °F				13.0			
ASTM Color		0.5		L-3.5			
RCR, W %							15.49
Vanadium, ppm	76						
Nickel, ppm	28						
Viscosity, SUS @210°F			123		302		
SFS @210°F							308

# DESULFURIZATION

Table B-8. OPERATING CONDITIONS, YIELDS, AND PRODUCT PROPERTIES

Run Number	185-249-4
Catalyst Age, BBL/LB	0.44
Feed	80-85% Demetallized Bachaquero Export
	Vacuum Residuum
HRI Identification No.	L-408
	(17.5 °API, 1.00 W % S)
Catalyst	American Cyanamid Co-Mo
	0.02" diameter beads
HRI No.	3104

## OPERATING CONDITIONS

Hydrogen Pressure, psig	2000
Temperature, °F	760
Liquid Space Velocity, V/Hr/V	1.11
Catalyst Space Velocity, B/D/LB	0.12
Reactor Type	Downflow
Hydrogen Rate, SCF/BBL	4360
Hydrogen Consumption, SCF/BBL	
975°F+ Conversion, V %	10.4

<u>YIELDS</u>	<u>W %</u>	<u>V %</u>
H <sub>2</sub> S & NH <sub>3</sub>	0.58	
C <sub>1</sub> -C <sub>3</sub>	0.48	
C <sub>4</sub> -400°F	1.56	1.94
400-650°F	10.42	11.53
650-975°F	28.10	29.13
975°F+	59.23	57.06
Total	100.37	
C <sub>4</sub> +	99.31	99.66
Gravity, °API		18.0
Sulfur, W %	0.55	

<u>FRACTION, °F</u>	<u>Coll. Liq.</u>	<u>IBP- 400°F</u>	<u>400°F+ 400°F</u>	<u>400- 650°F</u>	<u>650°F+ 650°F</u>	<u>650- 975°F</u>	<u>975°F+ 975°F</u>
V % on Collected Liquid	100	1.7	98.3	11.6	86.7	29.3	57.4
Gravity, ° API	17.9	49.4	18.7	32.6	14.9	22.2	11.4
Sulfur, W %	0.51		0.45	<0.02	0.59	0.19	0.82
Carbon, W %	86.30						
Hydrogen, W %	11.71						
H/C Atomic Ratio	1.62						
Nitrogen, ppm	3201						
Bromine No. cgs/gm		2.67		5.19			
Aniline Point, °F							
Flash Point, °F			410		490		
Pour Point, °F			20		35		
Smoke Point, °F				12.0			
ASTM Color							
RCR, W %							15.9
Vanadium, ppm	63						
Nickel, ppm	20						
Viscosity, SUS @210°F			165				
SFS @ 122°F			175			745	
SFS @ 210°F					34		184

# DESULFURIZATION

Table B-9. OPERATING CONDITIONS, YIELDS, AND PRODUCT PROPERTIES

Run Number	185-249-15
Catalyst Age, BBL/LB	1.76
Feed	80-85% Demetallized Bachaquero Export Vacuum Residium
HRI Identification No.	L-408 (17.5 °API, 1.00 W % S)
Catalyst	American Cyanamid Co-Mo 0.02" diameter beads
HRI No.	3104

## OPERATING CONDITIONS

Hydrogen Pressure, psig	2000
Temperature, °F	761
Liquid Space Velocity, V/Hr/V	1.07
Catalyst Space Velocity, B/D/LB	0.11
Reactor Type	Downflow
Hydrogen Rate, SCF/BBL	4160
Hydrogen Consumption, SCF/BBL	
975°F+ Conversion, V %	10.7

YIELDS	W %	V %
H <sub>2</sub> S & NH <sub>3</sub>	0.47	
C <sub>1</sub> -C <sub>3</sub>	0.52	
C <sub>4</sub> -400°F	1.64	1.90
400-650°F	10.78	11.98
650-975°F	28.25	29.25
975°F+	58.60	56.90
Total	100.25	
C <sub>4</sub> +	99.27	100.08
Gravity, °API		18.7
Sulfur, W %	0.64	

FRACTION, °F	Coll. Liq.	IBP- 400°F	400°F+	400- 650°F	650°F+	650- 975°F	975°F+
V % on Collected Liquid	100	1.7	98.3	12.0	86.3	29.3	57.0
Gravity, ° API	18.6	39.2	17.9	32.8	16.9	21.5	12.0
Sulfur, W %	0.47		0.66	≤0.02	0.55	0.21	0.97
Carbon, W %	86.84						
Hydrogen, W %	11.67						
H/C Atomic Ratio	1.60						
Nitrogen, ppm	3377						
Bromine No. cgs/gm		2.1		5.8			
Aniline Point, °F			140		165		
Flash Point, °F			320		480		
Pour Point, °F			25		40		
Smoke Point, °F				12.5			
ASTM Color							15.0
RCR, W %							
Vanadium, ppm	63						
Nickel, ppm	26						
Viscosity, SUS @210°F			177				
SFS @122°F			270		606		
SFS @210°F							166

# DESULFURIZATION

Table B-10. OPERATING CONDITIONS, YIELDS, AND PRODUCT PROPERTIES

Run Number	185-250-14
Catalyst Age, BBL/LB	1.61
Feed	60-65% Demetallized Lloydminster Vacuum Residuum
HRI Identification No.	L-422
Catalyst	(13.2 °API, 2.83 W % S) American Cyanamid Co-Mo 0.02" diameter beads
HRI No.	3104

## OPERATING CONDITIONS

Hydrogen Pressure, psig	2000
Temperature, °F	764
Liquid Space Velocity, $V_F/H_r/V_R$	1.21
Catalyst Space Velocity, B/D/LB	0.13
Reactor Type	Downflow
Hydrogen Rate, SCF/BBL	3950
Hydrogen Consumption, SCF/BBL	420
975°F+ Conversion, V %	6.1

YIELDS	W %	V %
H <sub>2</sub> S & NH <sub>3</sub>	2.22	
C <sub>1</sub> -C <sub>3</sub>	0.66	
C <sub>4</sub> -400	1.81	2.32
400-650°F	6.51	7.34
650-975°F	28.39	30.16
975°F+	61.06	61.02
Total	100.65	
C <sub>4</sub> +	97.77	100.84
Gravity, °API		17.8
Sulfur, W %	0.94	

FRACTION, °F	Coll. Liq.	IBP- 400°F	400°F+	400- 650°F	650°F+	650- 975°F	975°F+
V % on Collected Liquid	100	2.0	98.0	7.3	90.7	30.0	60.7
Gravity, °API	17.6	50.2	16.9	31.0	14.5	21.7	12.6
Sulfur, W %			0.90	<0.03	0.96	0.19	1.41
Carbon, W %	86.95						
Hydrogen, W %	11.61						
H/C Atomic Ratio	1.60						
Nitrogen, ppm	3347						
Aniline Point, °F		121		127		167	
Flash Point, °F			430		485		
Pour Point, °F			35		55		
RCR, W %							13.9
Vanadium, ppm	43						
Nickel, ppm	34						
Viscosity, SUS @210°F			215				
SFS @210°F					39		

# DESULFURIZATION

Table B-11. OPERATING CONDITIONS, YIELDS, AND PRODUCT PROPERTIES

Run Number	185-250-25
Catalyst Age, BBL/LB	2.89
Feed	60-65% Demetallized Lloydminster Vacuum Residuum
HRI Identification No.	L-422
Catalyst	(13.2 °API, 2.83 W % S) American Cyanamid Co-Mo 0.02" diameter beads
HRI No.	3104

## OPERATING CONDITIONS

Hydrogen Pressure, psig	1980
Temperature, °F	760
Liquid Space Velocity, $V_F/Hr/V_R$	1.04
Catalyst Space Velocity, B/D/LB	0.11
Reactor Type	Downflow
Hydrogen Rate, SCF/BBL	5150
Hydrogen Consumption, SCF/BBL	520
975°F+ Conversion, V %	11.9

<u>YIELDS</u>	<u>W %</u>	<u>V %</u>
H <sub>2</sub> S & NH <sub>3</sub>	2.28	
C <sub>1</sub> -C <sub>3</sub>	0.66	
C <sub>4</sub> -400°F	1.93	2.47
400-650°F	7.18	8.04
650-975°F	31.04	32.85
975°F+	57.71	57.26
Total	100.80	
C <sub>4</sub> +	97.86	100.62
Gravity, °API		17.3
Sulfur, W %	0.94	

<u>FRACTION, °F</u>	<u>Coll. Liq.</u>	<u>IBP- 400°F</u>	<u>400°F+</u>	<u>400- 650°F</u>	<u>650°F+</u>	<u>650- 975°F</u>	<u>975°F+</u>
V % on Collected Liquid	100	2.3	97.7	8.0	89.7	32.7	57.0
Gravity, °API	17.2	50.7	16.1	29.7	14.6	20.8	11.3
Sulfur, W %		0.12	1.0	40.03	1.21	0.23	1.46
Carbon, W %	86.56						
Hydrogen, W %	11.70						
H/C Atomic Ratio	1.61						
Nitrogen, ppm	2665						
Aniline Point, °F		117		128		170	
Flash Point, °F			425		495		
Pour Point, °F			25		55		
RCR, W %							14.7
Vanadium, ppm	45						
Nickel, ppm	33						
Viscosity, SUS @210°F			223				
SFS @210°F					39		

# DESULFURIZATION

Table B-12. OPERATING CONDITIONS, YIELDS, AND PRODUCT PROPERTIES

Run Number	185-251-4
Catalyst Age, BBL/LB	0.49
Feed	85% Demetallized Lloydminster Vacuum Residium
HRI Identification No.	L-424
Catalyst	(16.4 °API, 1.88 W % S) American Cyanamid Co-Mo 0.02" diameter beads
HRI No.	3104

## OPERATING CONDITIONS

Hydrogen Pressure, psig	2000
Temperature, °F	761
Liquid Space Velocity, $V_F/Hr/V_R$	1.11
Catalyst Space Velocity, B/D/LB	0.12
Reactor Type	Downflow
Hydrogen Rate, SCF/BBL	4720
Hydrogen Consumption, SCF/BBL	460
975°F+ Conversion, V %	14.6

<u>YIELDS</u>	<u>W %</u>	<u>V %</u>
H <sub>2</sub> S & NH <sub>3</sub>	1.65	
C <sub>1</sub> -C <sub>3</sub>	0.79	
C <sub>4</sub> -400°F	1.18	1.50
400-650°F	10.30	11.38
650-975°F	34.29	35.63
975°F+	52.51	51.50
Total	100.72	
C <sub>4</sub> +	98.28	100.00
Gravity, °API		19.0
Sulfur, W %	0.49	

<u>FRACTION, °F</u>	<u>Coll.</u> <u>Liq.</u>	<u>IBP-</u> <u>650°F</u>	<u>650°F+</u>	<u>650-</u> <u>975°F</u>	<u>975°F+</u>
V % Collected Liquid	100	12.7	87.3	35.7	51.6
Gravity, °API	18.9	31.7	16.1	21.4	12.8
Sulfur, W %	0.49	0.03	0.55	0.15	0.85
Carbon, W %	86.92				
Hydrogen, W %	11.96				
H/C Atomic Ratio	1.64				
Nitrogen, ppm	2495				
Aniline Point, °F		129		167	
Flash Point, °F			485		
Pour Point, °F			45		
RCR, W %					12.8
Vanadium, ppm	18				
Nickel, ppm	16				
Viscosity, SUS @210°F			259		

# DESULFURIZATION

Table B-13. OPERATING CONDITIONS, YIELDS, AND PRODUCT PROPERTIES

Run Number	185-251-20
Catalyst Age, BBL/LB	2.44
Feed	85% Demetallized Lloydminster Vacuum Residuum
HRI Identification No.	L-424
Catalyst	(16.4 °API, 1.88 W % S) American Cyanamid Co-Mo 0.02" diameter beads
HRI No.	3104

## OPERATING CONDITIONS

Hydrogen Pressure, psig	1990
Temperature, °F	760
Liquid Space Velocity, $V_F/Hr/V_R$	1.13
Catalyst Space Velocity, B/D/LB	0.12
Reactor Type	Downflow
Hydrogen Rate, SCF/BBL	3670
Hydrogen Consumption, SCF/BBL	310
975°F+ Conversion, V %	8.0

## YIELDS

	W %	V %
H <sub>2</sub> S & NH <sub>3</sub>	1.49	
C <sub>1</sub> -C <sub>3</sub>	0.53	
C <sub>4</sub> -400°F	1.45	1.82
400-650°F	9.04	9.98
650-975°F	31.19	32.53
975°F+	56.79	55.48
Total	100.49	
C <sub>4</sub> +	98.47	99.91
Gravity, °API		18.6
Sulfur, W %	0.59	

FRACTION, °F	Coll. Liq.	IBP- 400°F	400°F+	400- 650°F	650°F+	650- 975°F	975°F+
V % on Collected Liquid	100	1.7	98.3	10.0	88.3	32.7	55.6
Gravity, °API	18.5	49.9	17.7	30.5	16.6	21.6	11.9
Sulfur, W %	0.59		0.63	< 0.03	0.69	0.20	1.02
Carbon, W %	86.85						
Hydrogen, W %	11.53						
H/C Atomic Ratio	1.58						
Nitrogen, ppm	3011						
Aniline Point, °F		119		129		167	
Flash Point, °F			385		470		
Pour Point, °F			20		50		
RCR, W %							
Vanadium, ppm	20						14
Nickel, ppm	24						
Viscosity, SUS @122°F			133				
SUS @210°F					246		
Smoke Point				12.0			

<b>TECHNICAL REPORT DATA</b> <i>(Please read Instructions on the reverse before completing)</i>		
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16. ABSTRACT <b>The report gives results of Phase III work to optimize operating conditions in the demetallization step for overall desulfurization of heavy petroleum residual oils. Bachaquero and Lloydminster vacuum residua were demetallized to different levels of vanadium removal, the products desulfurized over commercial hydrodesulfurization catalyst at various operating conditions, and minimum operating costs were calculated to produce low sulfur fuel oil. The report describes test units, operating conditions, and procedures, and includes run summaries and tables of feedstock, product, and catalyst inspections. Graphs and tables depicting operating costs for producing 0.3, 0.5, and 1.0 wt % sulfur fuel oil are given, along with various correlations between demetallization levels, catalyst deactivation, demetallization rate constant, and contaminant metals deposited on catalyst.</b>		
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